POLYMER MODIFICATION

via

1,3-DIPOLAR CYCLOADDITION

REACTIONS

by

IAN STOBIE, B.Sc.

Thesis presented for the degree

of

DOCTOR of PHILOSOPHY

University of Edinburgh

April 1983
Modification of \textit{cis}-1,4-polyisoprene and \textit{cis}-1,4-polybutadiene by the 1,3-dipolar cycloaddition of p-nitrobenzonitrile oxide has been studied. The nitrile oxide was generated in situ from the corresponding hydroximoyl chloride under conditions which had previously been optimised using cyclooctene and 1-methylcyclohexene as models for the unsaturation present in the polymers. Strong support for the formation of polymeric 2-isoxazoline units was provided by comparison of the $^{13}$C n.m.r. spectra of the products with those of the model compounds. Reduction of the resulting polymer-bound nitro groups was effected by treatment with triiron dodecacarbonyl and sodium hydroxide in a two phase system using benzyltriethylammonium chloride as a phase transfer agent. Formation of amine groups was evident from the change in the i.r. spectrum and was demonstrated by characteristic reactions with acetyl chloride and p-tolyl isocyanate.

1,3-Dipolar cycloaddition of the nitrile units of acrylonitrile/styrene and acrylonitrile/vinylidene chloride copolymers with p-nitrobenzonitrile oxide has also been investigated. Proof that a 1,3-dipolar cycloaddition had occurred, producing the corresponding 1,2,4-oxadiazole, is provided by comparison of the $^{13}$C n.m.r. spectra of the products with those of a model compound.

The generation and reactions of polymer-bound nitrile sulphides was investigated by copolymerising a suitable precursor, a 1,3,4-oxathiazol-2-one, containing a pendant alkene group with styrene and with methyl methacrylate. Thermal decarboxylation of these copolymers
yielded polymer-bound nitrile sulphides which were trapped as their 1,3-dipolar cycloadducts with dimethyl acetylenedicarboxylate and ethyl cyanoformate. Proof that the corresponding isothiazole and 1,2,4-thiadiazole rings had been formed was obtained by comparison of the $^{13}$C n.m.r. spectra of the products with those of model compounds. An alternative approach to the synthesis of these copolymers involving the reaction of the 5-alkenyl-1,3,4-oxathiazol-2-ones with dimethyl acetylenedicarboxylate and ethyl cyanoformate prior to copolymerisation with styrene and methyl methacrylate was also examined. Thermolysis of the 5-alkenyl-1,3,4-oxathiazol-2 one copolymers in the absence of a dipolarophile yielded the corresponding nitrile containing copolymers by the fragmentation of the nitrile sulphides produced. The composition of all the copolymers produced were evaluated from their elemental analyses.
DECLARATION

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself and that it has not been submitted in any previous application for a higher degree.

The thesis describes results of research carried out in the Department of Chemistry, University of Edinburgh and I.C.I. Organics Division, Manchester under the joint supervision of Dr. R. M. Paton and Dr. R. M. Mortier since 1st October 1979, the date of my admission as a research student.

The following courses have been attended:

Organic Chemistry Seminars, Edinburgh University Chemistry Department (3 years attendance);
Biosynthesis (5 lectures), Dr. J. Simpson;
Flash Vacuum Pyrolysis (5 lectures), Dr. H. McNab;
Industrial Inorganic Chemistry (5 lectures), Dr. H.L. Roberts;
Current Topics in Organic Chemistry, (10 lectures), various lecturers;
Molecular Interaction in Industrial Food Research (5 lectures), Unilever Research;
Bioorganic Chemistry (5 lectures), various lecturers.
I would like to thank Dr. R. M. Paton and Dr. R. M. Mortier for their excellent supervision and guidance throughout the course of this project.

Thanks and appreciation are also due to teaching and technical staff of the Chemistry Department of Edinburgh University especially Mr. J. Miller for his help in obtaining such excellent polymer $^{13}$C n.m.r. spectra.

I would also like to thank the Science and Engineering Research Council for the award of a Studentship for the period during which this research was carried out.

The excellent typing is a tribute to the skill and patience of my mother, Mrs. C. G. Stobie.
# CONTENTS

## INTRODUCTION

<table>
<thead>
<tr>
<th>Preamble</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 1,3-DIPOLAR CYCLOADDITION</td>
<td>4</td>
</tr>
<tr>
<td>1.1.1 The 1,3-Dipole</td>
<td>4</td>
</tr>
<tr>
<td>1.1.2 1,3-Dipolar Cycloaddition Reactions</td>
<td>5</td>
</tr>
<tr>
<td>1.1.2a Mechanism</td>
<td>5</td>
</tr>
<tr>
<td>1.1.3 Frontier Molecular Orbital Theory</td>
<td>7</td>
</tr>
<tr>
<td>1.1.3a Dipolarophile Energy Levels</td>
<td>9</td>
</tr>
<tr>
<td>1.1.3b 1,3-Dipole Energy Levels</td>
<td>11</td>
</tr>
<tr>
<td>1.1.3c Classification of Reactions</td>
<td>12</td>
</tr>
<tr>
<td>1.1.3d Regioselectivity</td>
<td>13</td>
</tr>
</tbody>
</table>

## NITRILE OXIDES

| 1.2 NITRILE OXIDES | 15 |
| 1.2.1 History | 15 |
| 1.2.2 Generation of Nitrile Oxides | 16 |
| 1.2.2a From Hydroximoyl Chlorides | 16 |
| 1.2.2b From Aldoximes | 17 |
| 1.2.2c From Nitroparaffins | 17 |
| 1.2.2d From 1,2,5-Oxadiazole-N-Oxides | 18 |
| 1.2.2e Other Sources | 19 |
| 1.2.3 Properties of Nitrile Oxides | 20 |
| 1.2.3a Structure | 20 |
| 1.2.3b Stability | 21 |
| 1.2.4 1,3-Dipolar Cycloadditions of Nitrile Oxides | 22 |
| 1.2.4a Cycloaddition to Simple Aliphatic Nitriles | 24 |
| 1.2.5 1,3-Addition Reactions leading to Open-Chain Structures | 25 |
1.3 NITRILE SULPHIDES

1.3.1 Thermal Generation of Nitrile Sulphides

1.3.1a From 1,3,4-Oxathiazol-2-ones

1.3.1b From N-Thiocarbonyl Diphenylsulphimides

1.3.1c From Iminosulphur Difluorides

1.3.1d From 1,4,2-Dithiazol-5-one

1.3.2 Photolytic Generation of Nitrile Sulphides

1.3.3 Reactions of Nitrile Sulphides

1.3.3a Cycloaddition to Carbon-Carbon Multiple Bonds

1.3.3b Cycloaddition to Nitriles

1.4. 1,3-DIPOLAR CYCLOADDITIONS INVOLVING POLYMERS

1.4.1 Polymer Formation using 1,3-Dipoles

1.4.2 Modification of Polymers via 1,3-Dipolar Cycloaddition Reactions

1.4.2a Polymer Crosslinking

1.4.2b Addition of Active and Reactive Groups

1.4.2c Modification of Physical Properties

1.4.2c.i Nitrile Imines

1.4.2c.ii Nitrile Oxides

1.4.2c.iii Nitrones

1.4.3 Preparation and the Reactions of Polymers containing 1,3-Dipole Precursors
# CONTENTS

**EXPERIMENTAL**

<table>
<thead>
<tr>
<th>SYMBOLS AND ABBREVIATIONS</th>
<th>PAGE NO.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>46</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>INSTRUMENTATION</th>
<th>PAGE NO.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>47</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PREPARATION OF SOLVENTS</th>
<th>PAGE NO.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>49</td>
</tr>
</tbody>
</table>

| 2.1 Preparation of p-Nitrobenzohydroximoyl Chloride | 50       |
| 2.2 Preparation of 3,5-Di(p-nitrophenyl)1,2,4-oxadiazole | 51       |
| 2.3 Preparation of 3,4-Di(p-nitrophenyl)furazan-N-oxide | 51       |
| 2.4 Reaction of p-Nitrobenzohydroximoyl Chloride with Cyclooctene | 51       |
| 2.5 Reaction of p-Nitrobenzohydroximoyl Chloride with 1-Methylcyclohexene | 52       |
| 2.6 Reaction of p-Nitrobenzohydroximoyl Chloride with 1,5-Cyclooctadiene | 53       |
| 2.7 Reduction of 11-(p-Nitrophenyl)-9-oxa-10-aza-bicyclo-[6,3,0]-undec-10-ene | 54       |
| 2.7a Reduction with Tin and Hydrochloric acid | 54       |
| 2.7b Reduction with Triiron Dodecacarbonyl | 54       |
| 2.8 Reduction of 6-Methyl-9-(p-nitrophenyl)-7-oxa-8-azabicyclo-[4,3,0]-non-8-ene | 55       |
| 2.9 Reduction of 11-(p-Nitrophenyl)-9-oxa-10-aza-bicyclo-[6,3,0]-undeca-4,10-diene | 56       |
| 2.9a Reduction with Triiron Dodecacarbonyl | 56       |
| 2.9b Reduction with Hydrogen over a Palladium catalyst | 56       |
| 2.10 Reaction of 11-(p-Nitrophenyl)-9-oxa-10-aza-bicyclo-[6,3,0]-undec-4,10-diene with p-Toluenesulphonyl Hydrazide | 57       |
2.11 Preparation of the Acetyl derivative of 11-(p-Aminophenyl)-9-oxa-10-azabicyclo[6,3,0]-undec-10-ene

2.12 Preparation of the p-Tolyl urea derivative of 11-(p-Aminophenyl)-9-oxa-10-azabicyclo[6,3,0]-undec-4,10-ene

2.13 Reaction of p-Nitrobenzhydroximoyl Chloride with Isobutyronitrile

2.13a Reaction in Toluene

2.13b Reaction in γ-Butyrolactone

2.14 Preparation of Amides

2.15 Preparation of Chlorocarbonylsulphenyl Chloride

2.16 Preparation of 1,3,4-oxathiazol-2-ones

2.16a 5-(Prop-1-enyl)-1,3,4-oxathiazol-2-one

2.16b 5-Isopropenyl-1,3,4-oxathiazol-2-one

2.16c 5-Styryl-1,3,4-oxathiazol-2-one

2.16d 5-Isopropyl-1,3,4-oxathiazol-2-one

2.16e 5-Vinyl-1,3,4-oxathiazol-2-one

2.17 Synthesis of Isothiazoles and 1,2,4-Thiadiazoles from 1,3,4-oxathiazol-2-ones

2.17a Dimethyl 3-(Prop-1-enyl)isothiazole-4,5-dicarboxylate

2.17b Dimethyl 3-Isopropenylisothiazole-4,5-dicarboxylate

2.17c Dimethyl 3-Styrylisothiazole-4,5-dicarboxylate

2.17d Dimethyl 3-Isopropylisothiazole-4,5-dicarboxylate

2.17e Ethyl 3-(Prop-1-enyl)-1,2,4-thiadiazole-5-carboxylate

2.17f Ethyl 3-Isopropenyl-1,2,4-thiadiazole-5-carboxylate

2.17g Ethyl 3-Styryl-1,2,4-thiadiazole-5-carboxylate

2.17h Ethyl 3-Isopropyl-1,2,4-thiadiazole-5-carboxylate
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.18</td>
<td>Polymerisation of Styrene and Methyl Methacrylate and preparation of their copolymers with 1,3,4-Oxathiazol-2-ones, 1,2,4-Thiadiazoles and Isothiazoles containing an Alkenyl substituent</td>
</tr>
<tr>
<td>2.18a</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>2.18b</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>2.18c</td>
<td>Styrene/5-Vinyl-1,3,4-oxathiazol-2-one</td>
</tr>
<tr>
<td>2.18d</td>
<td>Styrene/5-Isopropenyl-1,3,4-oxathiazol-2-one</td>
</tr>
<tr>
<td>2.18e</td>
<td>Methyl Methacrylate/5-Vinyl-1,3,4-oxathiazol-2-one</td>
</tr>
<tr>
<td>2.18f</td>
<td>Methyl Methacrylate/5-Isopropenyl-1,3,4-oxathiazol-2-one</td>
</tr>
<tr>
<td>2.18g</td>
<td>Methyl Methacrylate/5-Isopropenyl-1,3,4-oxathiazol-2-one as a 20% solution using 1% initiator</td>
</tr>
<tr>
<td>2.18h</td>
<td>Methyl Methacrylate/5-Styryl-1,3,4-oxathiazol-2-one</td>
</tr>
<tr>
<td>2.18i</td>
<td>Methyl Methacrylate/5-(Prop-1-enyl)-1,3,4-oxathiazol-2-one</td>
</tr>
<tr>
<td>2.18j</td>
<td>Styrene/Ethyl 3-Isopropenyl-1,2,4-thiadiazole-5-carboxylate</td>
</tr>
<tr>
<td>2.18k</td>
<td>Styrene/Dimethyl 3-Isopropenylisothiazol-4,5-dicarboxylate</td>
</tr>
<tr>
<td>2.18l</td>
<td>Methyl Methacrylate/Dimethyl 3-Isopropenylisothiazole-4,5-dicarboxylate</td>
</tr>
<tr>
<td>2.19</td>
<td>Thermolysis of copolymers of Styrene and Methyl Methacrylate with 5-Vinyl-1,3,4-oxathiazol-2-one and 5-Isopropenyl-1,3,4-oxathiazol-2-one in an inert solvent</td>
</tr>
<tr>
<td>2.19a</td>
<td>Styrene/5-Vinyl-1,3,4-oxathiazol-2-one</td>
</tr>
<tr>
<td>2.19b</td>
<td>Styrene/5-Isopropenyl-1,3,4-oxathiazol-2-one</td>
</tr>
<tr>
<td>2.19c</td>
<td>Methyl Methacrylate/5-Vinyl-1,3,4-oxathiazol-2-one</td>
</tr>
<tr>
<td>2.19d</td>
<td>Methyl Methacrylate/5-Isopropenyl-1,3,4-oxathiazol-2-one</td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>2.20</td>
<td>Thermolysis of copolymers of Styrene and Methyl Methacrylate with 5-Vinyl-1,3,4-oxathiazol-2-one and 5-Isopropenyl-1,3,4-oxathiazol-2-one in the presence of Ethyl Cyanoformate and Dimethyl Acetylenedicarboxylate</td>
</tr>
<tr>
<td>2.20a</td>
<td>Styrene/5-Vinyl-1,3,4-oxathiazol-2-one</td>
</tr>
<tr>
<td>2.20a(i)</td>
<td>With Ethyl Cyanoformate</td>
</tr>
<tr>
<td>2.20a(ii)</td>
<td>With Dimethyl Acetylenedicarboxylate</td>
</tr>
<tr>
<td>2.20b</td>
<td>Styrene/5-Isopropenyl-1,3,4-oxathiazol-2-one</td>
</tr>
<tr>
<td>2.20b(i)</td>
<td>With Ethyl Cyanoformate</td>
</tr>
<tr>
<td>2.20b(ii)</td>
<td>With Dimethyl Acetylenedicarboxylate</td>
</tr>
<tr>
<td>2.20c</td>
<td>Methyl Methacrylate/5-Vinyl-1,3,4-oxathiazol-2-one</td>
</tr>
<tr>
<td>2.20c(i)</td>
<td>With Ethyl Cyanoformate</td>
</tr>
<tr>
<td>2.20c(ii)</td>
<td>With Dimethyl Acetylenedicarboxylate</td>
</tr>
<tr>
<td>2.20d</td>
<td>Methyl Methacrylate/5-Isopropenyl-1,3,4-oxathiazol-2-one</td>
</tr>
<tr>
<td>2.20d(i)</td>
<td>With Ethyl Cyanoformate</td>
</tr>
<tr>
<td>2.20d(ii)</td>
<td>With Dimethyl Acetylenedicarboxylate</td>
</tr>
<tr>
<td>2.21</td>
<td>Reaction of p-Nitrobenzohydroximoyl Chloride with Acrylonitrile/Styrene and Acrylonitrile/Vinylidene Chloride copolymers</td>
</tr>
<tr>
<td>2.21a</td>
<td>Acrylonitrile/Styrene copolymer</td>
</tr>
<tr>
<td>2.21a(i)</td>
<td>Modification with 10 moles of Hydroximoyl Chloride per mole of nitrile</td>
</tr>
<tr>
<td>2.21a(ii)</td>
<td>Modification of 0.25 moles of Hydroximoyl Chloride per mole of nitrile</td>
</tr>
<tr>
<td>2.21b</td>
<td>Acrylonitrile/Vinylidene Chloride copolymer</td>
</tr>
<tr>
<td>2.21b(i)</td>
<td>Modification with 10 moles of Hydroximoyl Chloride per mole of nitrile</td>
</tr>
<tr>
<td>2.21b(ii)</td>
<td>Modification with 0.25 moles of Hydroximoyl Chloride per mole of nitrile</td>
</tr>
<tr>
<td>2.22</td>
<td>Reaction of p-Nitrobenzohydroximoyl Chloride with cis-1,4-Polyisoprene and cis-1,4-polybutadiene</td>
</tr>
<tr>
<td>Section</td>
<td>Substance</td>
</tr>
<tr>
<td>-----------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>2.22a</td>
<td>cis-1,4-Polyisoprene</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>2.22b</td>
<td>cis-1,4-Polybutadiene</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>2.23</td>
<td>Reduction of p-Nitrobenzohydroximoyl Chloride modified cis-1,4-Polyisoprene and cis-1,4-Polybutadiene</td>
</tr>
<tr>
<td>2.23a</td>
<td>cis-1,4-Polyisoprene</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>2.23b</td>
<td>cis-1,4-Polybutadiene</td>
</tr>
</tbody>
</table>
## CONTENTS

<table>
<thead>
<tr>
<th>DISCUSSION</th>
<th>PAGE NO.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Modification of cis-1,4-Polyisoprene and cis-1,4-Polybutadiene with Nitrile Oxides.</td>
</tr>
<tr>
<td>3.1.1</td>
<td>Reaction of cyclooctene and 1-methylcyclohexene with p-nitrobenzohydroximoyl chloride.</td>
</tr>
<tr>
<td>3.1.2</td>
<td>Reaction of p-nitrobenzohydroximoyl chloride with cis-1,4-polyisoprene and cis-1,4-polybutadiene.</td>
</tr>
<tr>
<td>3.1.3</td>
<td>Reduction of polymer-bound nitro groups.</td>
</tr>
<tr>
<td>3.1.3a</td>
<td>Reduction with triirondodecacarbonyl.</td>
</tr>
<tr>
<td>3.1.3b</td>
<td>Reduction by catalytic hydrogenation.</td>
</tr>
<tr>
<td>3.2</td>
<td>Modification of Polymers containing Pendant Nitrile Groups with p-Nitrobenzohydroximoyl Chloride.</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Reaction of p-nitrobenzohydroximoyl chloride with acrylonitrile/styrene copolymer.</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Reaction of p-nitrobenzohydroximoyl chloride with acrylonitrile/vinylidene chloride copolymer.</td>
</tr>
<tr>
<td>3.3</td>
<td>Preparation and Reactions of Polymer-Bound Nitrile Sulphides.</td>
</tr>
<tr>
<td>3.3.1</td>
<td>Synthesis of 5-isopropyl-1,3,4-oxathiazol-2-one.</td>
</tr>
<tr>
<td>3.3.2</td>
<td>Thermolysis of 5-isopropyl-1,3,4-oxathiazol-2-one in the presence of ethyl cyanoformate and dimethyl acetylenedicarboxylate.</td>
</tr>
<tr>
<td>3.3.3</td>
<td>Synthesis of 1,3,4-oxathiazol-2-ones containing a pendant alkene group.</td>
</tr>
<tr>
<td>3.3.4</td>
<td>Thermolysis of 5-alkenyl-1,3,4-oxathiazol-2-ones in the presence of ethyl cyanoformate and dimethyl acetylenedicarboxylate.</td>
</tr>
<tr>
<td>3.3.5</td>
<td>Copolymerisation of 5-alkenyl-1,3,4-oxathiazol-2-ones with styrene and methyl methacrylate.</td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>3.3.6</td>
<td>Attempted copolymerisation of 5-(prop-1-enyl)-1,3,4-oxathiazol-2-one and 5-styryl-1,3,4-oxathiazol-2-one with styrene and methyl methacrylate.</td>
</tr>
<tr>
<td>3.3.7</td>
<td>Copolymerisation of ethyl 3-isopropenyl-1,2,4-thiadiazole-5-carboxylate and dimethyl 3-isopropenylisothiazole-4,5-dicarboxylate with styrene and methyl methacrylate.</td>
</tr>
<tr>
<td>3.3.8</td>
<td>Generation and reaction of polymer-bound nitrile sulphides from copolymers of 5-vinyl-1,3,4-oxathiazol-2-one and 5-isopropenyl-1,3,4-oxathiazol-2-one with methyl methacrylate and styrene.</td>
</tr>
<tr>
<td>3.3.8a</td>
<td>Thermolysis in an inert solvent.</td>
</tr>
<tr>
<td>3.3.8b</td>
<td>Thermolysis in the presence of ethyl cyanoformate and dimethyl acetylenedicarboxylate.</td>
</tr>
</tbody>
</table>

References

Published Papers
INTRODUCTION

Preamble

Chemical modification of polymers is becoming increasingly important, with many industrial processes being dependant on such reactions. An illustration of the value of this is the use of polymers as photoresists; these have many applications including printing, textile patterns, name plates and integrated circuits.

One method of producing integrated circuits involves the crosslinking of partly cyclised polyisoprene (1) using nitrenes generated from a bis-azide (2)\textsuperscript{1,2}.

\begin{align*}
(1) & \quad H_3C-\begin{array}{c}
\text{CH}_3 \\
\text{H}_2C-\begin{array}{c}
\text{CH}_2 \\
\end{array}
\end{array} \\
(2) & \quad \text{NR-CH=CH-CN}
\end{align*}

The silicon wafer is engraved by first coating the previously oxidised surface with a layer of cyclised polyisoprene (1) containing the bis-nitrene (2). Exposure to ultraviolet radiation leads to the production of a bis-nitrene which reacts with two polymer molecules to yield a crosslink. Thus exposure through a mask representing the desired circuitry leads to crosslinked areas which remain when the exposed resist is treated with a solvent for (1). These residual areas of crosslinked polymer then resist the action of the etch solution which exposes the unprotected regions of silicon. The resist is now removed and the regions of silicon exposed through the overlying layer of silica can now be doped with the desired electronically active impurities. This total sequence of oxidation, resist exposure, development, removal and
doping is usually repeated many times to produce the circuit.

The crosslinking of polymers with bis-nitrenes, especially bis-(sulphonyl nitrenes), has been used extensively to produce foams. The mechanism for the production of the crosslink is thought to involve insertion of the nitrenes into the C-H bond of two polymer molecules (Scheme 1).

**Scheme 1**

\[
\begin{align*}
N_3SO_2-\text{RSO}_2N_3 & \xrightarrow{\Delta} \text{NSO}_2-\text{RSO}_2N \\
\end{align*}
\]

Polymers or copolymers of vinyl chloride\(^4,5,6\), ethylene\(^7,8\), butadiene\(^9\), propylene\(^8,9,10\), styrene\(^6,11\), vinyl ethers\(^12\) and acrylates\(^13\) have been crosslinked in this way.

It has been claimed\(^14,15\) that nitrenes have been used to covalently link antioxidant groups to polymers. The advantage claimed for this is that it produces non-leachable antioxidant groups. The nitrenes, generated from the corresponding azides \((3)^{15}\) and \((4)^{14}\), were thought to insert into the C-H bonds of the polymers as before.
A number of modifications of polymers containing double bonds have been carried out in order to change the physical properties of the polymer, especially the thermal stability and the elasticity.

**cis-1,4-Polyisoprene** and **cis-1,4 - polybutadiene** have been reported to react with, for example, chlorosulfonfyl isocyanate\(^\text{16,17,18}\), monoperphthalic acid\(^\text{16}\), acetic anhydride\(^\text{16}\), trichlorosilane\(^\text{16}\), borohydranes\(^\text{16}\) and toluene-\(p\)-sulphenyl chloride\(^\text{19}\). **Trans-1,4-polybutadiene** and **3,4-polyisoprene** have also been shown to react with chlorosulfonfyl isocyanate\(^\text{17}\). A summary of these reactions is presented in Scheme 2.

The unsaturation present in some polymers has been used to add 1,3-dipoles\((a-b-c)\)

\[\text{\begin{tabular}{c}
  \(\sim C\equiv C\sim\) \\
  +
  \(a-b-c\)
  \end{tabular}\}

\[\xrightarrow{a-b-c} \text{\begin{tabular}{c}
  \(\sim H\equiv C\sim\)
  \\
  +
  \(a-b-c\)
  \end{tabular}\}

The 1,3-dipoles used contained substituents which became permanently bound to the polymer. In some cases the substituent was another 1,3-dipole, i.e. a bis-1,3-dipole, and the crosslinked polymer was obtained. In others, the substituent was a reactive group, allowing a reactive handle to be attached to the polymer. 1,3-Dipoles have also been added to polymers to modify their physical properties.

Polymer modification reactions via 1,3-dipoles will be discussed in detail in Section 1.4 after the concept of 1,3-dipolar cycloaddition has been described (Section 1.1). The preparation and reactions of two classes of 1,3-dipoles, nitrile oxides and nitrile sulphides, are of particular importance to this thesis and will be discussed in detail in Section 1.2 and 1.3 respectively.
1.1 1,3-DIPOLE CYCLOADDITIONS

1.1.1 The 1,3-Dipole

A 1,3-dipole may be defined as a system $a-b-c$, in which $a$ has an electron sextet, and carries a formal positive charge and $c$ is an anionic centre having a free electron pair. The reactive system $a-b-c$ is not normally capable of long lived existence unless there is a lone pair of electrons on $b$ which can fill the electron gap at $a$ by forming an additional bond, giving an all-octet structure as shown below.

$$\overset{+}{a} - \overset{+}{b} \overset{-}{c} \longleftrightarrow \overset{+}{a} = \overset{+}{b} - \overset{-}{c}$$

1,3-Dipoles containing a double bond must necessarily have nitrogen as the central atom $b$, as this is the only element capable of supplying an unshared electron pair while in the trivalent neutral state. Systems without a double bond may also contain oxygen as the central atom $b$.

1,3-Dipoles containing a double bond with nitrogen as the central atom $b$ are of particular importance to this thesis and are illustrated in Table 1.

**Table 1** Nitrogen centred 1,3-dipoles containing a double bond

<table>
<thead>
<tr>
<th>Structure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{-}$</td>
<td>Nitrile ylids</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{-}$</td>
<td>Diazo compounds</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Structure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{-}$</td>
<td>Nitrile ylids</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{-}$</td>
<td>Diazo compounds</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Structure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{-}$</td>
<td>Nitrile ylids</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{-}$</td>
<td>Diazo compounds</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Structure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{-}$</td>
<td>Nitrile ylids</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{-}$</td>
<td>Diazo compounds</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Structure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{-}$</td>
<td>Nitrile ylids</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{-}$</td>
<td>Diazo compounds</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Structure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{-}$</td>
<td>Nitrile ylids</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{-}C=\overset{-}{N}=\overset{-}{C}&lt;\overset{+}{\pi}$</td>
<td>Nitrile imines</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{-}$</td>
<td>Diazo compounds</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
<tr>
<td>$\overset{+}{N}=\overset{-}{N}=\overset{-}{N}&lt;\overset{+}{\pi}$</td>
<td>Azides</td>
</tr>
</tbody>
</table>
The ground state of 1,3-dipoles where \(a\) is carbon, \(b\) is nitrogen and \(c\) is oxygen or sulphur (i.e. nitrile oxides and nitrile sulphides) can be described by resonance structures 5a-e.

\[
\begin{align*}
\text{(5a)} & \quad -a\equiv b\equiv c \\
\text{(5b)} & \quad -a\equiv b\equiv c \\
\text{(5c)} & \quad -a\equiv b\equiv c \\
\text{(5d)} & \quad -a\equiv b\equiv c \\
\text{(5e)} & \quad -a\equiv b\equiv c
\end{align*}
\]

The all-octet structures 5a and 5b, being the most stable, are well represented in the ground state of the molecule, while 5c and 5e indicate that the formal charges are interchangeable and it is therefore expected that 1,3-dipoles will have a low dipole moment.

1.1.2 1,3-Dipolar Cycloaddition Reactions

1,3-Dipoles (\(a\equiv b\equiv c\)) react with multiple bond systems (d\(\equiv\)e), the dipolarophile, in a stereospecific manner to yield a five-membered compound (6) which carries no nett charge.

\[
\begin{align*}
\text{(6)} & \quad a\equiv b\equiv c \\
\text{d\(\equiv\)e} & \quad b\equiv c
\end{align*}
\]

The role of the dipolarophile can be filled by a variety of unsaturated groups including C\(\equiv\)C, C\(\equiv\)N, C=O, C=S, N=\(\equiv\)N, CEC and C\(\equiv\)N. In view of the wide range of atoms \(a\), \(b\) and \(c\) the scope for the synthesis of heterocycles is immense.

1.1.2a Mechanism

Huisgen\(^{20,22,23}\), has suggested that these reactions proceed by a concerted process in which two new \(\sigma\) bonds are formed simultaneously, but not necessarily in a synchronous manner (Path A, Scheme 3); in the
transition state (7) the new $\sigma$-bonds are both partially formed to
different extents.

An alternative two-step mechanism (Path B) has been postulated
by Firestone$^{24,25,26,27}$ which involves the reversible formation of
a discrete spin-paired diradical intermediate (8)

**Scheme 3**

The main point of disagreement is whether the energy barrier for
rotation ($E_r$) around bond d-e in intermediate (8) is greater than
the activation energy ($E_a$) for ring closure. Huisgen$^{22}$ claims that
$E_r < E_a$ and that if the reaction proceeded by Path B a mixture of
isomers would be obtained (Scheme 4).

**Scheme 4**

At the moment most workers$^{28,29,30}$ in this area favour the
concerted mechanism proposed by Huisgen.
1.1.3 Frontier Molecular Orbital Theory

Frontier molecular orbital theory has been used to rationalise the effect of substituents attached to the 1,3-dipole and the dipolarophile on the reactivity and regioselectivity of 1,3-dipolar cycloaddition reactions. Much of the work in this field is due to Houk \textsuperscript{31,32,33}, Bastide \textsuperscript{34,35,36} and Sustmann \textsuperscript{37,38}. Their examinations indicate that the relative reactivity of a given 1,3-dipole towards a series of dipolarophiles is determined primarily by the magnitude of the stabilization energy gained in the transition state by the interaction of the frontier orbitals of the two reactants.

The stabilization energy ($\Delta E$) produced in bond formation between centres a and c of the 1,3-dipole and centres d and e of the dipolarophile as they approach each other has been deduced from second-order molecular orbital perturbation theory as shown in Figure 1.
\[ \Delta E = \frac{2 \left[ c_a c'_e b_{ae} c_c c'_d b_{cd} \right]^2}{\Delta \gamma} + \frac{2 \left[ c'_a c_e b_{ae} c'_c c'_d b_{cd} \right]^2}{\Delta \gamma'} \]

\( \Delta \gamma \) and \( \Delta \gamma' \) represent the differences in the orbital energies (i.e. \( \Delta \gamma = E\psi_2 - E\psi_5 \), \( \Delta \gamma' = E\psi_A - E\psi_3 \), \( C \) and \( C' \) are atomic coefficients of the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) respectively. The resonance integral \( \beta \) is a function of the distance between the reacting centres involved; \( \beta \) is larger for the formation of C-C than C-N or C-O bonds.
1,3-Dipolar cycloaddition reactions become more favourable as the stabilization energy of the transition state increases. The largest stabilization energy ($\Delta E$) is obtained when the maximum overlap of atomic orbitals occur, i.e. when the atoms with the largest atomic orbital coefficients and the atoms with the smallest atomic orbital coefficients interact. The interaction of that HOMO and LUMO of the 1,3-dipole and the dipolarophile which results in the smallest change of orbital energy, $\Delta \gamma$ or $\Delta \gamma'$, will be favoured as it gives rise to the largest $\Delta E$.

1.1.3a Dipolarophile Energy Levels

The effects of substituents on the energy levels of the dipolarophile are two fold: they effect the orbital energy levels, and the atomic coefficients are modified (Figure 2).
Introduction of electron donating groups ($\tilde{X}, R$), raises the energy levels of both LUMO and HOMO by approximately the same amount. Purely electron withdrawing groups have the opposite effect; i.e. lowering both LUMO and HOMO energy levels to the same extent.

Conjugating substituents ($R'$) compress the frontier orbital levels by raising the HOMO and lowering the LUMO. Groups which are both electron withdrawing and conjugating ($Z$) have an effect composed from their two parts; this results in a small lowering of the LUMO energy level and a large lowering of the HOMO energy level.

Substitution of one of the carbon atoms of the double bond by a heteroatom leads to a lowering of the HOMO and LUMO energy levels with respect to the corresponding ethene. This has been attributed to the greater electronegativity of the heteroatoms (e.g. N and O).

Electron releasing groups (alkyl, OR, NR$_2$) increase the atomic coefficient at the point of attachment in the LUMO and lowers it in
the HOMO. Purely electron withdrawing groups (e.g., CCl₃) have exactly the opposite effect. Conjugating (-CH=CH₂, Ph etc.) or conjugating accompanied by electron withdrawing substituents (CHO, CO₂R, CN etc.) give rise to smaller atomic coefficients at the point of attachment in both LUMO and HOMO orbitals. When a heteroatom (O or N) has been substituted for a carbon in the double bond, the larger atomic coefficient is found on the heteroatom in the HOMO and on the carbon atom in the LUMO.

1.1.3b 1,3-Dipole Energy Levels

The HOMO/LUMO energy levels and the atomic orbital coefficients for 1,3-dipoles have been obtained using CNDO/2 calculations; the results for unsubstituted carbonyl ylid (9), nitrile imine (10), nitrile oxide (11) and benzonitrile sulphide (12), with respect to ethene, are given in Figure 3.

Figure 3
Substituent effects on 1,3-dipoles have been less well studied than those on dipolarophiles, although they are known to have the same general effect on the energy levels.

1.1.3c Classification of Reactions

According to Sustman, 1,3-dipolar cycloadditions can be classified into three types (Figure 4).

Type (1), where the interaction of the HOMO of the dipole with the LUMO of the dipolarophile is greatest, eg carbonyl ylids (9) (Figure 3).

Type 2, where both frontier orbital interactions must be taken into account, eg nitrile imines (10) (Figure 3).

Type 3, where interaction of the LUMO of the dipole with the HOMO of the dipolarophile predominates, eg nitrile oxides (11) (Figure 3).
1.1.3d Regioselectivity

According to Fukui\textsuperscript{39}, cycloaddition reactions take place in the direction which allows the maximum overlap of frontier molecular orbitals. The two possible orientations for the 1,3-dipolar cycloaddition reaction of dipole $\tilde{a}$-b-$\tilde{c}$ with dipolarophile d=e are shown in Figure 5.

Formation of bond a-e will be favoured over bond a-d in the transition state as this produces a greater overlap of atomic orbitals and therefore a larger stabilization energy. This leads to a greater proportion of the product having orientation (a) than (b).
Frontier molecular orbital theory has been applied successfully to explain the differences in regioselectivity of benzonitrile oxide towards methyl acrylate\textsuperscript{40} and vinyl ethers\textsuperscript{41} (Scheme 5).

Scheme 5

\begin{equation}
\begin{array}{c}
\text{CH}_2=\text{CHCO}_2\text{Me} \\
\text{PhC}=\text{N}=\text{O} \\
\text{CH}_2=\text{CHOR}
\end{array}
\begin{array}{c}
\text{Ph} \\
\text{Ph}\text{C}=\text{N}=\text{O} \quad (13) \text{95-97\%} \\
\text{Ph} \quad (14) \text{3-5\%} \\
\text{Ph} \quad (15) \text{100\%}
\end{array}
\end{equation}

Benzonitrile oxide reacts with methyl acrylate to give a mixture of the 3-phenyl-2-isoxazoline 4- and 5-carboxylate, (13) and (14), whereas the corresponding reaction with vinyl ethers yields only the 5-substituted compound (15). The atomic orbital energies for benzonitrile oxide, methyl acrylate and vinyl ether are shown in Figure 6.

Figure 6
The electron deficient double bond of vinyl ethers have the larger coefficient at the unsubstituted carbon in both $\psi_A$ and $\psi_B$. Frontier molecular orbital theory predicts that the 5-substituted isoxazoline (15) should be produced via the dominant $\psi_A - \psi_3$ interaction, and this was found experimentally, with no 3-phenyl-4-substituted isoxazoline being obtained.

For the reaction of benzonitrile oxide with methyl acrylate it is predicted, from the union of the largest atomic coefficients, that 5-substituted isoxazoline (13) should be produced and this is the major regioisomer found. However, as the coefficients at carbon and oxygen in $\psi_3$ are comparable and the difference between the $\alpha$ and $\beta$ - coefficients of methyl acrylate is small, the formation of a small amount of 3-phenyl-4-substituted isoxazoline (14) is not surprising. The interaction $\psi_2 - \psi_B'$ must also be taken into account. Despite the greater value of $\Delta \psi (= \psi_2 - \psi_B')$ which is in the denominator, the larger coefficients at the ends of the dipole and at the end of the $\alpha$ and $\beta$ carbons of the acrylate ester increase the numerator. This latter interaction favours the formation of the minor isomer (14).

1.2 NITRILE OXIDES

1.2.1 History

Nitrile oxides were first discovered, although not fully understood, as salts with mercury and silver by Howard$^{42}$ in 1800. The first purely organic nitrile oxide, fulminic acid, was synthesised by Neff$^{43}$ from nitromethane, although the structure was not fully
elucidated until the work of Ley\textsuperscript{44} in 1899. Theoretical support for Ley's formulation (11a) was given by Pauling\textsuperscript{45}, when he calculated the potential energies for structures (11a) and (16), showing (11a) to be favoured over (16).

\begin{align*}
\text{H} - \text{O} - \text{N} &= \text{C} : & \text{H} - \text{C} &= \text{N} - \text{O} \\
(16) & & (11a) & & (11b)
\end{align*}

The last important obstacle, the ability of (11) to account for the known reactions of nitrile oxides was finally cleared by Huisgen's\textsuperscript{23} concept of 1,3-dipolar reactivity. In this he proposed that the correct representation was a resonance hybrid of structures (11a) and (11b).

1.2.2 Generation of Nitrile Oxides

Nitrile oxides have been generated by a variety of methods, the two most important being the dehydrohalogenation of hydroximoyl halides (usually chlorides), and the dehydrogenation of aldoximes.

1.2.2a From Hydroximoyl Chlorides

Dehydrohalogenation of hydroximoyl chlorides has been achieved by heating in an inert solvent or by the action of base.\textsuperscript{49} The hydroximoyl chlorides themselves are prepared by chlorination of the corresponding aldoxime (formed from the reaction of the aldehyde with hydroxylamine), either directly with chlorine or by the use of nitrosyl chloride.
Hydroximoyl chlorides are excellent precursors as most are indefinitely stable at room temperature, and will generate the nitrile oxide rapidly when required.

1.2.2b From Aldoximes

Aldoximes have been reported to generate nitrile oxides on dehydrogenation with an alkaline solution of hypobromite. Dehydrogenation occurs from the syn-aldoxime only, although under the reaction conditions most anti-aldoximes undergo facile rearrangement to the syn form. This method has proved to be especially useful in cases where the nitrile oxide cannot be prepared via the hydroximoyl chloride because of side reactions during the chlorination step.

The above method failed when alkali-labile groups, or groups unstable towards the oxidising agent were present. A milder and more selective dehydrogenation has been achieved using N-bromosuccinimide in the presence of alkali alkoxides or tertiary bases. This modification has allowed the preparation of heterocyclic and polyfunctional nitrile oxides and is considered to be one of the most generally applicable procedures.

1.2.2c From Nitroparaffins

Nitrile oxides can be generated from nitroparaffins by treatment with base and dehydration with, for example, isocyanates (Scheme 6).
1.2.2d From 1,2,5-Oxadiazole-N-Oxides

Nitrile oxides can be generated by thermolysis of 1,2,5-oxadiazole-N-oxides (furoxans) which are readily synthesised from bis-aldoximes\textsuperscript{50-53}, alkenes\textsuperscript{54} and 1,2-dinitroalkenes\textsuperscript{55} (Scheme 7.)

In the case where R and R' are linked, bis-nitrile oxides are formed. If the thermolysis is carried out in the presence of a suitable
dipolarophile, i.e. phenyl acetylene^{52}, a bis-heterocyclic compound (17) is formed. If no suitable dipolarophile is present, a polymeric furoxan (18) is obtained^{56} (Scheme 8).

**Scheme 8**

1.2.2e **Other Sources**

Nitrile oxides can be generated in several other ways i.e. from furazans (19)^{50,57-59}, nitrolic acids (20)^{49}, 1,3,2,4-dioxiathiazole-2-oxides (21)^{14,15,60} and potassium salts of dinitroalkanes (22)^{61} (Scheme 9).
These methods are seldom used as the nitrile oxides can be more easily obtained by the methods described previously.

1.2.3 Properties of Nitrile Oxides

1.2.3a Structure

The most generally accepted representation of a nitrile oxide is a resonance hybrid (I1a-e)\(^{49}\).
The all octet structures (11a) and (11c) represent the preferred electron distribution in the ground state, while the sextet structure (11b) expresses best most of the reactions of nitrile oxides, especially 1,3-dipolar cycloadditions.

1.2.2b Stability

All simple aliphatic and most aromatic nitrile oxides are indefinitely stable only at low temperatures (normally below -70°C). When the temperature is allowed to rise the nitrile oxides spontaneously dimerise to the 1,2,5-oxadiazole-\(N\)-oxide (furoxan) (23) or rearrange to isocyanate (24).

\[
\begin{align*}
R - C = N & - O \\
\begin{array}{c}
> -70^\circ C \\
R \neq H
\end{array} & \rightarrow \begin{array}{c}
R \\
N=O
\end{array} + R - N = C = O \\
(23)
\end{align*}
\]

The ratio of furoxan to isocyanate varies with temperature and the nature of the nitrile oxide. The more thermally unstable the nitrile oxide, the greater the proportion of furoxan. An increase in temperature in general leads to a larger proportion of isocyanate.
Aromatic nitrile oxides substituted in the o,o-positions with bulky groups are sterically hindered towards dimerisation. These tend to be long lived at room temperature although they rearrange to isocyanates on heating.

1.2.4 1,3-Dipolar Cycloadditions of Nitrile Oxides

1,3-Dipolar cycloaddition reactions of nitrile oxides with multiple bond systems are well known and have been the subject of a recent review\textsuperscript{49}. The mechanism of such reactions has been discussed in Section 1.1.2a.

Cycloaddition occurs with alkenes, alkynes, activated carbonyls (actuated with electron withdrawing groups), thiocarbonyls, aldimines and ketimines, aromatic nitriles, activated aliphatic nitriles (actuated with electron withdrawing groups) and some other unsaturated systems (Scheme 10). The order of reactivity is $\text{C=O} > \text{C=C} > \text{C=S} > \text{C=N}$. Nitrile oxides have also been shown to react with compounds (25) to (27) although the rings formed normally cleave and undergo a further reaction.

\[
\begin{align*}
\text{N} - \text{CO}_2\text{R} \\
\text{N} - \text{CO}_2\text{R} \\
\text{N} - \text{CO}_2\text{R}
\end{align*}
\]

\[
\begin{align*}
\text{R}^- \quad \text{P} & \quad \text{Ar} - \text{N} = \text{PPH}_3
\end{align*}
\]

1.2.4a Cycloaddition to Simple Aliphatic Nitriles

The reaction of 1,3-dipoles with aliphatic nitriles is of particular importance to this thesis. Unlike the corresponding
reactions with alkenes which are well documented, no recent review is available on this subject. A comprehensive summary of these reactions is therefore presented at this stage.

The reactions of nitrile oxides with aromatic and heterocyclic nitriles as well as aliphatic nitriles activated with electron withdrawing groups are well established. The reaction with simple aliphatic nitriles has been reported to yield only the furoxan (23), with no 1,2,4-oxadiazole being formed. In these cases the nitrile oxide was generated either in situ from the hydroximoyl chloride by refluxing in toluene or by the addition of the nitrile oxide (from the hydroximoyl chloride plus triethylamine) to the neat refluxing nitrile.

The reaction with simple aliphatic nitriles has been reported to yield the 1,2,4-oxadiazole in the presence of a catalytic amount of boron trifluoride. The function of the boron trifluoride is to polarize the cyano group, resulting in an increase in electron density at the carbon, with a corresponding decrease at nitrogen. The reaction is thought not to be a concerted cycloaddition, rather a two stage process involving a zwitterion intermediate.

Evidence for this proposal has been presented by Meyers and Sircar, based on the work of Morrocchi et al and Tielmann. The reaction of benzonitrile oxide with ethyl cyanoacetate under alkaline conditions has been reported to yield only the isoxazole (28). Repeating the reaction in the presence of boron trifluoride yielded the 1,2,4-oxadiazole (29) in 14% yield. Meyers and Sircar proposed that both products arise from a common zwitterion (30).
The first successful concerted cycloaddition of nitrile oxides with simple aliphatic nitriles was reported in 1963 by Leandrol et al.\textsuperscript{71} Thermolysis of p-phenylbenzohydroximoyl chloride (31) in the presence of 1-cyano-2-methylpropane (32) gave the corresponding 1,2,4-oxadiazole (33).

\[
\text{PhC} \equiv \text{N}^+ \text{O}^- + \text{CH}_2(\text{CO}_2\text{Et})\text{CN} \rightarrow \text{PhC} \equiv \text{N}^+ \text{CH}_2\text{CO}_2\text{Et}
\]

(30)

\[
\begin{array}{c}
\text{PhC} \equiv \text{N}^+ \text{O}^- \ \text{no BF}_3 \\
\text{Ph} \text{HCC} \equiv \text{N}^- \text{O}^+ \text{CH}_2\text{CO}_2\text{Et} \\
\text{Ph} \text{N} \text{N} \text{O} \text{CH}_2\text{CO}_2\text{Et} \text{NH}
\end{array}
\]

(28)

(29)

More recently Beltrame et al.\textsuperscript{72} have reacted a series of aromatic nitrile oxides with simple aliphatic nitriles (Scheme II).
1.3-Addition Reactions Leading to Open-Chain Structures

Owing to the electrophilicity of the carbon atom of nitrile oxides, the reaction with a generalized nucleophile $B\cdot H$ leads to a product where the nucleophilic part of the reagent has joined the carbon atom of the nitrile oxide and oxygen bears the remaining proton.

$$ R - C \equiv N - O + B\cdot H \rightarrow R - C(B) = NOH $$

$(BH = H_2O/H^+, \text{ PhOH, RSH, RNH}_2$ etc)

This reaction, which is general for a wide range of nucleophiles, has been the subject of a review by Grundmarrn and Grünanger\textsuperscript{49}. 

The order of reactivity is given as $CH_3 < Et = n - Pr < i-Pr$.
NITRILE SULPHIDES

In contrast to the extensively studied nitrile oxides, discussed in Section 1.2, nitrile sulphides have a relatively short history, the first evidence for their existence being obtained by Franz and Black in 1970\(^7\). The investigation of nitrile sulphides has progressed slowly since then as can be seen by the small amount of material in the literature (ca 25 papers).

The only direct evidence for their existence has come from low temperature (85K) spectroscopic studies\(^7\), while the remainder is largely circumstantial, coming from the identification of adducts formally derived by 1,3-dipolar cycloaddition reactions when suitable "traps" were present. This evidence is different for each method of generation and will be discussed in detail in conjunction with the preparative technique.

1.3.1 Thermal Generation of Nitrile Sulphides

Four thermal routes to nitrile sulphide have been reported. These involve the pyrolysis of labile precursors viz 1,3,4-oxathiazol-2-ones\(^7\), N-thiocarbonyl diphenylsulphimides\(^7\), iminosulphur difluorides\(^7\) and 1,4,2-diathiazol-5-ones\(^7\).

1.3.1a From 1,3,4-Oxathiazol-2-ones

The chemistry of nitrile sulphides was initiated by Franz and Black\(^7\) in 1970 when a solution of 5-phenyl-1,3,4-oxathiazole-2-one (34a) was thermolysed in an inert solvent. The products of the reaction were benzonitrile, sulphur and carbon dioxide.
The possible intermediacy of the thermally labile nitrile sulphide (35a) was tested by carrying out the reaction in the presence of dimethyl acetylenedicarboxylate (DMAD). Isolation of the 1,3-dipolar cycloadduct, dimethyl 3-phenylisothiazole-4,5-dicarboxylate (36a), in good yield (90%) provided strong support for the formation of benzonitrile sulphide (35a).

A further indication of the intermediacy of nitrile sulphide (35a) was obtained by reacting (34) with ethyl propiolate and isolating isothiazole-4 and 5-carboxylates (37) and (38) respectively. Both regioisomers were formed in 35% yield.

Three possible mechanisms for these reactions were considered by Howe to explain the formation of these isothiazoles (Scheme 12).
Path C, involving the heterolysis of a C-S bond producing the ionic species (39), followed by Michael addition to ethyl propiolate is inconsistent with the formation of both (37) and (38). Kinetic studies indicated that the rate of disappearance of oxathiazolone was independent of the concentration of DMAD, consistent only with Path A.

Oxathiazol-2-ones have been used to generate nitrile sulphides containing a large number of substituents and are the most widely used source. They are stable at room temperature and are rapidly synthesised from the corresponding amide and chlorocarboxymethylsulphenyl chloride in good yield.
**1.3.1b From N-Thiocarbonyl Diphenylsulphimides**

N-Thiocarbonyl diphenylsulphimides (41), formed by the reaction of diphenylsulphimide (41) with dithiobenzoates (42), have been reported to give diphenyl sulphide and sulphur when heated at 70°C. Thermolysis in the presence of an excess of electron deficient acetylenes yielded the corresponding isothiazole (36) in moderate yields (25 - 50%).

\[
\text{Ph}_2S-\text{NH} + \text{RS-}C\text{-Ar} \xrightarrow{\text{S}} \text{Ph}_2S=\text{N-}C\text{Ar} \quad (40)
\]

Kinetic data shows that the rate of decomposition of (40) is first order and that for the reactions with acetylenes the rate of disappearance of (40) equals the rates of appearance of both isothiazole (36) and nitrile. The rate of consumption of N-thiocarbonyl diphenylsulphimide is independent of the dipolarophile concentration but greatly affected by its electrophilic activity, with rates for R = PhCO > MeOOC > Ph. The activation entropy was found to be positive, ruling out transition states such as (43), where there was an increase in order.
The mechanism proposed\textsuperscript{75} (Scheme 13), involves initial formation of thiazirine (44), followed by either fragmentation to nitrile and sulphur (Path A), or ring opening to the nitrile sulphide, which then undergoes 1,3-dipolar cycloaddition with the acetylene (Path B). As the rate of appearance of nitrile was unaffected by the dipolarophile concentration it was concluded, in conflict to the work of Franz and Black\textsuperscript{73}, that (Path C) was unlikely.

Scheme 13

\[
\begin{align*}
\text{Ph}_2\text{S} + \text{N} & \rightleftharpoons \text{Ph}_2\text{S} + \text{N} \\
\text{A}r & \rightleftharpoons \text{A}r \\
\text{N} & \rightleftharpoons \text{N} \\
\end{align*}
\]

1.3.1c From Iminosulphur Difluorides

Thermolysis of (N-benzylimino)sulphur difluoride (45) in a sealed tube has been reported\textsuperscript{79,81} to yield sulphur, benzonitrile and 2,4,6-triphenyl-1,3,5-triazine (46); formation of (46) is thought to occur by acid-catalysed trimerisation of benzonitrile\textsuperscript{76}. 
The intermediacy of benzonitrile sulphide in this reaction was demonstrated by heating (45) and DMAD in the presence of two equivalents of sodium fluoride and 0.1 equivalents of 18-crown-6-polyether, and isolating the isothiazole (36a) in 65% yield.

The crown ether is believed to partially solubilise sodium fluoride, allowing fluoride ion to catalyse the elimination of hydrogen fluoride from (45)\textsuperscript{76}.

\[ \text{Ph-CN} + \text{S} \rightarrow \text{Ph-CN} + \text{S} \]

1.3.1d From 1,4,2-Dithiazol-5-one

Thermolysis of 1,4,2-dithiazol-5-ones have been reported\textsuperscript{77} to generate nitrile sulphides. Heating 3-phenyl-1,4,2-dithiazol-5-one (47)
in the presence of DMAD at 160°C gave 3-phenylisothiazole-4,5-dicarboxylate (36a) in 52% yield.

\[
\begin{align*}
\text{Ph-C=S} + \text{Cl}_3\text{CSCL} & \rightarrow \text{Ph-N=S} + \text{Ph-N=NPh} \\
\text{Ph-CO}_2\text{Me} & \rightarrow \Delta \text{DMAD} \rightarrow \text{Ph-N=S} - \text{N=O}
\end{align*}
\]

(36a) (47)

Nitrile sulphides have also been generated from 1,3,4-oxathiazoles (48) and 1,2,4-thiadiazolines (49), which are prepared by the reaction of 1,3,4-oxathiazol-2-ones with ketones and imines respectively by rare retro-1,3-dipolar cycloadditions.

\[
\begin{align*}
\text{R'N=S} & \rightarrow \text{R''N=S} \\
\text{R'O} & \rightarrow \text{R'O}
\end{align*}
\]

(48) (49)

The methods of generating nitrile sulphides discussed in sections 1.3.1b-d offer little or no advantage over the use of 1,3,4-oxathiazol-2-ones and are seldom used synthetically.
1.3.2 Photolytic Generation of Nitrile Sulphides

A variety of phenyl substituted five-membered heterocyclic compounds containing C, N and S have been examined with a view to photolytically generating nitrile sulphides \(74,82,84-91\). These compounds were photolysed in an inert solvent and in the presence of DMAD\(^8\). The presence of the intermediate was demonstrated by the isolation of sulphur and nitrile, and the 3-phenylisothiazole-4,5-dicarboxylate respectively. The heterocycles which fulfilled this criterion were of three types, differing in the ring positions of the nitrile sulphide forming nitrogen and sulphur atoms (Scheme 14).

\(\text{Scheme 14}\)

**Type I**

Type II

\[
\ce{Ph\(\rightarrow\)N.S(X.Y) \rightarrow \text{hv} \rightarrow \left[\text{Ph-C\(=\)N-S}\right]} \quad \Delta \quad \text{hv} > 140K \rightarrow \left[\text{Ph-C\(=\)N-S}\right] \rightarrow \text{PhC\(=\)N S} \quad (50)
\]

Type III

Photolytic fragmentation of the heterocyclic compounds of Types I - III, with formation of nitrile sulphide, apparently takes place by
Table 2  Yields of isothiazole (36a) formed by photolysis of compounds of Types I - III in neat dimethyl acetylenedicarboxylate

\[
\text{I-III} \xrightarrow{hv} \left[ \text{Ph-C≡N-S} \right] \xrightarrow{DMAD} \text{Ph} \begin{array}{c} \text{C} \end{array} \text{Me} \quad \text{N} \begin{array}{c} \text{C} \end{array} \text{O} \begin{array}{c} \text{Me} \end{array}
\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>% Yield (36a)</th>
<th>Compound</th>
<th>% Yield (36a)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type I</strong></td>
<td></td>
<td><strong>Type III</strong></td>
<td></td>
</tr>
<tr>
<td>Ph₅S₅O₅</td>
<td>19</td>
<td>Ph₅N₅S₂</td>
<td>8</td>
</tr>
<tr>
<td>(34a)</td>
<td></td>
<td>(51)</td>
<td></td>
</tr>
<tr>
<td>Ph₅S₅S₅</td>
<td>11</td>
<td>Ph₅N₅S₂⁺⁻</td>
<td>8</td>
</tr>
<tr>
<td>(52)</td>
<td></td>
<td>(53)</td>
<td></td>
</tr>
<tr>
<td><strong>Type II</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ph₅O₅N₁</td>
<td>8</td>
<td>Ph₅N₅O₂</td>
<td>9</td>
</tr>
<tr>
<td>(54)</td>
<td></td>
<td>(55)</td>
<td></td>
</tr>
<tr>
<td><strong>Type III</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ph₅N₅⁺⁻</td>
<td>21</td>
<td>Ph₅N₅S₂⁺⁻</td>
<td>10</td>
</tr>
<tr>
<td>(56)</td>
<td></td>
<td>(57)</td>
<td></td>
</tr>
<tr>
<td>Ph₅N₅S₂⁻</td>
<td>9</td>
<td>Ph₅N₅S₂⁻</td>
<td>5</td>
</tr>
<tr>
<td>(58)</td>
<td></td>
<td>(59)</td>
<td></td>
</tr>
<tr>
<td>Ph₅N₅S₂⁻</td>
<td>7</td>
<td>Ph₅N₅S₂⁻</td>
<td>12</td>
</tr>
<tr>
<td>(60)</td>
<td></td>
<td>(61)</td>
<td></td>
</tr>
</tbody>
</table>
the extrusion of a small fragment $X=Y$ (e.g., CO, CO$_2$, COS, CS$_2$, N$_2$).
In each case initial formation of thiazirine (50) has been assumed
(Scheme 14) although the reaction may take place with direct formation
of nitrile sulphide without intermediates or, less likely, proceed via
individual mechanisms in each case.

Irradiation of compounds of Types I - III in neat DMAD yielded
3-phenylisothiazole-4,5-dicarboxylate (36a); some examples are
listed in Table 2.

1.3.3 Reactions of Nitrile Sulphides

Nitrile sulphides have been reported to react with a wide
variety of dipolarophiles. The discussion presented here will be
confined to reactions in which the nitrile sulphide is generated
thermally, especially from 1,3,4-oxathiazol-2-ones, although the
same products are normally isolated from photolytic sources.

Compared with the analogous thermal reactions, photochemical
yields are low (5-22%)$^{87}$; for example, the photochemical reaction of
5-phenyl-1,3,4-oxathiazol-2-one (34a) with DMAD gave a 22% yield of
the corresponding isothiazole (36a), whereas the yield was 90.5% for
the thermal reaction. It has been suggested$^{87}$ that the lower photo-
chemical yields are due to the destruction of the benzonitrile
sulphide, yielding benzonitrile and sulphur, as a result of energy
transfer.

1.3.3a Cycloaddition to Carbon-Carbon Multiple Bonds

Nitrile sulphides have been reported to undergo 1,3-dipolar
cycloaddition reactions with electron poor double and triple bonds,
including DMAD\textsuperscript{73}, phenyl propiolate\textsuperscript{92}, 5-norbonene-\textit{cis}, endo-2,3-dicarboxylate\textsuperscript{92} and 1,4-naphthoquinone\textsuperscript{93} (Scheme 15). In all cases, sulphur and nitrile were formed as by-products due to the competing decomposition of the nitrile sulphide.

Scheme 15

Product (64) is thought to be formed by an initial 1,3-dipolar cycloaddition to the alkene bond of naphthaquinone, forming an isothiazoline, which is subsequently oxidised to the isothiazole with a second molecule of naphthaquinone.
1.3.3b Cycloaddition to Nitriles

Nitrile sulphides have been reported\textsuperscript{94,95} to react with nitriles containing substituents which are conjugating and/or electron withdrawing, to yield the corresponding thiadiazoles (66) in good yield (28-73\%).

\[
\begin{align*}
R & \quad \overset{\Delta}{\rightarrow} \quad [R-\text{C} & \equiv & \text{N} & \equiv & \text{S}] & \quad \overset{R-C \equiv N}{\rightarrow} & \quad R' \\
\text{R} & \quad \text{N} & \quad \text{S} & \quad \text{R} & \quad \text{N} & \quad \text{S} & \quad \text{R} & \quad \text{N} & \quad \text{S}
\end{align*}
\]

In some cases the by-product (67) was isolated in 2-8\% yield, it was thought\textsuperscript{94} to have resulted from direct sulphur atom transfer between RCNS and R′CN, with subsequent cycloaddition with another molecule of R′CN.

\[
\begin{align*}
[R-\text{C} & \equiv & \text{N} & \equiv & \text{S}] & \quad \overset{R'-C \equiv N}{\rightarrow} & \quad [R-\text{C} & \equiv & \text{N} & \equiv & \text{S}] & \quad \overset{R'-C \equiv N}{\rightarrow} & \quad R' \\
\text{R} & \quad \text{N} & \quad \text{S} & \quad \text{R} & \quad \text{N} & \quad \text{S} & \quad \text{R} & \quad \text{N} & \quad \text{S}
\end{align*}
\]
Recently it has been reported\(^9\) that thermolysis of oxathiazol-2-ones in the presence of activated carbonyl compounds yields the corresponding oxathiazoles (48) in reasonable yields (18-76\%).

\[ R-CN \xrightarrow{\Delta} \left[ R-C=N^- - S \right] \xrightarrow{RC=O} R' + R-C=N + S \]

\( R' = \text{CCl}_3 \text{ or CF}_3 \)

\( R'' = \text{H, Ph, CCl}_3 \)

In general for all these cycloaddition reactions, the yield of the cycloadduct increased as: the molar excess of dipolarophile increased, the electron deficiency of the dipolarophile increased and the reaction temperature increased.

The effect of the molar excess of dipolarophile was shown by Howe\(^9\), who investigated the effect, on the yield of isothiazole, of varying the molar excess of nitrile present during the thermolysis of oxathiazolone; the results are given in Table 3.

<table>
<thead>
<tr>
<th>Molar ratio of nitrile to oxathiazolone</th>
<th>Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 : 1</td>
<td>14</td>
</tr>
<tr>
<td>35 : 1</td>
<td>39</td>
</tr>
<tr>
<td>100 : 1</td>
<td>72</td>
</tr>
</tbody>
</table>

Howe suggested that during the reaction, sulphur chains grow by either reacting with RCNS, or by combining with other sulphur chains. Since the sulphur species originate from RCNS, a decrease
in the ratio of oxathiazolone to nitrile will give a lower concentration of sulphur chains relative to nitrile, resulting in a greater yield of thiadiazole. Howe therefore suggests that the yield of cycloadduct can be maximised by adding the oxathiazolone dropwise to a solution of the dipolarophile at elevated temperature.

The reactions of nitrile sulphides are HOMO controlled with respect to the dipole (see Section 1.1.3c for definition). The presence of electron withdrawing groups in the dipolarophile increases the rate of the cycloaddition reaction, while leaving the rate of the competing decomposition to nitrile and sulphur unaffected.

It has been proposed that the rate of cycloaddition increases more rapidly with temperature than the competing decomposition reaction, leading to an increase in yield with temperature.

1.4 1,3-Dipolar Cycloadditions involving Polymers

1,3-Dipoles have been used to modify polymers and to produce new polymers. Selected examples of each case will be discussed.

1.4.1 Polymer Formation using 1,3-Dipoles

Thermally stable poly (1,2,4-oxadiazoles) (68), polyisoxazoles (69) and poly (2-isoxazolines) (70) have been produced by the reactions of bis-nitrile oxides with bis-nitriles, bis-acetylenes and bis-alkenes respectively. These are shown in (Scheme 16) along with the polyfuroxan (71) formed by
Scheme 16

\[
\begin{align*}
[ & C_6H_5/\overset{\text{N}}{\text{N}} \backslash C_6H_4/\overset{\text{O}}{\text{O}} \backslash C_6H_4/\overset{\text{N}}{\text{N}} \backslash C_6H_5/ ]_{n}. \\
\text{N=}=C-C_6H_4=\overset{\text{N}}{\text{C}}
\end{align*}
\]

\[
\begin{align*}
\text{CCl}=\overset{\text{NOH}}{\text{O}} & \text{ C=N} \overset{\text{+}}{\text{O}} \\
\text{CCl}=\overset{\text{NOH}}{\text{O}} & \text{ C=N} \overset{\text{+}}{\text{O}} \\
\end{align*}
\]

Scheme 17

\[
\begin{align*}
\text{Ph}=\overset{\text{N}}{\text{N}} \overset{\text{=}C_6H_4=N} \overset{\text{N}}{\text{N}} \overset{\text{=}N} \overset{\text{N}}{\text{N}} \overset{\text{=}N} \overset{\text{Ph}}{\text{Ph}} & \overset{\text{\Delta}}{\text{N}} & \text{Ph}=\overset{\text{N}}{\text{N}} \overset{\text{=}C-C_6H_4=C=\overset{\text{N}}{\text{N}} \overset{\text{=}N} \overset{\text{N}}{\text{N}} \overset{\text{=}N} \overset{\text{Ph}}{\text{Ph}} \\
\text{N=}=C-C_6H_4=\overset{\text{N}}{\text{C}}
\end{align*}
\]
dimerisation of the bis-nitrile oxides in the absence of a suitable
dipolarophile\textsuperscript{102-104} . Similar reactions have also been carried out
with bis-nitrile imines, generated from bis-1,2,3,4-tetrazoles, with
bis-nitriles, to give the polytriazoles (72)\textsuperscript{105} (Scheme 17).

1.4.2 Modification of Polymers via 1,3-Dipolar
Cycloaddition Reactions

1,3-Dipolar cycloaddition reactions have been carried out on
polymers for three reasons: to cause crosslinking, to attach active
or reactive groups and to modify the physical properties of the
polymer.

1.4.2a Polymer Crosslinking

Several polymers and copolymers containing unsaturation\textsuperscript{106},
including polybutadiene\textsuperscript{107,108}, have been crosslinked with bis-nitrile
oxides. The bis-nitrile oxides used were generated, either from the
corresponding bis-hydroximoyl chloride (73) or by thermolysis of
cyclic furoxans (74). Cycloaddition with the alkene bonds present
in two different polymer chains yielded a crosslinked material (75).

\[
\begin{align*}
\text{ONO} &= \text{CCl}_2\text{R}-\text{CCl}_2=\text{NOH} \\
(73) \\
\xrightarrow{\text{+}} & \quad \cdots \text{CH=CH}\quad \cdots \\
-\text{O}-\text{N} &= \text{C-R}-\text{C} = \text{N-O} \\
(74) \\
\xrightarrow{\text{+}} & \quad \cdots \text{CH=CH}\quad \cdots \\
\text{R} \\
(75)
\end{align*}
\]
1.4.2b Addition of Active and Reactive Groups

Reactive groups, such as carboxylic acids and esters, have been attached to cis-1,4-polyisoprene and cis-1,4-polybutadiene via 1,3-dipolar cycloaddition reactions of nitrile oxides. Some transformations have also been performed on the substituents thus introduced; for example esters have been converted to amides and carboxylic acids\textsuperscript{109}.

As with nitrenes, it is claimed that antioxidant groups may be attached to cis-1,4-polyisoprene by 1,3-dipolar cycloaddition with substituted nitrones\textsuperscript{110}; the advantage claimed being that it produces a non-leachable antioxidant.

1.4.2c Modification of Physical Properties

1,3-Dipolar cycloadditions of nitrile imines, nitrile oxides and nitrones to polymers containing unsaturation have been used to modify their physical properties (thermal stability and elasticity) as discussed below.

1.4.2c.i Nitrile Imines

Modification of polymers containing activated double bonds with diphenyl nitrile imine has been reported to occur in good yield\textsuperscript{111-114}, giving polymer (76) (Table 4)

\[
\begin{array}{c}
\begin{array}{c}
\text{PhN=NCPh} \\
\text{Ph}
\end{array}
\end{array}
\rightarrow
\begin{array}{c}
\begin{array}{c}
\text{PhN=NCPh} \\
\text{Ph}
\end{array}
\end{array}
\]

R=; see Table 4
Table 4  Reaction of diphenylnitrile imine with polymers containing activated carbonyl bonds

<table>
<thead>
<tr>
<th>R</th>
<th>Ratio of nitrile imines to double bond units</th>
<th>% of double bonds modified</th>
</tr>
</thead>
<tbody>
<tr>
<td>-O-CH$_2$CH$_2$O-</td>
<td>1:1</td>
<td>95-100</td>
</tr>
<tr>
<td>-O-C$_6$H$_4$-C(CH$_3$)$_2$-C$_6$H$_4$-O-</td>
<td>1:1</td>
<td>95-100</td>
</tr>
<tr>
<td>-O-CH$_2$CH$_2$CH$_2$CH$_2$O-</td>
<td>1:1</td>
<td>95-100</td>
</tr>
<tr>
<td>-N=N-</td>
<td>2:1</td>
<td>95-100</td>
</tr>
<tr>
<td>-NH-NH-</td>
<td>2:1</td>
<td>95-100</td>
</tr>
<tr>
<td>-O-[(CH$_2$)$_2$-NH]C-NH-C-C-H$_2$O-</td>
<td>2:1</td>
<td>95-100</td>
</tr>
</tbody>
</table>

* The yield was calculated with respect to the nitrile imine, and was based on the percentage which became attached to the polymer.

Modifications of non-specific polybutadiene and trans-1,4-polyisoprene with diphenylnitrile imine have been reported to occur in much lower yields$^{113}$ (reaction at a nitrile imine to double bond ratio of 2:1 resulted in 10% of the alkene units being modified) (Scheme 18). Natural rubber, cis-1,4-polyisoprene, has been reported not to give any cycloaddition products under similar conditions$^{113}$. It has been shown
that the majority of the reaction of diphenylnitrile imine with a non-stereospecific polybutadiene occurs at the trans sites\(^{113}\).

**Scheme 18**

![Scheme 18](image)

1.4.2c.ii Nitrile Oxides

Nitrile oxides, generated from the corresponding hydroximoyl chloride in situ, have been reported to undergo cycloaddition with the alkene double bonds of cis-1,4-polybutadiene\(^{16,115}\), cis-1,4 and trans-1,4-polyisoprene\(^{112,115}\), polychloroprene\(^{16}\), unsaturated polyesters\(^{116}\) and non-stereospecific polybutadiene\(^ {116}\). The degree of modification of the polydiene depends on the initial molar excess of hydroximoyl chloride and the substituent attached to it. Typically, the use of 1 mole of hydroximoyl chloride per double bond unit resulted in 20-80% of the double bonds being modified. The generalised reaction is shown in Scheme 19.
The reaction of polymers containing pendant or terminal acetylenes with benzonitrile oxide has been reported to occur in good yield (Scheme 20).

Scheme 20

\[ \text{Scheme 19} \]

\[ R-\text{CCI=NOH} \xrightarrow{\Delta} R-C=\text{N-O} \]

\[ \text{CH}_2\text{CH}=\text{CR}'\text{CH}_2 \]

\[ \text{CH}_2\text{CH}=\text{CR'CH}_2 \]

\[ R' = \text{CH}_3, \text{H} \]

\[ R = p-\text{MeO}_2\text{C}_6\text{H}_4, 3,4,5-(\text{MeO})_3\text{C}_6\text{H}_2, \]

\[ 2,4,6-(\text{MeO})_3\text{C}_6\text{H}_2, \text{MeO}_2\text{C}, \]

\[ p-\text{MeO(CH)}_n\text{C}_6\text{H}_4; n = 2,6,7. \]

\[ \text{PH-C=\text{N-O}} \]
1.4.2c.iii  **Nitrones**

cis-1,4-Polybutadiene has been modified with nitrones in good yield\textsuperscript{112} (Scheme 21). Reaction with 1 mole of nitrene precursor per twenty double bond units in the polymer, resulted typically in cycloaddition to 3.1\% of the double bond units; corresponding to a 62\% yield with respect to the nitrene\textsuperscript{112}.

Scheme 21

![Chemical structure](image)

R=Ph,Et

1.4.3  **Polymers Containing 1,3-Dipole Precursors**

Two reports exist in the literature of reactions of polymers containing 1,3-dipole precursors. Stille\textsuperscript{119} copolymerised a nitrile imine precursor, a tetrazole, with cis-1,4-polyisoprene to give copolymer (77). On thermolysis a nitrile imine was produced, which underwent cycloaddition with a double bond from another polymer molecule, yielding a crosslink (Scheme 22).
Cohen et al.\textsuperscript{120} prepared poly (vinylbenzene azide) by treating poly (vinylbenzene chloride) with sodium azide. Formation of the azide was demonstrated by its characteristic reaction with acetylene-dicarboxylic acid and its methyl ester, producing the corresponding 1,2,3-triazoles.
SYMBOLS AND ABBREVIATIONS

b.p.  boiling point
m.p.  melting point
h.p.l.c.  high performance liquid chromatography
g.l.c.  gas liquid chromatography
t.l.c.  thin layer chromatography
M⁺  parent ion
m/e  mass/charge ratio
n.m.r.  nuclear magnetic resonance
MW  weight average molecular weight
Mn  number average molecular weight
INSTRUMENTATION

Melting Points Melting points of compounds were determined using a Kofler hot-stage apparatus.

Nuclear Magnetic Resonance Spectra

(a) \(^1H\,n.m.r\). Routine spectra were recorded on a Varian EM360 (60 MHz) spectrometer. The spectra of all new compounds were obtained using a Varian HA-100 spectrometer operated by Mr. J. Millar or a Bruker WH-360 spectrometer operated by Dr. I. H. Sadler. Chemical shifts (\(\delta_H\)) were measured in parts per million (ppm) relative to tetramethylsilane (TMS) as standard (\(\delta=0\)).

(b) \(^13C\,n.m.r\). Spectra were generally recorded on a Varian CFT-20 spectrometer operated by Mr. J. Millar or on a Varian XL-100 spectrometer operated by Mr. L. Bell. In a few cases, a Bruker WH-360 spectrometer operated by Dr. I. H. Sadler was used. Chemical shifts (\(\delta_C\)) were measured in ppm relative to TMS (\(\delta=0\)).

Infra-red Spectroscopy I. R. Spectra were recorded on a Perkin-Elmer 157G Grating Spectrophotometer. Liquid and polymer samples were run as thin films and solid samples as Nujol mulls.

Elemental Analysis Microanalyses were carried out on a Perkin-Elmer Elemental Analyser 240 by Mr. J. Grunbaum.
Mass Spectroscopy  Mass spectra and exact masses were obtained on an AEI MS-902 double focusing mass spectrometer operated by Mr. D. Thomas.

Gas Liquid Chromatography  G.L.C. investigations were carried out on a Pye 104 chromatograph, with a flame ionisation detector.

High Performance Liquid Chromatography  Analytical and qualitative h.p.l.c. investigations were carried out using polished stainless steel columns (32 and 16x 0.5 cm internal diameter) packed with 5 micron spherisorb silica and 5 micron octadecyl silicate (ODS-Hypersil) supplied by Shandon Southern Ltd. Product detection was by a Cecil Instruments CE 12 u.v. monitor. Quantitative measurements were made after calibration of the instrument with known mixtures of authentic sample and internal standard. All authentic samples and internal standards were purified before use. Both straight phase (silica) and reverse phase (ODS) h.p.l.c. were employed.

Straight Phase  Silica columns were deactivated by pumping methylene chloride containing 20 percent water through the system. All solvents were mixtures of methylene chloride and hexane.

Reverse Phase  Solvents were prepared by mixing analar methanol and distilled water, and were degassed by refluxing for five minutes under reduced pressure.
Thin Layer Chromatography  Chromatographs were developed on 0.3 mm layers of alumina (Merck, Aluminium Oxide G) or silica gel (Merck, silica Gel G) containing Woelm fluorescent green indicator (0.5%). Components of the chromatogram were detected by their quenching of fluorescence under u.v. light, or by their absorption of iodine.

Gel Permeation Chromatography  Gel permeation chromatography was carried out on a 60 cm x 7 mm internal diameter column packed with a styrene/divinylbenzene copolymer supplied by T. L. Gell Polymer Laboratories. The column was eluted with tetrahydrofuran at a rate of 1 ml per minute and was coupled to a Waters 401 differential diffractive index detector.

SOLVENTS AND REAGENTS

Toluene and Xylene were distilled and stored over sodium wire. Chloroform was distilled from P₂O₅ and stored over molecular sieve. Diethyl ether was stored over sodium wire. Triethylamine was stored over sodium hydroxide pellets. Hexane was redistilled and stored over molecular sieve. Y-Butyrolactone was redistilled prior to use. Methylene Chloride was redistilled and stored over molecular sieve.
2.1 Preparation of p-Nitrobenzohydroximoyl Chloride

p-Nitrobenzohydroximoyl chloride was prepared by the method of Chiang \cite{121} by the reaction of p-nitrobenzaldehyde and hydroxyammonium chloride to form the oxime which was then chlorinated directly.

To a suspension of p-nitrobenzaldehyde (6.5 g) in a 0.5M sodium hydroxide solution (250 ml) was added hydroxyammonium chloride (6.0 g) and the mixture was heated until a clear solution was obtained. The oxime was precipitated by the addition of dry ice and the solution left to cool. The oxime was filtered off, dissolved in methylene chloride (50 ml) and dried overnight with anhydrous magnesium sulphate. The drying agent was filtered off and the oxime purified by evaporating the solution to ca 20 ml and precipitating with petrol (b.p. 60-80°C) (100 ml). The solution was filtered to give the p-nitrobenzaldoxime as a white powder (5.1 g, 74%), m.p. 130°C (lit. 122-133°C); ν\text{max} (Nujol) 1510, 1345 (NO\textsubscript{2}) cm\textsuperscript{-1}. m/e (100°C) M\textsuperscript{+}, 166.

p-Nitrobenzohydroximoyl chloride was prepared from the oxime (2.4 g) by dissolving in methylene chloride (200 ml) containing 0.75% ethanol (1.5 ml), cooling below 0°C on a salt ice bath and bubbling chlorine through the solution for 20 minutes. A colour change from yellow through blue and green back to yellow was observed; the solution was kept cool for 2 hours and allowed to stand overnight. The solvent was removed under reduced pressure and the product purified by dissolving in a minimum volume of warm methylene chloride and precipitating with petrol (b.p. 60-80°C). The solution was filtered yielding the p-nitrobenzohydroximoyl chloride as a white powder (2.8 g, 95%), m.p. 126°C (lit. 121-126-7°C); ν\text{max} (Nujol) 1510, 1345 (NO\textsubscript{2}) cm\textsuperscript{-1}. m/e (90°C) M\textsuperscript{+}, 202, 200.
2.2 Preparation of 3,5-Di(p-nitrophenyl)-1,2,4-oxadiazole

To a solution of p-nitrobenzonitrile (1.48 g, 10 mmol) in toluene (200 ml) was added p-nitrobenzohydroximoyl chloride (2.0 g, 10 mmol) and the mixture heated under reflux (ca 140°C) until h.p.l.c. analysis indicated complete consumption of the hydroximoyl chloride (after 24 hours). The solvent was removed under reduced pressure and the solid obtained recrystallised from toluene giving the 3,5-di(p-nitrophenyl)-1,2,4-oxadiazole as yellow needles (1.54 g, 42%), m.p. 237°C (lit.123 244°C); \( \nu_{\text{max}} \) (Nujol) 1520, 1345 (NO\(_2\)) cm\(^{-1}\). m/e (170°C) \( M^+ \), 312.

2.3 Preparation of 3,4-Di(p-nitrophenyl)furazan-N-oxide

To a solution of p-nitrobenzohydroximoyl chloride (1.0 g) in ether (200 ml) was added triethylamine (0.5 g). A precipitate of triethylamine hydrochloride formed and was removed by filtration. Heating the filtrate under reflux for 7 hours and cooling gave a brown solid which was recrystallised from glacial acetic acid to yield 3,4-di(p-nitrophenyl)furazan-N-oxide as a white solid (0.42 g, 51%), m.p. 200°C (lit.124 199-200°C); \( \nu_{\text{max}} \) (Nujol) 1510, 1345 (NO\(_2\)) cm\(^{-1}\). m/e (180°C) \( M^+ \), 328.

2.4 Reaction of p-Nitrobenzohydroximoyl Chloride with Cyclooctene

To a solution of cyclooctene (27.5 g, 250 mmol) dissolved in xylene (500 ml) was added p-nitrobenzohydroximoyl chloride (5.0 g, 25 mmol) and the mixture heated under reflux (ca 140°C) until h.p.l.c. analysis indicated complete consumption of the hydroximoyl chloride (after 4 hours). The solvent and excess cyclooctene were removed by distillation under reduced pressure. Chromatography on alumina eluting with toluene produced first a white solid, which was identified as
3,5-di(p-nitrophenyl)-1,2,4-oxadiazole (2%) from t.l.c. and quantitative h.p.l.c. by comparison with an authentic sample. The second fraction, a brown solid, was recrystallised from toluene to give 11-(p-nitrophenyl)-9-oxa-10-azabicyclo-[6,3,0]-undec-10-ene as yellow needles (4.85 g, 70%), m.p. 142°C; (Found: C, 65.8; H, 6.8; N, 10.3. C_{15}H_{18}N_{2}O_{3} requires C, 65.7; H, 6.6; N, 10.2%). ν\text{max} (Nujol) 1515, 1335 (NO_2) cm^{-1}. S_H (CDCl_3) 8.22 (d, 2H, half an AB system, J = 9Hz, ArH); 7.80 (d, 2H, half an AB system, J = 9Hz, ArH); 4.70-4.44 (m, 1H, C_8H); 3.60-3.40 (m, 1H, C_1H); 2.20-1.00 (m, 12H C_7H). S_C (CDCl_3) 160.5 (isoxazoline ring C); 148.0, 135.5 (Ar ring C), 127.4, 123.8 (Ar ring CH); 86.5 (C_8); 49.4 (C_1); 29.8, 25.2, 25.1, 25.0, 24.6, 24.4, (C_2-7). m/e (150°C) 274(M^+, 100%), 257 (12), 245 (13) 231 (15), 218 (20), 217 (21), 203 (48), 191 (24), 190 (22), 189 (20) 175 (42), 129 (34) 95 (24), 91 (30), 67 (36) 41 (66).

2.5 Reaction of p-Nitrobenzohydroximoyl Chloride with 1-Methylcyclohexene

To a solution of 1-methylcyclohexene (5.0 g, 51 mmol) in xylene (100 ml) was added p-nitrobenzohydroximoyl chloride (1.0 g, 5 mmol) and the mixture heated under reflux (ca 140°C) until h.p.l.c. analysis indicated complete consumption of the hydroximoyl chloride (after 4 hours). The solvent and excess 1-methylcyclohexene were removed by distillation under reduced pressure. Chromatography on alumina eluting with toluene produced first a white solid, which was identified as 3,5-di(p-nitrophenyl)-1,2,4-oxadiazole (4%) from its m.p. 235°C and mixed m.p. 230°C (lit. 244°C) by comparison with an authentic sample. The second fraction, a yellow solid, was recrystallised from toluene to give 6-methyl-9-(p-nitrophenyl)-7-oxa-8-azabicyclo-[4,3,0]-non-8-ene as white needles (0.52 g, 41%), h.p.l.c. yield 52%), m.p. 115°C; (Found. C, 64.6; H, 6.2;
N, 10.8. \( \text{C}_{14}\text{H}_{16}\text{N}_{2}\text{O}_{3} \) requires C, 64.6; H, 6.0; N, 10.5\%\). \( \nu_{\text{max}} \) (Nujol) 1510, 1345 (\( \text{NO}_{2} \)) cm\(^{-1}\). \( \delta_{\text{H}} \) (CDCl\(_3\)) 8.30 (d, 2H, half an AB system, \( J = 9 \) Hz, ArH); 7.92 (d, 2H, half an AB system, \( J = 9 \) Hz, ArH); 3.25-2.90 (m, 1H, C\(_1\)H); 2.45-1.25 (m, 8H, C\(_2\)-5H); 1.34 (s, 3H, CH\(_3\)). \( \delta_{\text{C}} \) (CDCl\(_3\)) 160.6 (isoxazoline ring C); 147.9, 135.8 (Ar ring C), 127.2, 123.7 (Ar ring CH), 86.5 (C\(_6\)); 49.0 (C\(_1\)); 31.1, 26.5, 25.8, 20.6, 20.0 (C\(_2\)-5, CH\(_3\)). m/e (120°C) 260 (M\(^+\), 80), 245 (75) 231 (15) 217 (100\%), 216 (22), 175(40), 143 (15), 129 (18), 95 (15), 94 (14), 81 (25), 43 (45), 41 (30).

2.6 Reaction of p-Nitrobenzohydroximoyl Chloride with 1,5-Cyclooctadiene

To a solution of 1,5-cyclooctadiene (10.8 g, 100 mmol) in xylene (300 ml) was added p-nitrobenzohydroximoyl chloride (2.0 g, 10 mmol) and the mixture heated under reflux (ca 140°C) until h.p.l.c. analysis indicated complete consumption of the hydroximoyl chloride (after 4 hours). The solvent and excess 1,5-cyclooctadiene were removed by distillation under reduced pressure. Chromatography on silica eluting with ether/toluene (1:40) produced first a white solid, which was identified as 3,5-di(p-nitrophenyl)-1,2,4-oxadiazole (0.06 g, 1.8\%) from its m.p. 234°C and mixed m.p. 232°C (lit.\(^5\) 244°C) by comparison with an authentic sample. The second fraction, a yellow solid, was recrystallised from ethanol to give 11-(p-nitrophenyl)-9-oxa-10-azabicyclo-[6,3,0]undeca-4,10-diene as white needles (1.38 g, 51\%), m.p. 106°C; (Found: C, 66.1; H, 5.7; N, 10.3. \( \text{C}_{15}\text{H}_{16}\text{N}_{2}\text{O}_{3} \) requires C, 66.2; H, 5.9; N, 10.3\%). \( \nu_{\text{max}} \) (Nujol) 1520, 1340 (\( \text{NO}_{2} \)) cm\(^{-1}\). \( \delta_{\text{H}} \) (CDCl\(_3\)) 8.22 (d, 2H, half an AB system, \( J = 9 \) Hz, ArH); 7.80 (d, 2H, half an AB system, \( J = 9 \) Hz, ArH); 5.84-5.46 (m, 2H, C\(_4\)-5H). 4.44 (m, 1H, C\(_8\)H); 3.76-3.46 (m, 1H, C\(_1\)H); 2.90-1.68 (m, 8H, C\(_2\)-3H, C\(_6\)-7H). \( \delta_{\text{C}} \) (CDCl\(_3\)) 161.3 (isoxazoline ring C);
2.7 Reduction of 11-(p-Nitrophenyl)-9-oxa-10-aza-bicyclo-[6,3,0]-undec-10-ene

(a) Reduction with Tin and Hydrochloric Acid

To a suspension of the nitro compound (0.25 g, 0.91 mmol) in conc. hydrochloric acid (2.5 ml) was added tin (1.0 g) and the mixture shaken thoroughly. The mixture was warmed to 30°C for 15 minutes and refluxed until the compound had all dissolved. The solution was allowed to cool, neutralised with sodium hydroxide and extracted with methylene chloride. The extracts were dried overnight with magnesium sulphate. Removal of the solvent under reduced pressure yielded 11-(p-aminophenyl)-9-oxa-10-aza-bicyclo-[6,3,0]-undec-10-ene as a brown oil (125 mg, 45%), \( M^+ \), 244.158961. \( C_{15}H_{20}N_{2}O \) requires \( M^+ \), 244.157555. \( \nu_{max} \) (Nujol) 3490, 3400, 3220 \( \text{cm}^{-1} \). \( \delta_H \) (CDCl\( _3 \)) 7.40 (d, \( 2H \), half an AB system, \( J = 7 \text{ Hz}, \text{ArH} \)), 6.59 (d, \( 2H \), half an AB system, \( J = 7 \text{ Hz}, \text{ArH} \)); 4.48-4.20 (m, \( 1H \), \( C_1H \)); 4.50-3.50 (bs, \( 2H, \text{NH}_2 \)); 3.44-3.12 (m, \( 1H \), \( C_6H \)); 2.15-1.00 (m, \( 12H \), \( C_2-H \)). m/e (130°C) 244 (\( M^+ \), 100%), 215 (7), 201 (5), 187 (7), 173 (12), 145 (21), 134 (22), 132 (11), 118 (24), 106 (11), 54 (85).

(b) Reduction with Triiron Dodecacarbonyl

To a solution of the nitro compound (0.55 g, 2.0 mmol) in toluene (20 ml) was added triiron dodecacarbonyl (0.89 g, 2.0 mmol) and benzyl-triethylammonium chloride (0.045 g). The solution was stirred with a 1M sodium hydroxide solution (20 ml) for two hours. The organic layer was
separated on a centrifuge and the solvent removed under reduced pressure giving a dark oil. The oil was extracted into 1M hydrochloric acid from methylene chloride, neutralised with 1M sodium hydroxide and reextracted into methylene chloride. Removal of the solvent under reduced pressure yielded 11-(p-aminophenyl)-9-oxa-10-azabicyclo-[6,3,0]-undec-10-ene as a yellow oil (0.25 g, 61%); ν max (CHCl₃) 3495, 3400, 3225 (NH₂) cm⁻¹. δ H (CDCl₃) 7.40 (d, 2H, J = 7 Hz, ArH); 6.59 (d, 2H, J = 7 Hz, ArH); 4.48-4.20 (m, 1H, C₁₁); 4.50-3.50 (bs, 2H, NH₂); 3.44-3.12 (m, 1H, C₈H), 2.15-1.00 (m, 12H, C₂₋₇H). S C (CDCl₃) 162.3 (isoxazoline ring C); 147.8, 119.0 (Ar ring C); 128.1, 114.7 (Ar ring CH); 84.7 (C₁), 50.3 (C₈); 30.0, 25.3, 25.1, 25.0, 24.5 (C₂₋₇). m/e (130°C) M⁺, 244.

2.8 Reduction of 6-Methyl-9-(p-nitrophenyl)-7-oxa-8-azabicyclo-[4,3,0]-non-8-ene

To a solution of this nitro compound (0.8 g, 3.5 mmol) in toluene (30 ml) was added triiron dodecacarbonyl (2.0 g, 3.9 mmol) and benzyl-triethylammonium chloride (0.08 g). The solution was stirred with a 1M sodium hydroxide solution (40 ml) for two hours. The organic layer was separated on a centrifuge and the solvent removed under reduced pressure giving a dark oil. The oil was extracted into 1M hydrochloric acid from methylene chloride, neutralised with sodium hydroxide and reextracted into methylene chloride. Removal of the solvent under reduced pressure yielded 6-methyl-9-(p-aminophenyl)-7-oxa-8-azabicyclo-[4,3,0]-non-8-ene as a brown oil which gave a yellow solid on Kugelrohr distillation (150°C/0.02 mm Hg) (0.47 g, 60%), m.p. 115°C; (Found: C, 72.8; H, 7.9; N, 11.9. C₁₁H₁₃N₂O requires C, 73.0; H, 7.9; N, 12.2%). ν max (CHCl₃) 3500, 3400, 3220 (NH₂), 1650 (NH₂) cm⁻¹. δ H (CDCl₃) 7.46 (d, 2H, half an AB system, J = 9 Hz, ArH), 6.64 (d, 2H, half an AB system, J = 9 Hz, ArH);
4.00-3.40 (bs, 2H, NH₂); 3.10-2.88 (m, 1H, C₁H); 2.25-1.20 (m, 8H, C₂₅H). δ₁(CDCl₃) 162.5 (isoxazoline ring C); 148.0, 119.5 (Ar ring C); 128.1, 114.6 (Ar ring CH); 84.3 (C₁); 49.9 (C₆); 31.6, 26.9, 26.7, 21.4, 20.6 (C₂₅H, CH₃). m/e (110°C) 230 (M⁺, 100%), 215 (26), 187 (36), 173 (5), 159 (10), 145 (42), 134 (27), 132 (19), 106 (15), 92 (17), 65 (10).

2.9 Reducott of 11-(p-Nitrophenyl)-9-oxa-10-azabicyclo-
[6,3,0]-undeca-4,10-diene

(a) Reduction with Triiron Dodecacarbonyl

To a solution of the nitro compound (0.27 g, 1.0 mmol) in toluene (10 ml) was added triiron dodecacarbonyl (0.55 g, 1.1 mmol) and benzyltriethylammonium chloride (0.06 g). The solution was stirred with a 1M sodium hydroxide solution (10 ml) for two hours. The organic layer was separated on a centrifuge and the solvent removed under reduced pressure giving a dark oil. The oil was extracted into 1M hydrochloric acid from methylene chloride, neutralised with 1M sodium hydroxide and reextracted into methylene chloride. Removal of the solvent under reduced pressure yielded 11-(p-aminophenyl)-9-oxa-10-azabicyclo-
[6,3,0]-undeca-4,10-diene as a brown oil (0.17 g, 70%), (Found: M⁺, 242.143149. C₁₉H₁₈N₂O requires M⁺, 242.143149). ν max (Nujol) 3500, 3400, 3220 (NH₂), 1625 (NH₂) cm⁻¹. δ₁(CDCl₃) 7.42 (d, 2H, half an AB system, J = 8 Hz, ArH); 6.60 (d, 2H, half an AB system, J = 8 Hz, ArH); 5.74-5.45 (m, 2H, CH=CH); 4.54-4.24 (m, 1H, C₁H); 4.16-3.80 (bs, 2H, NH₂); 3.65-3.38 (m, 1H, C₆H); 2.80-0.70 (m, 12H, C₂₅H, C₆H₆). m/e (120°C) 242 (M⁺, 95), 213 (15) 199 (10), 185 (14), 173 (20), 171 (16), 161 (28), 145 (68), 134 (10), 132 (20), 119 (30), 92 (36), 65 (100%).

(b) Reduction with Hydrogen over a Palladium Catalyst

To a solution of the nitro compound (230 mg, 0.88 mmol) in toluene (5 ml) was added palladium on charcoal (15 mg). The solution was
stirred under a slight positive pressure of hydrogen until \(^1\)H n.m.r. showed complete conversion to the amino compound (60 hours). The palladium charcoal was removed by filtering through alumina and the solvent removed under reduced pressure. The oil produced was dissolved in methylene chloride and extracted into 1M hydrochloric acid, neutralised with 1M sodium hydroxide and reextracted into methylene chloride.

Removal of the solvent under reduced pressure yielded 11-(p-aminophenyl)-9-oxa-10-azabicyclo-[6,3,0]-undeca-4,10-diene as a red oil (180 mg, 88%), \(\nu_{\text{max}}\) (Nujol) 3490, 3400, 3220 (NH\(_2\)) cm\(^{-1}\). \(\delta_H\) (CDCl\(_3\)) 7.40 (d, 2H); 6.59 (d, 2H), 4.48-4.20 (m, 1H), 4.50-3.50 (bs, 2H); 3.44-3.12 (m, 1H); 2.15-1.00 (m, 12H), m/e (120°C) \(M^+\), 244.

2.10 Reaction of 11-(p-Nitropheny1)-9-oxa-10-azabicyclo-[6,3,0]-undeca-4,10-diene with p-Toluenesulphonyl Hydrazide

To a solution of the nitro compound (250 mg, 1.0 mmol) in xylene (50 ml) was added p-toluenesulphonyl hydrazide (370 mg, 2.0 mmol) and the solution heated to reflux for 3 hours. The solvent was removed under reduced pressure and the oil produced crystallised with ethanol overnight in the fridge to yield 11-(p-nitropheny1)-9-oxa-10-azabicyclo-[6,3,0]-undeca-4,10-diene as a white solid (165 mg, 66%), m.p. 140°C; \(\nu_{\text{max}}\) (Nujol) 1515, 1335 (NO\(_2\)) cm\(^{-1}\). \(\delta_H\) (CDCl\(_3\)) 8.22 (d, 2H); 7.80 (d, 2H); 4.70-4.44 (m, 1H); 3.60-3.40 (m, 1H); 2.20-1.00 (m, 12H). Quantitative reverse phase h.p.l.c. indicated the presence of 11-(p-aminopheny1)-9-oxa-10-azabicyclo-[6,3,0]-undeca-4,10-diene (0.3%) and 11-(p-aminopheny1)-9-oxa-10-azabicyclo-[6,3,0]-undeca-4,10-diene (1.5%) by comparison with authentic samples.

2.11 Preparation of the Acetyl derivative of 11-(p-Aminophenyl)-9-oxa-10-azabicyclo-[6,3,0]-undeca-4,10-diene

To a solution of the amine (0.09 g, 0.4 mmol) in toluene (2 ml)
were added simultaneously acetyl chloride (0.03 g, 0.04 mmol) in toluene (1 ml) and triethylamine (0.035 g, 0.04 mmol) in toluene (1 ml). The solution was warmed on a water bath at 50°C for 1 hour and left to stand overnight. The acetyl derivative crystallised out, was filtered off and recrystallised from ethanol as a white solid (0.10 g, 95%), m.p. 166°C; (Found: C, 71.1; H, 7.7; N, 9.6. \( \text{C}_{13} \text{H}_{22} \text{N}_2 \text{O}_2 \) requires C, 71.3; H, 7.7; N, 9.8%). \( \gamma_{\text{max}} \) (Nujol) 3355 (NH), 1695, 1670 (C=O) cm\(^{-1}\). \( \delta_{\text{H}} \) (CDCl\(_3\)) 7.55 (s, 4H, ArH); 4.60-4.26 (m, 1H, C\(_8\)H); 3.52-3.26 (m, 1H, C\(_1\)H); 2.16 (s, 3H, Cl\(^+\)); 2.15-1.20 (m, 12H, C\(_2\)H). m/e (170°C) 286 (M\(^+\), 100%), 244 (20), 215 (10), 201 (8), 187 (12), 173 (5), 145 (9), 134 (10), 132 (8), 118 (10) 106 (8), 55 (20).

2.12 Preparation of the p-Tolylurea Derivative of 11-(p-Aminophenyl)-9-oxa-10-azabicyclo-[6,3,0]undec-10-ene

To a solution of the amine (0.15 g, 0.6 mmol) in toluene (5 ml) was added p-tolyl isocyanate (0.08 g, 0.6 mmol) and the solution warmed on a water bath for 1 hour. The urea derivative precipitated out on standing overnight, was filtered off and recrystallised from ethanol as a white solid (0.09 g, 40%), m.p. 240°C; (Found: C, 72.9; H, 7.3; N, 11.1. \( \text{C}_{23} \text{H}_{27} \text{N}_3 \text{O}_2 \) requires C, 73.2; H, 7.2; N, 11.1%). \( \gamma_{\text{max}} \) (Nujol) 3370 (NH), 1700 (C=O) cm\(^{-1}\). \( \delta_{\text{H}} \) (CDCl\(_3\)) 8.90 (s, 1H, NH); 8.70 (s, 1H, NH); 7.57 (d, 2H, half an AB system; J = 8 Hz, ArH attached to C\(_{11}\)); 7.52 (d, 2H, half an AB system, J = 8 Hz, ArH attached to C\(_{11}\)); 7.34 (d, 2H, half an AB system, J = 9 Hz, ArH of p-tolyl group); 7.08 (d, 2H, half an AB system, J = 9 Hz, ArH of p-tolyl group); 4.46-4.43 (m, 1H, C\(_8\)H); 4.46-4.37 (m, 1H, C\(_1\)H); 2.24 (s, 3H, CH\(_3\)); 1.96-1.15 (m, 12H C\(_2\)H). m/e (220°C) 377(M\(^+\),50), 270 (34) 244 (62), 227 (6), 215 (7), 199 (11), 173 (12), 171 (17), 145 (17), 134 (15), 133 (40), 132 (31), 107 (100%), 106 (87).
2.13 Reaction of p-Nitrobenzohydroximoyl Chloride with Isobutyronitrile

(a) Reaction in Xylene

To a solution of isobutyronitrile (3.45 g, 50 mmol) dissolved in xylene (100 ml) was added p-nitrobenzohydroximoyl chloride (1.02 g, 5 mmol) and the mixture heated under reflux (ca 140°C) until no p-nitrobenzohydroximoyl chloride remained by h.p.l.c. (reaction time 4 hours). The solvent and excess isobutyronitrile were removed under reduced pressure giving a dark oil. Chromatography on alumina eluting with toluene produced 3-(p-nitrophenyl)-5-isopropyl-1,2,4-oxadiazole, which was recrystallised from toluene as a white solid (0.24 g, 20%), m.p. 130°C; (Found: C, 56.7; H, 4.7; N, 17.8. \( \text{C}_{11}\text{H}_{11}\text{N}_{3}\text{O}_{3} \) required C, 56.6; H, 4.8; N, 18.0%). \( \text{\nu}_{\text{max}} \) (Nujol) 1520, 1340 cm\(^{-1}\). \( \delta_{\text{H}} \) (CDCl\(_3\)) 8.27 (s, 4H, ArH); 3.55-3.10 (m, 1H, J = 7 Hz, \( \text{CH} (\text{CH}_3)_2 \)); 1.47 (d, 6H, J = 7 Hz, \( \text{CH} (\text{CH}_3)_2 \)). \( \delta_{\text{C}} \) (CDCl\(_3\)) 184.7, 166.5 (oxadiazole ring C); 149.2, 132.8 (Ar ring C); 128.2, 123.9 (Ar ring CH); 27.4 (CH (CH\(_3\))\(_2\)); 20.0 (CH(CH\(_3\))\(_2\)). m/e (110°C) 233 (M\(^+\), 100%), 164 (87), 134 (20), 88 (25), 43 (37) 32 (27).

(b) Reaction in \( \gamma \)-Butyrolactone

To a solution of isobutyronitrile (1.04 g, 15 mmol) in \( \gamma \)-butyrolactone (45 ml) was added p-nitrobenzohydroximoyl chloride (300 mg, 1.5 mmol) and the mixture heated at 140°C for 4 hours. The \( \gamma \)-butyrolactone and residual isobutyronitrile were removed at reduced pressure (0.5 mm Hg) giving a dark oil. Chromatography on alumina eluting with toluene gave 3-(p-nitrophenyl)-5-isopropyl-1,2,4-oxadiazole, which was recrystallised from toluene as a white solid (75 mg, 20%), m.p. 130°C; \( \text{\nu}_{\text{max}} \) (Nujol) 1520, 1340 cm\(^{-1}\).
Synthesis of 1,3,4-Oxathiazol-2-ones

2.14 Preparation of Amides

Where amides were not commercially available they were prepared from the acid chlorides as described in Vogel. The amides formed in this way are listed in Table 1.

Table 1  Synthesis of Amides

<table>
<thead>
<tr>
<th>R</th>
<th>% Yield</th>
<th>M.p.(°C)</th>
<th>(recrystallisation solvent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH_3CH=CH-</td>
<td>55</td>
<td>157(126 161)</td>
<td>(water)</td>
</tr>
<tr>
<td>PhCH=CH-</td>
<td>67</td>
<td>146-147(126 145-146.5)</td>
<td>(aqueous ethanol)</td>
</tr>
</tbody>
</table>

2.15 Preparation of Chlorocarbonylsulphenyl Chloride

Chlorocarbonylsulphenyl chloride was prepared by the method of Weiss. To water (8.6 ml), stirring on a salt ice bath, was cautiously added conc. H\_2SO\_4 (100 ml). When the temperature had fallen below 25°C, trichloromethane sulphenyl chloride (88.6 g) was added and the mixture heated at 40-50°C for 3 hours with vigorous stirring. The reaction mixture was allowed to cool and form into two layers. The top layer, chlorocarbonylsulphenyl chloride, was separated and stored over molecular sieve (43.3 g, 61%), \( \nu \text{ max } (\text{film}) 1785 \text{ (C=O) cm}^{-1} \).

2.16 Preparation of 1,3,4-Oxathiazol-2-ones

These were prepared by reaction of chlorocarbonylsulphenyl chloride (Cl\_2CO\_2SCl) and the appropriate amide following the general approach described in the literature, but modified to take account of the lower thermal
stability of the unsaturated products.

(a) 5-(Prop-1-enyl)-1,3,4-oxathiazol-2-one

This compound was prepared by the above method from crotonamide (20.0 g, 240 mmol) and C1COSC1 (30.0 g, 230 mmol) in chloroform (450 ml). The solution was refluxed for 48 hours and the solvent was removed under reduced pressure. Chromatography on silica eluting with petrol/methylene chloride (4:1) yielded 5-(prop-1-enyl)-1,3,4-oxathiazol-2-one as a white crystalline solid, which was recrystallised from ethanol (7.8 g, 22%), m.p. 45-47°C (lit. 128 b.p. 82°C at 10 mmHg); (Found: M⁺, 143.001619. C₅H₅NO₂S requires M, 143.004098). νmax (Nujol) 1775 (C=O), 1650 (C=C) cm⁻¹. δH (CDCl₃) 6.75 (dq, 1H, JBA = 17 Hz, JBC = 7 Hz, HACCHBCFI3C); 6.02 (dq, 1H, JAB = 17 Hz, JAC = 2 Hz, HA); 1.94 (dd, 3H, JCB = 7 Hz, JCA = 2 Hz, CH C). δC (CDCl₃) 173.2 (C 2 ); 156.8 (C 5 ); 141.4, 117.3 (CH); 18.6 (CH₃). m/e (20°C) 143 (M⁺, 56), 115 (10), 99 (8), 76 (6), 69 (100%), 41 (34).

(b) 5-Isopropenyl-1,3,4-oxathiazol-2-one

A mixture of methylacrylamide (80.0 g, 0.94 mol) and C1COSC1 (122.5 g, 0.94 mol) dissolved in dry chloroform (800 ml) was heated under reflux for 18 hours. Evaporation of the solvent and distillation under reduced pressure (80°C, 10 mm Hg) yielded 5-isopropenyl-1,3,4-oxathiazol-2-one as a colourless oil which crystallised on cooling (23.8 g, 18%), m.p. 28-29°C; (Found: M⁺, 143.003191. C₅H₅NO₂S requires M, 143.004098). νmax (Nujol) 1770 (C=O), 1635 (C=C) cm⁻¹. δH (CDCl₃) 5.95 (s, 1H, =CH); 5.66 (q, 1H, J = 2 Hz, =CH); 2.05 (d, 3H, J = 2 Hz, CH₃). δC (CDCl₃) 173.1 (C 2 ); 158.1 (C 5 ); 130.7 (=C); 123.8 (=CH₂); 17.2 (CH₃). m/e (20°C) 143 (M⁺, 36), 115 (15), 103 (12), 99 (10), 85 (5), 76 (10), 69 (100%), 41 (85).
(c) **5-Styryl-1,3,4-oxathiazol-2-one**

A mixture of cinnamamide (7.35 g, 36 mmol) and ClCOCl (6.50 g, 50 mmol) dissolved in dry chloroform (175 ml) was heated under reflux for 14 hours. The solvent was removed under reduced pressure yielding a solid, which was chromatographed on silica eluting with methylene chloride to remove any residual amide. Recrystallisation from cyclohexane gave 5-styryl-1,3,4-oxathiazol-2-one as a white solid (4.24 g, 42%), m.p. 107°C; (Found: C, 58.5; H, 3.6; N, 6.9. C_{10}H_{7}NO_{2}S requires C, 58.6; H, 3.4; N, 6.8%). ν_{max} (Nujol) 1775 (CO), 1635 (C=CH) cm⁻¹.

Σ_{H} (CDCl₃) 7.6-7.2 (m, 5H, ArH); 7.44 (d, 1H, J = 16 Hz, =CH); 6.58 (d, 1H, J = 16 Hz, =CH). Σ_{C} (CDCl₃) 172.7 (C₂); 157.1 (C₅); 133.7 (Ar ring C); 141.3, 112.4 (=CH). m/e (20°C) 205 (M⁺, 96), 161 (16), 131 (100%), 129 (46), 107 (95), 77 (85), 51 (65).

(d) **5-Isopropyl-1,3,4-oxathiazol-2-one**

To a solution of 2-methylpropionamide (20.0 g, 140 mmol) in dry chloroform (250 ml) at 50°C was added ClCOCl (24.0 g, 180 mmol) and the solution refluxed for 8 hours. Evaporation of the solvent and distillation at reduced pressure (62°C, 10 mm Hg) yielded 5-isopropyl-1,3,4-oxathiazol-2-one as a colourless oil (29.4 g, 80%), (Found: M⁺, 145.020730. C₅H₇NO₂S requires M, 145.019748). ν_{max} (film) 1785, 1755 (C=O) cm⁻¹. Σ_{H} (CDCl₃) 2.91 (m, 1H, J = 7 Hz, (CH₃)₂ CH); 1.30 (d, 6H, J = 7 Hz, (CH₃)₂ CH). Σ_{C} (CDCl₃) 173.7 (C₂); 167.2 (C₅); 36.0 ((CH₃)₂ CH) 26.6 ((CH₃)₂ CH). m/e (20°C) 145 (M⁺, 16), 117 (6), 71 (40), 43 (100%), 41 (15).

(e) **5-Vinyl-1,3,4-oxathiazol-2-one**

To a solution of acrylamide (10.0 g, 140 mmol) in dry chloroform (100 ml) at 40°C was added ClCOCl (18.3 g, 140 mmol) and the solution
refluxed for 8 hours. The solvent and unreacted ClCOSCl were removed by evaporation under reduced pressure and precipitated acrylamide separated by filtration. The residue was chromatographed on silica eluting with petrol/methylene chloride (4:1) to yield 5-vinyl-1,3,4-oxathiazol-2-one as a yellow oil (4.0 g, 22%), (Found: M+, 128.989250. C4H3NO2S requires M, 128.98449). ν_max (film) 1770 (C=O), 1640 (C=C) cm⁻¹.

Δ H (CDCl3) 6.26 (d, 1H, J_BC = 17.5 Hz, H_B = CHC); 6.22 (d, 1H, J_AC = 7 Hz, H_A); 5.88 (dd, 1H, J_CA = 7 Hz, J_CB = 17.5 Hz, H_C).

Δ C (CDCl3) 172.6 (C2); 156.7 (C5); 122.6 (CH); 127.4 (=CH2). m/e (20°C) 129 (M+, 66), 101 (32), 91 (8), 88 (7), 76 (6), 55 (100%).

2.17 Synthesis of Isothiazoles and 1,2,4-Thiadiazoles from 1,3,4-Oxathiazol-2-ones

The general method was to heat under reflux a solution of the oxathiazole and the alkyne or nitrile in dry xylene as described below for dimethyl 3-(prop-1-enyl)isothiazole-4,5-dicarboxylate; the reaction being monitored by t.l.c. or h.p.l.c. After removal of the solvent and excess dipolarophile by evaporation under reduced pressure the product was purified by chromatography and distillation or recrystallisation.

(a) Dimethyl 3-(Prop-1-enyl)isothiazole-4,5-dicarboxylate

A solution of 5-(prop-1-enyl)-1,3,4-oxathiazol-2-one (1.41 g, 9.9 mmol) and dimethyl acetylenedicarboxylate (DMAD) (7.10 g, 50 mmol) in dry xylene (25 ml) was heated under reflux for 20 hours. The solvent and most of the excess dipolarophile were removed by evaporation under reduced pressure (65°C, 0.05 mm Hg) and the residual oil chromatographed on silica eluting with petrol/methylene chloride (1:4). Distillation of the product (100°C, 0.05 mm Hg) yielded dimethyl 3-(prop-1-enyl)
isothiazole-4,5-dicarboxylate as a colourless oil (1.62 g, 68%), (Found:
(C=O), 1655 (C=C) cm⁻¹. δ_H (CDCl₃) 6.81 (dq, 1H, J₁₂ = 15 Hz, J₁₃ = 6 Hz,
H₁₂ = CH B CH₃ C); 6.51 (dq, 1H, J₂₃ = 15 Hz, J₂₄ = 2 Hz, HA); 3.91 (s, 3H,
CH₃); 3.87 (s, 3H, CH₃); 1.91 (dd, 3H, J₁₀ = 6 Hz, J₁₁₉ = 2 Hz, CH₃ C).
δ_C (CDCl₃) 163.9*, 159.3 (C=O); 163.6* (C₂); 154.1 (C₅); 130.6 (C₄);
134.7, 122.3 (=CH); 52.7 (2OCH₃); 18.2 (CH₃). (* alternative assignments).
m/e (20°c) 241 (M⁺, 69), 210 (45) 209 (44), 182 (33), 151 (21), 150 (25),
123 (100%), 110 (20), 84 (36), 59 (60).

(b) Dimethyl 3-Isopropenylisothiazol-4,5-dicarboxylate

A solution of 5-isopropenyl-1,3,4-oxathiazol-2-one (1.43 g, 10 mmol)
and DMAD (1.42 g, 10 mmol) in dry xylene (20 ml) was heated under reflux
for 4 hours. The solvent was removed by evaporation under reduced pressure
and the oil produced chromatographed on silica eluting with hexane/
methylene chloride (1:1). This gave dimethyl 3-isopropenylisothiazol-4,5-
dicarboxylate as a colourless oil (0.81 g, 34%), (Found: M⁺, 241.040193.
C₁₀H₁₁NO₂S requires M, 241.040875). ν_max (film) 1735 (C=O), 1630 (C=C)
cm⁻¹. δ_H (CDCl₃) 5.42 (dq, 1H, J₂₃ = 0.5 Hz, HA₃ = CH₃ C); 5.36
(dq, 1H, J₁₂ = 1.5 Hz, J₁₃ = 0.5 Hz, H₃); 3.91 (s, 3H, CH₃); 3.88 (s, 3H,
CH₃); 3.18 (dd, 3H, J₁₀ = 1.5 Hz, J₁₁₉ = 0.5 Hz, CH₃ C). δ_C (CDCl₃) 166.4
(C₂); 164.9, 159.0 (C=O); 154.5 (C₅); 132.4 (C₄); 138.3 (=C); 117.6
(=CH₂); 52.9, 52.7 (OCH₃); 21.1 (CH₃). m/e 241 (M⁺, 50), 210 (60), 209
(100%), 151 (75), 125 (30), 84 (30), 59 (46).

c) Dimethyl 3-Styrylisothiazole-4,5-dicarboxylate

A solution of 5-styryl-1,3,4-oxathiazol-2-one (1.0 g, 4.9 mmol) and
DMAD (3.55 g, 25 mmol) in dry xylene (25 ml) was heated under reflux for
22 hours. The solvent and excess DMAD were removed by evaporation under reduced pressure (70°C, 0.03 mm Hg) and the residual oil chromatographed on silica eluting with petrol/methylene chloride (1:4). The yellow solid obtained was recrystallised from ethanol to give dimethyl 3-styrylisothiazole-4,5-dicarboxylate as a white solid (1.62 g, 50%), m.p. 85°C; (Found: C, 59.6; H, 4.5; N, 4.5. C_{15}H_{13}NO_{4}S requires C, 59.4; H, 4.3; N, 4.6%). ν max (Nujol) 1730 (C=O) cm⁻¹. δ H (CDCl₃) 7.69 (d, 1H, J = 16 Hz, =CH); 7.6-7.2 (m, 5H, ArH); 7.23 (d, 1H, J = 16 Hz, =CH); 3.97 (s, 3H, CH); 3.92 (s, 3H, CH₃). δ C (CDCl₃) 164.0, 159.6 (C=O); 163.6 (C₂); 156.9 (C₅); 131.2 (C₄); 136.5, 118.8 (Ar ring C); 135.9 (Ar ring C); 129.0, 128.7, 127.3 (Ar ring CH); 55.0, 52.9 (OCH₂). m/e (20°C) 303 (M⁺, 75), 302 (100%), 272 (10), 240 (13), 152 (16), 150 (20), 102 (10), 77 (15), 59 (10).

(d) Dimethyl 3-Isopropylisothiazole-4,5-dicarboxylate

A solution of 5-isopropyl-1,3,4-oxathiazole-2-one (1.45 g, 10 mmol) and DMAD (7.10 g, 50 mmol) in dry xylene (25 ml) was heated under reflux for 20 hours. The solvent and residual DMAD were removed by evaporation under reduced pressure (75°C / 0.05 mm Hg) and the oil produced chromatographed on silica eluting with petrol/methylene chloride (1:4). This gave dimethyl 3-isopropylisothiazole-4,5-dicarboxylate as a colourless oil (1.56 g, 64%), (Found: M⁺, 243.056698. C_{10}H_{13}NO_{4}S requires M⁺, 243.056524). ν max (film) 1740 (C=O) cm⁻¹. δ H (CDCl₃) 3.90 (s, 3H, OCH₃); 3.87 (s, 3H, OCH₃); 3.30 (m, 1H, J = 7 Hz, CH (CH₃)₂); 1.30 (d, 6H, J = 7 Hz, CH(CH₃)₂). δ C (CDCl₃) 174.5 (C₃); 164.2 (C=O); 159.4 (C=O); 155.4 (C₅); 131.5 (C₄); 52.6 (OCH₃); 31.1(CH (CH₃)₂); 21.3(CH (CH₃)₂). m/e (20°C) 243 (M⁺, 20), 228 (20) 213 (25), 212 (95), 211 (100%), 196 (85), 183 (30), 180 (28), 179 (60), 153 (21), 151 (25), 125 (16), 84 (21).
(e) Ethyl 3-(prop-1-enyl)-1,2,4-thiadiazole-5-carboxylate

A solution of 5-(prop-1-enyl)-1,3,4-oxathiazol-2-one (1.45 g, 10 mmol) and ethyl cyanoformate (ECF) (3.53 g, 35 mmol) in xylene (25 ml) was heated under reflux for 20 hours. The solvent and residual ECF were removed by evaporation under reduced pressure (30°C / 0.05 mm Hg). The oil produced was distilled under reduced pressure (100°C / 0.05 mm Hg) and chromatographed on silica eluting with petrol/methylene chloride (1:4) giving ethyl 3-(prop-1-enyl)-1,2,4-thiadiazole-5-carboxylate as a colourless oil (0.87 g, 64%), (Found: M⁺, 198.04671. C₈H₁₀N₂O₂S requires M, 198.046295). ν_max (film) 1760 (C=O) cm⁻¹. δ_H (CDCl₃) 7.24 (dq, 1H, J_BA = 15 Hz, J_BC = 7 Hz, H_A = CH₂CH₃), 6.62 (dq, 1H, J_AB = 15 Hz, J_AC = 2 Hz, H_A), 4.51 (q, 2H, CH₂), 1.96 (dd, 3H, J_CB = 7 Hz, J_CA = 2 Hz, CH₃C); δ_C (CDCl₃) 178.0 (C₅), 174.1 (C₃), 159.2 (C=O), 138.5, 123.3 (±CH), 63.0 (OCH₂), 18.1, 13.9 (CH₃). m/e (20°C) 198 (M⁺, 75), 169 (18), 153 (15), 124 (45), 99 (100%), 66 (42).

(f) Ethyl 3-Isopropenyl-1,2,4-thiadiazole-5-carboxylate

A solution of 5-isopropenyl-1,3,4-oxathiazol-2-one (5.0 g, 35 mmol) and ECF (14.3 g, 140 mmol) in dry xylene (130 ml) was heated under reflux for 48 hours. The solvent and residual ECF were removed by evaporation under reduced pressure (40°C / 0.05 mm Hg). The oil produced was distilled under reduced pressure (75°C / 0.05 mm Hg) and chromatographed on silica eluting with petrol/methylene chloride (1:4) giving ethyl 3-isopropenyl-1,2,4-thiadiazole-5-carboxylate as a colourless oil (1.61 g, 23%), (Found: M⁺, 198.045899. C₈H₁₀N₂O₂S requires M, 198.046295). ν_max (film) 1755 (C=O), 1630 (C=O) cm⁻¹. δ_H (CDCl₃) 6.41 (s, 1H, =CH); 5.20 (q, 1H, J = 1 Hz, =CH); 4.51 (q, 2H, CH₂); 2.27 (d, 3H, J = 1 Hz, CH₂); 1.44 (t, 3H, CH₃). δ_C (CDCl₃) 177.5 (C₅), 175.2 (C₃), 157.8 (C=O), 136.2
(g) **Ethyl 3-Styryl-1,2,4-thiadiazole-5-carboxylate**

A solution of 5-styryl-1,3,4-oxathiazol-2-one (1.0 g, 5 mmol) and ECF (1.76 g, 18 mmol) in dry xylene (25 ml) was heated under reflux for 22 hours. The xylene and residual ECF were removed by evaporation under reduced pressure (50°C / 0.05 mm Hg). The solid produced was recrystallised from ethanol to give ethyl 3-styryl-1,2,4-thiadiazole-5-carboxylate as a white solid (0.81 g, 64%), m.p. 81°C; (Found: C, 60.4; H, 4.8; N, 10.8. C\textsubscript{13}H\textsubscript{12}N\textsubscript{2}O\textsubscript{2}S requires C, 60.0; H, 4.6; N, 10.8%). ν\textsubscript{max} (Nujol) 1745 (C=O), 1640 (C=O) cm\textsuperscript{-1}. δ\textsubscript{H} (CDCl\textsubscript{3}) 7.94 (d, 1H, J = 16 Hz, =CH); 7.7-7.3 (m, 5H, ArH); 7.27 (d, 1H, J = 16 Hz, =CH); 4.52 (q, 2H, CH\textsubscript{2}); 1.44 (t, 3H, CH\textsubscript{3}). δ\textsubscript{C} (CDCl\textsubscript{3}) 177.9 (C\textsubscript{5}); 173.8 (C\textsubscript{3}); 158.0 (C=O); 139.1, 127.1 (=CH); 135.1 (Ar ring C); 128.9, 128.7, 128.4 (Ar ring CH); 62.8 (OCH\textsubscript{2}); 13.7 (CH\textsubscript{3}). m/e (20°C) 260 (M\textsuperscript{+}, 70), 259 (100%), 231 (16) 215 (7), 187 (26) 161 (13) 160 (15), 134 (15) 129 (30), 128 (40), 77 (25).

(h) **Ethyl 3-Isopropyl-1,2,4-thiadiazole-5-carboxylate**

A solution of 5-isopropyl-1,3,4-oxathiazol-2-one (1.45 g, 10 mmol) and ECF (3.53 g, 35 mmol) in dry xylene (25 ml) was heated under reflux for 20 hours. The solvent and excess ECF were removed by evaporation under reduced pressure (40°C / 0.02 mm Hg). The oil produced was chromatographed on silica eluting with petrol/methylene chloride (1:4) giving ethyl 3-isopropyl-1,2,4-thiadiazole-5-carboxylate as a colourless oil (1.23 g, 62%), (Found: M\textsuperscript{+}, 200.061241. C\textsubscript{8}H\textsubscript{12}N\textsubscript{2}O\textsubscript{2}S requires M, 200.061945). ν\textsubscript{max} (film) 1755, 1725 (C=O) cm\textsuperscript{-1}. δ\textsubscript{H} (CDCl\textsubscript{3}) 4.53 (q, 2H, J = 7 Hz, CO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}); 3.46 (m, 1H, J=7 Hz, CH (CH\textsubscript{3})\textsubscript{2}); 1.44 (t, 3H, J = 7 Hz, CO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}); 1.40 (d, 6H, J = 7 Hz, CH (CH\textsubscript{3})\textsubscript{2}). δ\textsubscript{C} (CDCl\textsubscript{3}) 183.5 (C\textsubscript{5});
178.3 (C\textsubscript{3}) 158.4 (C=O); 62.7 (CO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}); 32.6 (CH(CH\textsubscript{3})\textsubscript{2}); 21.1 (CH(CH\textsubscript{3})\textsubscript{2}); 13.8 (CO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}). m/e (70\textdegree C) 200 (M\textsuperscript{+}, 60), (100%), 157 (25), 155 (15), 139 (30), 111 (18), 101 (54), 100 (30), 86 (15), 69 (21), 59 (17), 54 (18).
2.18 Polymerisation of Styrene and Methyl Methacrylate and preparation of their copolymers with unsaturated 1,3,4-Oxathiazol-2-ones, 1,2,4-Thiadiazoles and Isothiazoles

The polymers were prepared from 30% solutions (by weight) of monomers in refluxing methyl ethyl ketone (MEK) (ca 80°C) initiating with azobisisobutyronitrile (ABIBN). 1 or 2% ABIBN on monomer was used; when 2% was used 1.3% was added initially and the remaining 0.7% after 2 hours. Multiple additions were used to keep the radical concentration approximately constant. The reaction was monitored by withdrawing 1 ml samples, precipitating, filtering, drying and weighing to establish the percentage conversion to polymer that had occurred. The reactions were stopped after 5 hours, by which time 95% of the possible polymerisation had occurred. A ratio of 1:4 by weight of heterocyclic monomer to styrene or methyl methacrylate (MMA) was used. The polymers or copolymers were purified by precipitating directly into a suitable non-solvent. The solvent/non-solvent mixture was decanted and the polymer redissolved in chloroform and reprecipitated. The above procedure was repeated; the product was filtered off and dried in a vacuum oven at 50°C/12 mm Hg) for 2 hours. During the copolymerisation of the oxathiazolones the presence of a small amount of nitrile formed from the decomposition of the oxathiazolone was observed by i.r. and $^{13}$C n.m.r. The degree of decomposition and the ratio of oxathiazolone to styrene or MMA were evaluated from the elemental analyses of the copolymers.

(a) Polystyrene

The polymerisation was carried out as above using styrene (5.0 g) in MEK (12 ml) with ABIBN (106.3 mg) as initiator. The polymer was precipitated into hexane (300 ml) (x3) giving 2.7 g (54%) of polystyrene. The i.r. spectrum of the product was identical to that of a
standard sample of polystyrene, (Found: C, 92.3; H, 7.7; N, 0.0.
(C₆H₅)₉ requires C, 92.3; H, 7.7; N, 0.0%). δₗ (CDCl₃) 7.2-5.8
(m, 5H, ArH); 2.2-0.6 (m, 3H, CH₂-CH). δ C (CDCl₃) 145.9-145.2
(Ar ring C); 127.8, 125.5 (Ar ring CH); 48.5-40.0 (CH₂-CH).
Mₘ, 14000; Mₘ/Mₙ, 1.94.

(b) Poly(Methyl Methacrylate)

The polymerisation was carried out as before with MMA (5.0 g) in
MEK (12 ml) with ABIBN (50.4 mg). The polymer was precipitated into
hexane (300 ml) (X3) giving 4.5 g (81%) of poly(methyl methacrylate).
The i.r. spectrum of the product was identical to that of poly(methyl
methacrylate) from the literature (Found: C, 59.7; H, 8.3, N, 0.0.
(C₅H₈O₂) requires C, 60.0; H, 8.0; N, 0.0%). δₗ (CDCl₃) 3.58-3.50
(bs, 3H, OCH₃); 2.1-1.5 (bs, 3H, CH₂-CCH₂); 1.3-0.5 (m, 2H, CH₂-CCH₂-CO₂CH₃).
δ C (CDCl₃) 178.0, 177.7, 177.4, 176.7, 176.5 (CO₂CH₃); 56.8-51.1
(CH₂-CCH₂); 51.4 (CO₂CH₃); 45.2, 44.6, 44.3 (CH₂-CCH₃); 18.5, 16.2
(CH₂-CCH₃). Mₘ, 19500; Mₘ/Mₙ, 4.6.

(c) Copolymerisation of Styrene with 5-Vinyl-1,3,4-oxathiazol-2-one

The copolymerisation was carried out as before with styrene
(60.0 g, 577 mmol) and 5-vinyl-1,3,4-oxathiazol-2-one (15.0 g, 117 mmol)
in MEK (180 ml), initiated with ABIBN (1.55 g). Precipitation into
hexane (1200 ml) (X3) gave styrene/5-vinyl-1,3,4-oxathiazol-2-one
copolymer as a white solid (16.7 g, 22%), (Found: C, 71.1; H, 6.2; N,
4.4; S, 9.6%; corresponding to a styrene:oxathiazolone:nitrile ratio
of 0.64:0.33:0.03). ν max (film) 2210 (C≡N), 1755 (C=O) cm⁻¹.
δₗ (CDCl₃) 7.48-6.20 (m, ArH); 2.52-0.60 (m, CH₂-CH of styrene,
oxathiazolone and nitrile units). δ C (CDCl₃) 173.3 (oxathiazolone C₂);
162.9 (oxathiazolone C); 148-141 (Ar ring C); 128.3, 127.1, 126.3 (Ar ring CH); 50-38, 30-27 (CH₂-CH of styrene, oxathiazolone and nitrile units). $\overline{M}_w$, 2900; $M_w/M_n$, 1.5.

(d) **Copolymerisation of Styrene with 5-Isopropenyl-1,3,4-oxathiazol-2-one**

The copolymerisation was carried out as before with styrene (24.0 g, 331 mmol) and 5-isopropenyl-1,3,4-oxathiazol-2-one (6.09 g, 42 mmol) in MEK (180 ml); initiated with ABIBN (0.60 g). Precipitation into hexane (1200 ml) (X3) gave styrene/5-isopropenyl-1,3,4-oxathiazol-2-one copolymer as a white solid (5.93 g, 19.7%), (Found: C, 67.2; H, 5.9; N, 5.3; S, 11.0%; corresponding to a styrene:oxathiazolone:nitrile ratio of 0.60:0.35:0.05).

$\nu_{\text{max}}$ (film) 2220 (C=O), 1750 (C=O) cm⁻¹. $\delta_H$ (CDCl₃) 7.60-6.10 (m, ArH); 2.60-0.60 (m, CH₂-CH, CH₂-CH₃ of oxathiazolone and nitrile units).

$\delta_C$ (CDCl₃) 172.7 (oxathiazolone C); 167-163 (oxathiazolone C₂); 147-143 (Ar ring C); 132-126 (Ar ring CH), 56-18 (CH₂-CH, CH₂-CH₃ of oxathiazolone and nitrile units). $\overline{M}_w$, 2900; $M_w/M_n$, 1.5.

(e) **Copolymerisation of Methyl Methacrylate with 5-Vinyl-1,3,4-oxathiazol-2-one**

The copolymerisation was carried out as before with MMA (60.0 g, 600 mmol) and 5-vinyl-1,3,4-oxathiazol-2-one (15.0 g, 117 mmol) in MEK (180 ml); initiated with ABIBN (1.55 g). Precipitation into methanol (1200 ml) (X3) gave MMA/5-vinyl-1,3,4-oxathiazol-2-one copolymer as a white solid (9.00 g, 12%), (Found: C, 56.2; H, 7.4; N, 2.0; S, 3.9%; corresponding to a MMA:oxathiazolone:nitrile ratio of 0.84:0.11:0.05).

$\nu_{\text{max}}$ (film) 2220 (C=O), 1725 (C=O) cm⁻¹. $\delta_H$ (CDCl₃) 3.80-3.42 (bs, OCH₃); 2.20-0.60 (m, CH₂-CH, CH₂-CH₃ of oxathiazolone and nitrile units). $\delta_C$ (CDCl₃) 177.5, 177.3, 176.5, 175.8, 175.7
(g) Copolymerisation of Methyl Methacrylate with 5-Isopropenyl-1,3,4-oxathiazol-2-one in a 20% solution using 1% initiator

The copolymerisation was carried out as before with MMA (4.0 g, 40 mmol) and 5-isopropenyl-1,3,4-oxathiazol-2-one (1.0 g, 70 mmol) in MEK (25 ml); initiated with ABIBN (51.6 mg). Precipitation into diethyl ether (200 ml) (x3) gave a white solid (0.68 g, 13%) which had an i.r. spectrum identical to that of the MMA/5-isopropenyl-1,3,4-oxathiazol-2-one copolymer prepared from a 30% solution with 2% ABIBN. \( \nu_{\text{max}} \) (film) 2220 (C=O) cm\(^{-1}\). \( \bar{m} \), 3800; \( \bar{M}_w/\bar{M}_n \), 2.1. The solvent/non-solvent mixture

(f) Copolymerisation of Methyl Methacrylate with 5-Isopropenyl-1,3,4-oxathiazol-2-one

The copolymerisation was carried out as before with MMA (40.0 g, 400 mmol) and 5-isopropenyl-1,3,4-oxathiazol-2-one (10.0 g, 70 mmol) in MEK (120 ml); initiated with ABIBN (1.05 g). Precipitation into methanol (1000 ml) (x3) gave MMA/5-isopropenyl-1,3,4-oxathiazol-2-one copolymer as a white solid (10.0 g, 20%), (Found: C, 50.9; H, 6.0; N, 5.1; S, 10.6%; corresponding to a MMA:oxathiazolone:nitrile ratio of 0.58:0.39:0.03). \( \nu_{\text{max}} \) (film) 2220 (C=O) cm\(^{-1}\). \( \bar{m} \) (CDCl\(_3\)) 180-177 (CO\(_2\)CH\(_3\)) cm\(^{-1}\), 167-162 (oxathiazolone C\(_2\)) of 57-16 (CH\(_2\)-CH\(_3\)-CO\(_2\)CH\(_3\), CH\(_2\)-CH\(_3\) of oxathiazolone and nitrile units). \( \bar{M}_w \), 9600; \( \bar{M}_w/\bar{M}_n \), 1.5.
containing polymer which had not been precipitated, together with unreacted oxathiazolone and MMA was evaporated under reduced pressure, \( ^1H \text{n.m.r.} \) analysis of the oil produced (0.66 g), indicated that it was composed of 96wt% oxathiazolone and 4wt% copolymer. This constituted a 95% recovery of unreacted oxathiazolone, and demonstrated that the purification technique was effective, precipitating 96% of the copolymer formed.

(h) **Attempted copolymerisation of Methyl Methacrylate with 5-Styryl-1,3,4-oxathiazol-2-one**

The copolymerisation was attempted by the method used before with MMA (4.0 g, 40 mmol) and 5-styryl-1,3,4-oxathiazol-2-one (1.0 g, 4.8 mmol) in MEK (20 ml, 20% solution). The reaction was initiated with ABIBN (49.5 mg) and monitored by withdrawing samples as before. The reaction kinetics appeared to be identical to those for the formation of poly(methyl methacrylate). The product was precipitated into hexane (150 ml)(X3) and it was found to have an i.r. spectrum identical to that of poly(methyl methacrylate). The mother liquor was concentrated under reduced pressure and the solid produced shown to be 5-styryl-1,3,4-oxathiazol-2-one (1.0 g, 100% recovered) by i.r. and \( ^1H \text{n.m.r.} \).

(i) **Attempted copolymerisation of Methyl Methacrylate with 5-(Prop-1-enyl)-1,3,4-oxathiazol-2-one**

The copolymerisation was attempted by the method used before with MMA (4.0 g, 40 mmol) and 5-(prop-1-enyl)-1,3,4-oxathiazol-2-one (1.0 g, 7.0 mmol) in MEK (20 ml, 20% solution). The reaction was initiated with ABIBN (51.5 mg) and monitored by withdrawing samples as before. The reaction kinetics appeared to be identical to those for poly(methyl methacrylate). The product was precipitated into hexane.
(150 ml)(X3) and was found to have an i.r. spectrum identical to that of poly(methyl methacrylate).

(j) **Copolymerisation of Styrene with Ethyl 3-Isopropenyl-1,2,4-thiadiazole-5-carboxylate**

The copolymerisation was carried out as before with styrene (4.0 g, 38 mmol) and ethyl 3-isopropenyl-1,2,4-thiadiazole-5-carboxylate (1.0 g, 5.0 mmol) in MEK (20 ml, 20% solution); initiated with ABIBN (49.4 mg). Precipitation into hexane (150 ml)(X3) gave styrene/ethyl 3-isopropenyl-1,2,4-thiadiazole-5-carboxylate copolymer as a yellow solid (0.75 g, 15%), (Found: C, 72.5; H, 6.5; N, 7.7; S, 3.8%; corresponding to a styrene/thiadiazole ratio of 0.64:0.36). $\nu_{\text{max}}$ (film) 1745, 1715 (C=O) cm$^{-1}$. $\delta_H$ (CDCl$_3$) 7.46-6.00 (m, 5H, ArH); 4.72-4.08 (bs, 0.83H, CO$_2$CH$_2$CH$_3$); 2.72-0.50 (m, CH$_2$-CH, CH$_2$-CCH$_3$, CO$_2$CH$_2$CH$_3$).

$\delta_C$ (CDCl$_3$) 184-182 (thiadiazole C$_5$); 178-176.5 (thiadiazole C$_3$); 161-159 (CO$_2$CH$_2$CH$_3$); 148-142 (Ar ring C); 130-123 (Ar ring CH); 62.5 (CO$_2$CH$_2$CH$_3$); 56-17 (CH$_2$-CH, CH$_2$-CCH$_3$); 14.1 (CO$_2$CH$_2$CH$_3$).

(k) **Copolymerisation of Styrene with Dimethyl 3-Isopropenylisothiazol-4,5-dicarboxylate**

The copolymerisation was carried out as before with styrene (1.00 g, 9.6 mmol) and dimethyl 3-isopropenylisothiazol-4,5-dicarboxylate (0.27 g, 1.1 mmol) in MEK (5 ml); initiating with ABIBN (24 mg). Precipitation into hexane (100 ml)(X3) gave styrene/dimethyl 3-isopropenylisothiazol-4,5-dicarboxylate copolymer as a yellow solid (190 mg, 15%), (Found: C, 82.4; H, 7.3; N, 1.9; S, 3.2%; corresponding to a styrene:isothiazole ratio of 0.85:0.15). $\nu_{\text{max}}$ (film) 1730 (C=O) cm$^{-1}$. $\delta_H$ (CDCl$_3$) 7.67-6.08 (m, 5H, ArH); 3.96-3.32 (m, 0.56H, CO$_2$CH$_3$); 2.48-0.60 (m, CH$_2$-CH, CH$_2$-CCH$_3$). $\delta_C$ (CDCl$_3$) 174-172 (isothiazole C$_3$);
165-164 (C=O); 159-158 (C = O); 157-153 (isothiazole C₅); 146-143 (Ar ring C);
132-118 (isothiazole C₄, Ar ring CH); 58-20 (OCH₃, CH₂-C₆H₅, CH₂-CCH₃
of isothiazole unit).

(1) Copolymerisation of Methyl Methacrylate with Dimethyl
3-Isopropenylisothiazole-4,5-dicarboxylate

The copolymerisation was carried out as before with MMA (1.00 g,
10 mmol) and dimethyl 3-isopropenylisothiazole-4,5-dicarboxylate
(0.25 g, 1.0 mmol) in MEK (4 ml); initiated with AIBN (25.0 mg).
Precipitation into hexane (50 ml) (X3) gave NMA/dimethyl 3-isopropenyl-
isothiazole-4,5-dicarboxylate copolymer as a white solid (380 mg, 30%),
(Found: C, 59.6; H, 7.7; N, 1.4 S, 3.6%; corresponding to a MMA:
isothiazole ratio of 0.88:0.12). ν_max (film) 1735 (C=O) cm⁻¹. S_H (CDCl₃)
4.15-3.05 (m, CO₂CH₃ of MMA and isothiazole units); 2.45-0.20
(m, CH₂-CCH₃ of MMA and isothiazole units). S_C (CDCl₃) 180.0-174.5
(CH₂-CCH₃CO₂CH₃); 174.0-172.0 (isothiazole C₅); 165.9-165.6, 159.0
(C=O); 154.9 (isothiazole C₅); 133.5 (isothiazole C₄); 68-4
(CH₂-CCH₃CO₂CH₃, CH₂-CCH₃ of isothiazole unit).

2.19 Thermolysis of copolymers of Styrene and Methyl Methacrylate
with 5-Vinyl-1,3,4-oxathiazol-2-one and 5-Isopropenyl-1,3,4-
oxathiazol-2-one in an inert solvent

Thermolysis was carried out by dissolving the copolymers (1.0 g)
in xylene (25 ml) and heating the solution under reflux (ca 140°C). The
reaction was followed by withdrawing a small sample, precipitating and
filtering. When i.r. showed the complete disappearance of the carbonyl
peak in the case of styrene copolymers or no further increase in the size
of the nitrile peak for MMA copolymers, the reaction was stopped. Reaction
times were found to be 4 hours for styrene copolymers and 6 hours for
MMA copolymers. The nitrile-containing copolymers were purified by multiple precipitations into hexane (25 ml)(X3); redissolving in chloroform between precipitations.

(a) **Styrene/5-Vinyl-1,3,4-oxathiazol-2-one copolymer**

The reaction was carried out as above yielding styrene/acrylonitrile copolymer as a white solid (0.78 g, 92%), (Found: C, 83.1; H, 7.02; N, 5.7; S, 3.0%; corresponding to a styrene:oxathiazolone:nitrile ratio of 0.63:0.07:0.30). $\nu_{\text{max}}$ (film) 2220 (C=CN) cm$^{-1}$. $\delta_H$ (CDCl$_3$) 7.6-5.8 (m, Ar ring); 3.3-0.3 (m, CH$_2$-CH$_6$H$_5$, CH$_2$-CH of oxathiazolone unit, CH$_2$-CHCN). $\delta_C$ (CDCl$_3$) 148-140 (Ar ring C); 136-126 (Ar ring CH); 123 (CH$_2$-CHCN); 51-27 (CH$_2$-CH$_6$H$_5$, CH$_2$-CH of oxathiazolone unit, CH$_2$-CHCN).

(b) **Styrene/5-Isopropenyl-1,3,4-oxathiazol-2-one copolymer**

The reaction was carried out as before yielding styrene/methacrylonitrile copolymer as a white solid (0.67 g, 80%), (Found: C, 81.7; H, 7.2; N, 7.0; S, 3.1%; corresponding to a styrene:oxathiazolone:nitrile ratio of 0.55:0.03:0.42). $\nu_{\text{max}}$ (film) 2220 (C=CN) cm$^{-1}$. $\delta_H$ (CDCl$_3$) 7.5-6.3 (m, Ar ring); 3.2-0.4 (m, CH$_2$-CH$_6$H$_5$, CH$_2$-CCH$_2$ of oxathiazolone unit, CH$_2$-CCH$_2$CN). $\delta_C$ (CDCl$_3$) 148-143 (Ar ring C); 134-127 (Ar ring CH); 124.5 (CH$_2$-CCH$_2$CN); 54-25 (CH$_2$-CH$_6$H$_5$, CH$_2$-CCH$_3$ of oxathiazolone unit, CH$_2$-CCH$_3$CN).

(c) **Methyl Methacrylate/5-Vinyl-1,3,4-oxathiazol-2-one copolymer**

The reaction was carried out as before yielding MMA/acrylonitrile copolymer as a white solid (0.80 g, 78%), (Found: C, 60.1; H, 7.4; N, 1.9; S, 1.2%; corresponding to a MMA:oxathiazolone:nitrile ratio of 0.88:0.04:0.08). $\nu_{\text{max}}$ (film) 2220 (C=CN), 1725 (C=O) cm$^{-1}$. $\delta_H$ (CDCl$_3$) 3.6-3.3 (bs, CO$_2$CH$_3$); 2.4-0.6 (m, CH$_2$-CCH$_3$CO$_2$CH$_3$, CH$_2$-CH of oxathiazolone...
unit, CH₂-CHCN). δ C (CDCl₃) 177.6, 177.4, 176.5, 175.8, 175.4 (CO₂CH₃); 123 (CH₂-CHCN); 57-15 (CH₂-CCH₃CO₂CH₃, CH₂-CH of oxathiazolone unit, CH₂-CHCN).

(d) Methyl Methacrylate/5-Isopropenyl-1,3,4-oxathiazol-2-one copolymer

The reaction was carried out as before yielding the MMA/methacrylonitrile copolymer as a white solid (0.68 g, 90%), (Found: C, 61.9; H, 7.7; N, 5.4; S, 2.7%; corresponding to a MMA:oxathiazolone:nitrile ratio of 0.65:0.08:0.27). ν max (film) 2220 (C=O), 1750 (C=O) cm⁻¹.

δ H (CDCl₃) 3.6-3.3 (bs, CO₂CH₃); 2.5-0.5 (m, CH₂-CCH₃CO₂CH₃, CH₂-CCH₃ of oxathiazolone unit, CH₂-CCH₃CN). δ C (CDCl₃) 181-175 (CO₂CH₃); 126-123 (CH₂-CCH₃CN); 58-27 (CH₂-CCH₃CO₂CH₃, CH₂-CCH₃ of oxathiazolone unit, CH₂-CCH₃CN).

2.20 Thermolysis of copolymers of 5-Vinyl-1,3,4-oxathiazol-2-one and 5-Isopropenyl-1,3,4-oxathiazol-2-one with Styrene and Methyl Methacrylate in the presence of Ethyl Cyanoformate and Dimethyl Acetylenedicarboxylate

These reactions were carried out by dissolving the copolymer in xylene and heating under reflux (ca 140°C) with a ten fold excess of ethyl cyanoformate (ECF) or dimethyl acetylenedicarboxylate (DMAD). The progress of the reaction was monitored by withdrawing a small sample, precipitating, filtering and examining the product by i.r.. When no further change in the carbonyl peak was evident (after 6 hours) heating was stopped and the thiadiazole - or isothiazole - containing polymers were purified by three precipitations into hexane (25 ml); redissolving in chloroform between precipitations. The products were filtered and dried in the vacuum oven at 45°C/12 mm Hg for 24 hours.
(a) **Styrene/5-Vinyl-1,3,4-oxathiazol-2-one copolymer**

(i) **Thermolysis with Ethyl Cyanoformate**

The reaction was carried out as before yielding styrene/ethyl 3-vinyl-1,2,4-thiadiazole-5-carboxylate/acrylonitrile terpolymer as a white solid (0.82 g, 91%), (Found: C, 79.7; H, 6.6; N, 6.5, S, 4.2%; corresponding to a styrene:thiadiazole:nitrile ratio of 0.66:0.13:0.21).

$\nu_{\text{max}}$ (film) 2220 (C=CN), 1750, 1720 (C=O) cm$^{-1}$. $\delta_H^1$ (CDCl$_3$) 7.52-6.00 (m, 5H, Ar ring); 4.64-4.22 (m, 0.2H, CO$_2$CH$_2$CH$_3$); 3.42-0.60 (m, CH$_2$-CHC$_6$H$_5$, CH$_2$-CH of thiadiazole unit, CH$_2$-CH-CN, CO$_2$CH$_2$CH$_3$);

$\delta_C$ (CDCl$_3$) 182-179 (thiadiazole C$_5$); 179-176 (thiadiazole C$_3$);

157-156 (CO$_2$CH$_2$CH$_3$); 147-142 (Ar ring C); 129-125 (Ar ring CH);

115 (CH$_2$-CH-CN); 62.6 (CO$_2$CH$_2$CH$_3$); 48-18 (CH$_2$-CHC$_6$H$_5$, CH$_2$-CH of thiadiazole unit, CH$_2$-CH-CN); 14.0 (CO$_2$CH$_2$CH$_3$).

(ii) **Thermolysis with Dimethyl Acetylenedicarboxylate**

The reaction was carried out as before yielding styrene/dimethyl 3-vinylisothiazole-4,5-dicarboxylate/acrylonitrile terpolymer as a yellow solid (0.94 g, 92%), (Found: C, 71.9; H, 6.1; N, 3.7; S, 4.6%; corresponding to a styrene:isothiazole:nitrile ratio of 0.66:0.17:0.17).

$\nu_{\text{max}}$ (film) 2230 (C=CN), 1725 (C=O) cm$^{-1}$. $\delta_H^1$ (CDCl$_3$) 7.52-6.16 (m, 5H, Ar ring); 4.10-3.08 (m, 6OH, CO$_2$CR); 2.80-0.6 (m, CH$_2$-CHC$_6$H$_5$,

CH$_2$-CH of isothiazole unit, CH$_2$-CH-CN). $\delta_C$ (CDCl$_3$) 171.6 (isothiazole C$_3$);

162.6, 159.0 (C=O); 157-154 (isothiazole C$_5$); 145-138 (Ar ring C);

132 (isothiazole C$_4$); 134-121 (Ar ring CH); 120.9 (CH$_2$-CH-CN); 52.4 (CO$_2$CH$_3$); 50-26 (CH$_2$-CHC$_6$H$_5$, CH$_2$-CH of isothiazole unit, CH$_2$-CH-CN).

(b) **Styrene/5-Isopropenyl-1,3,4-oxathiazol-2-one copolymer**

(i) **Thermolysis with Ethyl Cyanoformate**

The reaction was carried out as before yielding styrene/ethyl 3-isopropenyl-1,2,4-thiadiazole-5-carboxylate/methacrylonitrile terpolymer
as a white solid (0.88 g, 90%), (Found: C, 75.4; H, 6.9; N, 7.5; S, 5.8%
corresponding to a styrene:thiadiazole:nitrile ratio of 0.56:0.23:0.21).

\( \nu_{\text{max}} \) (film) 2220 (C=N), 1750, 1715 (C=O) cm\(^{-1}\). \( \delta \) \(_{\text{H}}\) (CDCl\(_3\)) 7.56-6.20
(m, 5H, Ar ring); 4.60-4.18 (m, 0.4H, CO\(_2\)CH\(_2\)CH\(_3\)); 3.36-0.60
(m, CH\(_2\)-CH\(_6\)H\(_5\), CH\(_2\)-CCH\(_3\) of thiadiazole unit, CH\(_2\)-CCH\(_3\)CN, CO\(_2\)CH\(_2\)CH\(_3\)).

\( \delta \) \(_{\text{C}}\) (CDCl\(_3\)) 185-181 (thiadiazole C\(_5\)); 179-176 (thiadiazole C\(_3\));
158-157 (CO\(_2\)CH\(_2\)CH\(_3\)); 149-142 (Ar ring C); 130-123 (Ar ring CH);
63 (CO\(_2\)CH\(_2\)CH\(_3\)); 46-18 (CH\(_2\)-CH\(_6\)H\(_5\), CH\(_2\)-CCH\(_3\) of thiadiazole unit,
CH\(_2\)-CCH\(_3\)CN); 13.9-13.6 (CO\(_2\)CH\(_2\)CH\(_3\)).

(ii) Thermolysis with Dimethyl Acetylenedicarboxylate

The reaction was carried out as before yielding styrene/dimethyl
3-isopropenylisothiazole-4,5-dicarboxylate/methacrylonitrile terpolymer
as a yellow solid (0.93 g, 88%), (Found: C, 71.8; H, 7.1; N, 4.1; S, 5.3%
corresponding to a styrene:isothiazole:nitrile ratio of 0.61:0.22:0.17).

\( \nu_{\text{max}} \) (film) 2220 (C=N), 1730 (C=O) cm\(^{-1}\). \( \delta \) \(_{\text{H}}\) (CDCl\(_3\)) 7.90-6.34
(m, 5H, Ar ring); 4.18-3.32 (m, 2.7H, CO\(_2\)CH\(_3\)); 3.20-0.60
(m, CH\(_2\)-CH\(_6\)H\(_5\), CH\(_2\)-CCH\(_3\) of isothiazole unit, CH\(_2\)-CCH\(_3\)CN). \( \delta \) \(_{\text{C}}\) (CDCl\(_3\))
174-171 (isothiazole C\(_3\)); 165.2, 158.9 (C=O); 157-154 (isothiazole C\(_5\));
148-142 (Ar ring C); 134-132 (isothiazole C\(_4\)); 132-122 (Ar ring CH);
122.5 (CH\(_2\)-CCH\(_3\)CN); 53 (CO\(_2\)CH\(_3\)); 52-14 (CH\(_2\)-CH\(_6\)H\(_5\), CH\(_2\)-CCH\(_3\) of
isothiazole unit, CH\(_2\)-CCH\(_3\)CN).

(c) Methyl Methacrylate/5-Vinyl-1,3,4-oxathiazol-2-one copolymer

(i) Thermolysis with Ethyl Cyanoforinate

The reaction was carried out as before yielding MMA/ethyl 3-vinyl-
1,2,4-thiadiazole-5-carboxylate/acrylonitrile terpolymer as a white
solid (0.87 g, 90%), (Found: C, 57.3; H, 7.3; N, 3.2; S, 1.6%
corresponding to a MMA:thiadiazole:nitrile ratio of 0.82:0.05:0.13). \( \nu_{\text{max}} \) (film)
2230 (C=N), 1730 (C=O) cm⁻¹.  \( \delta_H (\text{CDC}_3) \) 4.64-4.36 (q, 0.2H, CO₂CH₂CH₃); 3.50 (bs, 3H, CO₂CH₃); 2.46-0.60 (m, CH₂-CCH₃CO₂CH₃, CH₂-CH of thiadiazole unit, CH₂-CHCN, CO₂CH₂CH₃).  \( \delta_C (\text{CDC}_3) \) 182-174 (thiadiazole C₃ and C₅, CO₂CH₃); 158.0 (CO₂CH₂CH₃); 122-121 (CH₂-CHCN); 63.0 (CO₂CH₂CH₃); 58-17 (CH₂-CCH₃CO₂CH₃, CH₂-CH of thiadiazole unit, CH₂-CHCN); 13.9 (CO₂CH₂CH₃).

(ii) Thermolysis with Dimethyl Acetylenedicarboxylate

The reaction was carried out as before yielding MMA/dimethyl-3-vinylisothiazole-4,5-dicarboxylate/acrylonitrile terpolymer as a yellow solid (0.93 g, 84%); (Found: C, 59.1; H, 7.2; N, 1.7, S, 3.0%; corresponding to a MMA/isothiazole:nitrile ratio of 0.87:0.10:0.03).  \( \nu_{\text{max}} \) (film) 2220 (C=O), 1730 (C=O) cm⁻¹.  \( \delta_H (\text{CDC}_3) \) 4.65-3.25 (m, CH₂-CCH₃CO₂CH₃, CO₂CH₃ of isothiazole unit); 2.60-0.60 (m, CH₂-CCH₃CO₂CH₃, CH₂-CH of isothiazole unit, CH₂-CHCN).  \( \delta_C (\text{CDC}_3) \) 184-177 (CH₂-CCH₃CO₂CH₃); 175-173 (isothiazole C₃); 165-163, 162-159 (CO₂CH₃ of isothiazole unit); 158-156 (isothiazole C₅); 134-132 (isothiazole C₄); (CH₂-CHCN not visible); 58-14 (CH₂-CCH₃CO₂CH₃, CH₂-CH and CO₂CH₃ of isothiazole unit, CH₂-CHCN).

(d) Methyl Methacrylate/5-Isopropenyl-1,3,4-oxathiazol-2-one copolymer

(i) Thermolysis with Ethyl Cyanoforinate

The reaction was carried out as before yielding MMA/ethyl 3-isopropenyl-1,2,4-thiadiazol-5-carboxylate/methacrylonitrile terpolymer as a white solid (0.83 g, 82%), (Found: C, 56.7; H, 7.2; N, 5.9; S, 5.4%; corresponding to a MMA/thiadiazole:nitrile ratio of 0.64:0.20:0.16).  \( \nu_{\text{max}} \) (film) 2230 (C=O), 1730 (C=O) cm⁻¹.  \( \delta_H (\text{CDC}_3) \) 4.70-4.24 (m, 0.35H, CO₂CH₂CH₃); 3.80-3.14 (bs, 3H, CO₂CH₃); 2.40-0.60 (m, CH₂-CCH₃CO₂CH₃, CH₂-CCH₃ of thiadiazole unit, CH₂-CCH₃CN, CO₂CH₂CH₃).  \( \delta_C (\text{CDC}_3) \) 185-182 (thiadiazole C₅); 181-176 (thiadiazole C₇, CO₂CH₃);
170-169 ($CO_2CH_2CH_3$); 126-124 ($CH_2-CCH_2CN$); 63.1 ($CO_2CH_2CH_3$); 60-17 ($CH_2-CCH_3CO_2CH_3$, $CH_2-OCH_3$ of thiadiazole unit, $CH_2-CCH_3CN$); 14.0 ($CO_2CH_2CH_3$).

(ii) Thermolysis with Dimethyl Acetylenedicarboxylate

The reaction was carried out as before yielding MMA/dimethyl 3-isopropenyl-4,5-dicarboxylate/methacrylonitrile terpolymer as a yellow solid (0.85 g, 87%), (Found: C, 57.6; H, 6.7; N, 3.9; S, 4.3%; corresponding to a MMA:isothiazole:nitrile ratio of 0.67:0.17:0.16).

\[ \nu_{\text{max}} \text{ (film)} \, 2220 (\text{C=O}) \, \text{cm}^{-1}. \]

$\delta_H$ (CDCl$_3$) 4.5-3.4 (m, $CH_2-CCH_3CO_2CH_3$, $CO_2CH_3$ of isothiazole unit), 2.7-0.5 (m, $CH_2-CCH_3CO_2CH_3$, $CH_2-CCH_3$ of isothiazole unit, $CH_2-CCH_3CN$). $\delta_C$ (CDCl$_3$) 179-176 ($CH_2-CCH_3CO_2CH_3$); 174-172 (isothiazole C$_3$); 165.6, 159.0 ($CO_2CH_3$ of isothiazole unit); 157-155 (isothiazole C$_5$); 133.5 (isothiazole C$_4$); 126-123 ($CH_2-CCH_3CN$); 59-14 ($CH_2-CCH_3CO_2CH_3$, $CH_2-CCH_3$ and $CO_2CH_3$ of isothiazole unit, $CH_2-CCH_3CN$).

2.21 Reaction of p-Nitrobenzohydroximoyl Chloride with Acrylonitrile/Styrene and Acrylonitrile/Vinylidene Chloride copolymers

The copolymers used were supplied by the Aldrich Chemical Company. The acrylonitrile/styrene copolymer contained 25wt% acrylonitrile, the copolymer with vinylidene chloride contained 20wt% acrylonitrile.

Two different molar ratios (0.25:1 and 10:1) of hydroximoyl chloride to nitrile units were used. The reactions were carried out by dissolving the copolymer in $\gamma$-butyrolactone, adding the hydroximoyl chloride and heating on an oil bath at 130°C. For experiments using a ten fold excess, the hydroximoyl chloride was added in two equal portions at t=0 and t=2 hours. The reaction was stopped when i.r. indicated no further change in the size of the nitro peaks at 1530, 1340 cm$^{-1}$. The resulting polymer was precipitated from a suitable non-solvent (X3), filtered and dried in the vacuum oven at 90°C/12 mm Hg for 2-4 hours.
(a) Acrylonitrile/Styrene copolymer

(i) Modification with 10 moles of hydroximoyl chloride per mole of nitrile

The reaction was carried out as before with p-nitrobenzohydroximoyl chloride (7.5 g) and acrylonitrile/styrene copolymer (1.0 g) in γ-butyrolactone (35 ml) (reaction time 6 hours). The terpolymer produced was precipitated from methanol, redissolving between precipitations in dimethylformamide, as a white solid (6.0 g, 86%), (Found: C, 79.5; H, 6.6; N, 8.4%; starting polymer C, 85.6; H, 7.2, N, 6.7%; corresponding to conversion of 30% of the nitrile units to oxadiazole rings). $\nu_{\text{max}}$(film) 1530, 1340 (NO$_2$) cm$^{-1}$. $\delta$ H (CD$_3$NO) 8.3-7.6 (m, 1.OH, O$_2$NC$_6$H$_4$ ring CH); 7.1-6.2 (m, 5H, styrene ring CH); 3.3-0.8 (CH$_2$-CHC$_6$H$_5$, CH$_2$-CH of oxadiazole unit, CH$_2$-CHCN). $\delta$ C (CD$_3$NO) 182.6, 165.8 (oxadiazole ring C); 149.1, 132.1 (O$_2$NC$_6$H$_4$ ring C); 145-138 (styrene ring C); 130-122 (styrene ring CH, O$_2$NC$_6$H$_4$ ring CH); 121.3 (CH$_2$-CHCN); 51-32 (CH$_2$-CHC$_6$H$_5$, CH$_2$-CH of oxadiazole unit, CH$_2$-CHCN).

(ii) Modification with 0.25 moles of hydroximoyl chloride per mole of nitrile

The reaction was carried out as before with p-nitrobenzohydroximoyl chloride (2.0 g) and acrylonitrile/styrene copolymer (5.3 g) in γ-butyrolactone (75 ml) (reaction time 6 hours). The terpolymer produced was precipitated from methanol, redissolving between precipitations in dimethylformamide, as a white solid (5.1 g, 80%), (Found: C, 81.0; H, 6.9; N, 7.5%; corresponding to conversion of 8% of the nitrile units to oxadiazole rings). $\nu_{\text{max}}$(film) 1530, 1340 (NO$_2$) cm$^{-1}$. 
(b) **Acrylonitrile/Vinylidene Chloride copolymer**

(i) **Modification with 10 moles of hydroximoyl chloride per mole of nitrile**

The reaction was carried out as before with \( p \)-nitrobenzohydroximoyl chloride (5.66 g) and acrylonitrile/vinylidene chloride copolymer (0.75 g) in \( \gamma \)-butyrolactone (40 ml) (reaction time 6 hours). The terpolymer produced was precipitated from methanol, redissolving in \( \gamma \)-butyrolactone/nitromethane (1:1), as a grey solid (0.83 g, 85\%), (Found: C, 38.2; H, 2.7; N, 7.7\%; starting polymer C, 33.6; H, 2.8; N, 5.0\%; corresponding to conversion of 50\% of the nitrile units to oxadiazole rings). \( \nu_{\text{max}} \) (film) 1530, 1340 (NO\(_2\)) cm\(^{-1}\). \( \delta \) (C\(_2\)D\(_6\)SO) 8.2-7.6 (m, \( O_2NC_6\text{H}_4 \) ring \( \text{CH} \)); 4.2-1.4 (\( \text{CCl}_2\text{-CH}_2 \), \( \text{CH}_2\text{-CH} \) of oxadiazole unit, \( \text{CH}_2\text{-CHCN} \)). \( \delta \) (C\(_2\)D\(_6\)SO) 182.0, 166.6 (oxadiazole ring \( \text{C} \)); 149.3, 131.8 (\( O_2NC_6\text{H}_4 \) ring \( \text{C} \)); 128.5, 124.6 (\( O_2NC_6\text{H}_4 \) ring \( \text{CH} \)); 121.7 (\( \text{CH}_2\text{-CHCN} \)); 64-23 (\( \text{CH}_2\text{-CCl}_2 \), \( \text{CH}_2\text{-CH} \) of oxadiazole unit, \( \text{CH}_2\text{-CHCN} \)).

(ii) **Modification with 0.25 moles of hydroximoyl chloride per mole of nitrile**

The reaction was carried out as before with \( p \)-nitrobenzohydroximoyl chloride (2.0 g) and acrylonitrile/vinylidene chloride copolymer (6.6 g) in \( \gamma \)-butyrolactone (100 ml) (reaction time 6 hours). The terpolymer produced was precipitated from methanol, redissolving between precipitations in \( \gamma \)-butyrolactone/nitromethane (1:1), as a grey solid (7.3 g, 85\%), (Found: C, 35.0, H, 2.9; N, 5.6\%; corresponding to conversion of 10\% of the nitrile units to oxadiazole rings). \( \nu_{\text{max}} \) (film) 1530, 1340 (NO\(_2\)) cm\(^{-1}\).
Reaction of p-Nitrobenzohydroximoyl Chloride with 
cis-1,4-Polyisoprene and cis-1,4-Polybutadiene

Three different molar ratios (0.1:1, 0.2:1 and 1:1) of hydroximoyl chloride to double bond units in the polymer were used. The reactions were carried out by adding the p-nitrobenzohydroximoyl chloride to a solution of the polymer in xylene and heating under reflux (ca 140°C). The progress of the reaction was monitored by withdrawing small samples with time and precipitating into methanol. When i.r. indicated no further change in the size of the nitro peaks (at 1540, 1340 cm\(^{-1}\)) heating was stopped. The product was then precipitated into methanol (x3), redissolving between precipitations in chloroform and dried in the vacuum oven at 50°C/12 mm Hg for 2-4 hours.

(a) cis-1,4-Polyisoprene (PIP)

(i) Modification with 0.1 moles of hydroximoyl chloride per mole of double bond units in polyisoprene

The reaction was carried out as above using PIP (17.0 g) and p-nitrobenzohydroximoyl chloride (5.0 g) in xylene (750 ml) (reaction time 3 hours) yielding a brown sticky solid (15.5 g, 77%), (Found: C, 74.5; H, 9.0; N, 2.2%; corresponding to conversion of 7.5% of the isoprene units to isoxazoline rings). \(\nu_{\text{max}}\) (film) 1520, 1345 (NO\(_2\)) cm\(^{-1}\). 
\(\delta\)\(_H\) (CDCl\(_3\)) 8.28-8.12 (bd, 4H, ArH); 7.86-7.72 (bd, 2H, ArH); 5.10-4.98 (bs, 6.5H, CH=CCH\(_3\)); 2.44-1.00 (CH\(_2\)-CH=CH\(_2\), CH\(_2\)-CH-CCH\(_3\)-CH\(_2\) of isoxazoline units).

(ii) Modification with 0.2 moles of hydroximoyl chloride per mole of double bond units in polyisoprene

The reaction was carried out as above using PIP (1.7 g) and p-nitrobenzohydroximoyl chloride (1.0 g) in xylene (250 ml)
(reaction time 3 hours) yielding a brown sticky solid (1.64 g, 73%), (Found: C, 78.7; H, 9.1, N, 3.7%; corresponding to conversion of 12% of the isoprene units to isoxazoline rings). \( \nu_{\text{max}} \) (film) 1520, 1345 (NO\(_2\)) cm\(^{-1}\). \( \delta \) (CDCl\(_3\)) 8.32-8.12 (bd, 2H, ArH); 7.90-7.72 (bd, 2H, ArH); 5.26-4.92 (bs, 9.1H, CH=CH\(_2\)); 2.80-1.08 (CH\(_2\)-CH=CH\(_2\)-CH\(_2\), CH\(_2\)-CH=CH\(_3\)-CH\(_2\) of isoxazoline unit).

(iii) Modification with 1 mole of hydroximoyl chloride per mole of double bond units in the polymer

The reaction was carried out as before using PIP (0.75 g) and p-nitrobenzohydroximoyl chloride (2.6 g) in xylene (100 ml) (reaction time 3 hours) yielding a brown sticky solid (0.63 g, 70%), (Found: C, 71.2; H, 8.1; N, 8.8%; corresponding to conversion of 40% of the isoprene units to isoxazoline rings). \( \nu_{\text{max}} \) (film) 1520, 1345 (NO\(_2\)) cm\(^{-1}\). \( \delta \) (CDCl\(_3\)) 8.50-8.10 (bd, 2H, ArH); 7.90-7.70 (bd, 2H, ArH); 5.36-4.96 (bs, 0.62H, CH=CH\(_3\)); 2.80-1.00 (CH\(_2\)-CH=CH\(_2\)-CH\(_2\), CH\(_2\)-CH=CH\(_3\)-CH\(_2\) of isoxazoline unit). \( \delta \) (CDCl\(_3\)) 159.3-159.2 (isoxazoline C\(_3\)); 148.1, 137-133 (Ar ring C); 132-122 (Ar ring CH, CH\(_2\)-CH=CH\(_3\)-CH\(_2\), 89.9 (CH\(_2\)-CH=CH\(_3\) of isoxazoline unit); 54.0 (CH=CH\(_3\) of isoxazoline unit); 45-20 (CH=CH\(_3\) of isoxazoline unit, CH\(_2\)-CH=CH\(_3\)-CH\(_2\)).

(b) cis-1,4-Polybutadiene (PBD)

(i) Modification with 0.1 moles of hydroximoyl chloride per mole of double bond units in polybutadiene

The reaction was carried out as before using PBD (13.7 g) and p-nitrobenzohydroximoyl chloride (5.0 g) in xylene (750 ml) (reaction time 3 hours) yielding a brown solid (11.3 g, 67%), (Found: C, 79.3;
H, 9.0; N, 3.3%; corresponding to conversion of 75% of the butadiene units to isoxazoline rings. \( \nu_{\text{max}} \) (film) 1520, 1340 (NO\(_2\)) cm\(^{-1}\).

\( S\text{H}(\text{CDCl}_3) \) 8.3-8.0 (bd, 2H, ArH); 7.8-7.6 (bd, 2H, ArH); 5.7-5.0 (bs, 18CH, CH=CH); 2.8-1.3 (CH\(_2\)-CH=CH-CH\(_2\), CH\(_2\)-CH=CH-CH\(_2\) of isoxazoline unit).

(ii) **Modification with 0.2 moles of hydroximoyl chloride per mole of double bond units in polybutadiene**

The reaction was carried out as before using PBD (1.0 g) and p-nitrobenzohydroximoyl chloride (1.85 g) in xylene (250 ml) (reaction time 3 hours) yielding a brown solid (0.82 g, 72%)(Found: C, 77.2; H, 8.6; N, 4.6%; corresponding to conversion of 12% of the butadiene units to isoxazoline rings). \( \nu_{\text{max}} \) (film) 1520, 1340 (NO\(_2\)) cm\(^{-1}\). \( S\text{H}(\text{CDCl}_3) \) 8.2-7.9 (bd, 2H, ArH); 7.8-7.4 (bd, 2H, ArH), 5.6-4.9 (bs, 13.4H, CH=CH); 2.6-1.7 (m, CH\(_2\)-CH=CH-CH\(_2\), CH\(_2\)-CH=CH-CH\(_2\) of isoxazoline unit).

(iii) **Modification with 1.0 moles of hydroximoyl chloride per mole of double bond units in polybutadiene**

The reaction was carried out as before using PBD (0.75 g) and p-nitrobenzohydroximoyl chloride (2.77 g) in xylene (100 ml) (reaction time 3 hours) yielding a brown solid (0.71 g) which would not redissolve.

2.23 **Reduction of p-Nitrobenzohydroximoyl Chloride modified cis-1,4-Polyisoprene and cis-1,4-Polybutadiene**

(a) **cis-1,4-Polyisoprene**

(i) **Reduction with triiron dodecacarbonyl**

12% Modified polyisoprene (1.0 g) was dissolved in toluene (20 ml),
triiron dodecacarbonyl (2.0 g) and benzyltriethylammonium chloride (0.08 g) were added and the solution was stirred with a 1M sodium hydroxide solution (20 ml) for two hours. The mixture was allowed to separate into two layers; the organic layer was decanted and dried with magnesium sulphate. A small sample (2 ml) was precipitated into methanol; the product was dissolved in chloroform and reprecipitated twice into methanol to give a brown solid (0.75 g), (Found: C, 61.9; H, 7.9; N, 2.4; Fe, 12.5%). $\nu_{\text{max}}$ (film) 3450, 3370, 3220 (NH$_2$) cm$^{-1}$. The $^1$H n.m.r. of the product (150 mg in CDCl$_3$) showed no absorptions in the range 0-10 ppm.

The remaining solution (16 ml) was split into two equal portions (8 ml, each containing 400 mg of polymer). To one portion acetyl chloride (94 mg) in toluene (10 ml) and triethylamine (101 mg), also in toluene (10 ml), were added simultaneously. The solution was warmed on a water bath at 40°C for one hour and left to stand overnight. The product was precipitated into methanol (X2), redissolving between precipitations in chloroform. The other portion was reacted similarly with p-tolyl isocyanate (133 mg) in toluene (25 ml). The i.r. spectra of the products showed the disappearance of the NH$_2$ peaks at 3450, 3370 and 3220 cm$^{-1}$ and the appearance of the NH and carbonyl peaks at 3400-3300 cm$^{-1}$ and 1700-1650 cm$^{-1}$ respectively. The acetyl derivative had: C, 74.2; H, 9.2; N, 2.3%. $\nu_{\text{max}}$ (film) 3300 (NH), 1670 (C=O) cm$^{-1}$. The urea derivative had: C, 77.2; H, 7.6; N, 3.2%. $\nu_{\text{max}}$ (film) 3370 (NH), 1710 (C=O) cm$^{-1}$. $^1$H n.m.r. and $^{13}$C n.m.r. spectra could not be obtained.

Reduction of 7.5% modified polyisoprene yielded similar results including the reactions with acetyl chloride and p-tolyl isocyanate.
40% modified polyisoprene produced an insoluble gel on reaction with triiron dodecacarbonyl.

(ii) Reduction with hydrogen over a palladium catalyst

12% Modified polyisoprene (250 mg) was dissolved in toluene (5 ml) and palladium on charcoal (200 mg) was added. The solution was stirred over a slight positive pressure of hydrogen. The reaction was monitored by i.r. over a period of 7 days. A very small reduction in the size of the nitro peaks at 1530 and 1340 cm⁻¹ was observed as well as the appearance of small amine peaks at 3450, 3370 and 3220 cm⁻¹.

(iii) Reduction with hydrogen and triiron dodecacarbonyl after removal of residual double bonds with p-toluenesulphonyl hydrazide

12% Modified polyisoprene

To a solution of 12% modified polyisoprene (1.0 g) in xylene (150 ml) was added p-toluenesulphonyl hydrazide (8.8 g) and the solution heated under reflux for two hours. A further 8.8 g of p-toluenesulphonyl hydrazide was added and the solution refluxed for a further three hours. ¹H n.m.r. indicated complete removal of the alkene protons at 5.1-4.5 δ as well as a change in the aromatic region at 8.5-6.5 δ. The i.r. showed a marked decrease in the nitro peaks at 1530 and 1340 cm⁻¹ and the appearance of small amine peaks at 3450, 3370 and 3220 cm⁻¹. The product was precipitated into methanol (X3); redissolving between precipitations in chloroform and dried in the vacuum oven at 45°C/12 mm Hg for two hours. The resulting polymer (0.46 g) was dissolved in toluene (40 ml), triiron dodecacarbonyl (1.0 g) and benzyltrioethylammonium chloride were added and the solution was stirred with a 1M sodium hydroxide solution (20 ml)
for three hours. The mixture was allowed to separate, the organic layer was decanted and the polymer purified by precipitating into methanol (X3); redissolving between precipitations in chloroform. The product (0.52 g) was dried in the vacuum oven at 35°C/12 mm Hg for 2 hours. The i.r. spectrum of the product showed a reduction in the size of the nitro peaks at 1530 and 1340 cm⁻¹ and the appearance of the amine peaks at 3450, 3370 and 3220 cm⁻¹. No n.m.r. spectra could be obtained.

40% Modified polyisoprene

A solution of 40% modified polyisoprene (1.0 g) in xylene (150 ml) was treated as above with p-toluenesulphonyl hydrazide (5.2 g), producing a white polymer (0.88 g). The i.r. and ¹H n.m.r. of the product showed changes similar to those found with 12% modified PIP.

Attempts to reduce the nitro groups of the polymer produced with triiron dodecacarbonyl by the method used above produced only a crosslinked gel.

Hydrogenation of the PIP treated with p-toluenesulphonyl hydrazide, over a palladium catalyst was attempted by dissolving the polymer (0.4 g) in toluene (20 ml), adding palladium on charcoal (0.20 g), and stirring under a slight positive pressure of hydrogen for 4 days. The catalyst was removed and the polymer purified by precipitating into methanol (X3); redissolving between precipitations in chloroform. The i.r. of the product was found to be similar to that of the starting polymer.

(b) cis-1,4-Polybutadiene

(i) Reduction with triiron dodecacarbonyl

8% Modified polybutadiene (0.75 g) was dissolved in toluene (70 ml),
triiron dodecacarbonyl (1.2 g) and benzyltriethylammonium chloride (0.08 g) were added and the solution was stirred with a 1M sodium hydroxide solution (40 ml) for three hours. The mixture was allowed to separate and the organic layer decanted and dried with magnesium sulphate. The polymer produced was precipitated from methanol (x3); redissolving between precipitations in chloroform. The product was dried in the vacuum oven at 35°C/12 mm Hg for 2 hours, giving a brown solid (0.54 g), (Found: C, 61.9; H, 7.9; N, 2.4%). ν_max (film) 3470, 3370, 3200 (NH2) cm⁻¹. No n.m.r. spectra could be obtained.

Attempts to reduce more highly modified polybutadiene produced only crosslinked gel.
RESULTS AND DISCUSSION

3.1 Modification of cis-1,4-Polyisoprene and cis-1,4-Polybutadiene with Nitrile Oxides

Successful modifications of cis-1,4-polyisoprene (PIP) and cis-1,4-polybutadiene (PBD) with ethoxycarbonylnitrile oxide (78) have been reported\textsuperscript{115}, and are summarized in Section 1.4.2cii. The products of these reactions were unambiguously identified by comparison of their \textsuperscript{13}C n.m.r. spectra with those of carefully selected model compounds. The spectrum of the product (80) resulting from the reaction of (78) with PIP showed, in addition to the peaks assigned to PIP, others in positions characteristic of the 2-isoxazoline ring when compared with model system (79).

\[
\begin{align*}
\text{EtO}_2\text{C} - \text{CCl} = \text{NOH} & \xrightarrow{\Delta} \left[ \text{EtO}_2\text{C} - \text{C} = \text{N}^+ - \text{O} \right] \\
(78) & \\
\text{PIP} & \\
\rightarrow & \\
\text{EtO}_2\text{C} - \text{C} = \text{N}^+ - \text{O} & \\
(80)
\end{align*}
\]

The aim of the present work was to attach amino groups to PIP and PBD via 1,3-dipolar cycloaddition reactions.
Direct attachment of amine groups via nitrile oxides is not feasible due to the incompatibility of amine group reactivity with the preparation of nitrile oxides. This is due to dehydrohalogenation of the hydroximoyl chloride by the amine group. In order to avoid this obstacle it was decided to cycloadd a nitrile oxide containing a nitro group to the polymer, the hydroximoyl chloride of which is readily synthesised, and subsequently reduce this to the corresponding amine (81).

\[
\begin{align*}
\text{P-O}_2\text{NCH}_6\text{HCClNOH} & \xrightarrow{\Delta} \text{P-O}_2\text{NCH}_6\text{HCHN=O}^+ - \text{O}^- \\
\text{P} & \quad \text{PIP} \\
\text{H} & \quad \text{[H]} \\
\end{align*}
\]

(81)

The reactions of p-nitrobenzohydroximoyl chloride (82) with cyclooctene and 1-methylcyclohexene, the models selected for PBD and PIP respectively, were thoroughly investigated with a view to optimising the yield of cycloadduct before the reactions on the polymers were attempted.
3.1.1 Reaction of Cyclooctene and 1-Methylcyclohexene with p-Nitrobenzohydroximoyl Chloride

The reactions of p-nitrobenzohydroximoyl chloride (82) with cyclooctene and 1-methylcyclohexene were carried out as described in the literature\textsuperscript{115} for ethoxycarbonylhydroximoyl chloride. This involved dissolving the hydroximoyl chloride and the alkene at a molar ratio of 1:10 in toluene and heating under reflux (110°C) until the evolution of HCl had ceased. The reaction of (82) with cyclooctene, after 2.5 days, yielded the isoxazoline (83) (64%) and a trace (1%) of 3,5-di(p-nitrophenyl)-1,2,4-oxadiazole (84). Similarly the reaction with 1-methylcyclohexene gave the isoxazoline (85) (49%) and (84) (4%) after 9 days.

\[
\begin{align*}
\text{p-O}_2\text{NCH}_6\text{H}_4\text{N'O} & \xrightarrow{\Delta} \text{p-O}_2\text{NCH}_6\text{H}_4\text{C}-\text{Cl}=\text{N OH}+\text{p-O}_2\text{NCH}_6\text{H}_4\text{C}=\text{N-} \text{O} \\
(82) & \quad (83)
\end{align*}
\]

\[
\begin{align*}
\text{p-O}_2\text{NCH}_6\text{H}_4\text{C}-\text{Cl}=\text{N OH} & \xrightarrow{\Delta} \text{p-O}_2\text{NCH}_6\text{H}_4\text{C}=\text{N-} \text{O} \\
(82) & \quad (85)
\end{align*}
\]

Formation of the 1,2,4-oxadiazole (84) as a by-product of the reaction of nitrile oxides has been reported previously\textsuperscript{130}. This was rationalised in terms of an initial 1,3-dipolar cycloaddition of the
nitrile oxide to the hydroximoyl chloride.

The absence of furoxan (86) is not surprising as the nitrile oxide was generated in the presence of a large excess of dipolarophile. This gives a low steady state concentration of the 1,3-dipole, making dimerisation to (86) unlikely.

\[
\begin{align*}
\text{p-O} & \text{NCH}_4^+ \quad \text{N}=\quad \text{p-O} \quad \text{NCH}_4^- \\
\text{Cl} \quad \text{CHNO}_2- \quad \text{p} & \quad \text{Cl} \\
\end{align*}
\] 

(84)

In order to ascertain whether it was necessary to reflux these reaction mixtures for the times obtained by monitoring the evolution of HCl, h.p.l.c. analysis was employed. This allowed a more precise determination of the end point by following the disappearance of the hydroximoyl chloride directly. For the reaction of (82) with cyclooctene in toluene it was found that no hydroximoyl chloride remained after 12 hours reflux. This indicates that, either the method of monitoring the evolution of the HCl (litmus paper) is
so sensitive that it continued to give a positive test for HCl when
the reaction was near completion or that the HCl produced was not
readily removed from the system. In either case, this method was
abandoned in favour of h.p.l.c. for all subsequent experiments.

In an attempt to reduce the reflux time the reaction was
carried out at a higher temperature in xylene (ca 140°c). Under
these conditions, no hydroximoyl chloride could be detected after
3 hours. The yield of cycloadduct (83) was found to be 89% (cf 64%
in toluene at 110°c). Repeating the reaction of (82) with 1-methyl-
cyclohexene gave a 52% yield of cycloadduct (85) (cf 49% in toluene
at 110°c).

As with the modification of polydienes with ethoxycarbonyl-
hydroximoyl chloride reported in the literature 115, it was intended
to modify only a small proportion (~10%) of the alkene units.
In order to test the effect of possible reducing agents on the
residual alkene bonds, a third model was prepared by reacting
1 mole of (82) with 10 moles of 1,5-cyclooctadiene in xylene. After
3 hours under reflux, (87) was obtained in 52% yield; (84) was
formed as a by-product (2%).
Model compounds (83), (85) and (87) were fully characterised by i.r., $^1$H n.m.r., $^{13}$C n.m.r. and mass spectroscopy. The regioselectivity for the cycloaddition of the nitrile oxide to the alkene unit of 1-methylcyclohexene was evident from the $^{13}$C n.m.r. spectrum. The off-resonance decoupled spectrum of the product indicated that the peak with the highest $S$-value (160.6 ppm) had no hydrogens attached. This must be the peak due to the carbon attached to the most electronegative atom i.e. oxygen. This indicates that structure (85) is the correct one as it satisfies these criteria whereas the isomer (88) does not.
Isolation of (85) is in agreement with the predictions of molecular orbital theory. The reactions of nitrile oxides are LUMO controlled with respect to the dipole. By the union of the orbitals with the largest coefficients, the carbon of the dipole and the $\beta$-carbon of the dipolarophile, (85) should be produced.

The mass spectral fragmentation patterns of (83), (85) and (87) are similar to those reported in the literature for other isoxazolines\(^{130}\). This involves initial loss of COH, then loss of nitrogen, followed by sequential loss of CH\(_2\).

The \(^{13}\)C n.m.r. spectra of these model compounds have been fully assigned by comparison with similar molecules reported in the literature, (Table 5). This was done to ease the characterisation of the modified polymers, by comparing the position of the peaks produced with those expected for the isoxazoline ring.
Table 5  $^{13}$C n.m.r. data for model systems containing isoxazoline rings

<table>
<thead>
<tr>
<th>Compound</th>
<th>C₃</th>
<th>C₄</th>
<th>C₅</th>
<th>Ar ring C</th>
<th>Ar ring CH</th>
</tr>
</thead>
<tbody>
<tr>
<td>83</td>
<td>160.6</td>
<td>49.0</td>
<td>86.5</td>
<td>147.9, 135.8</td>
<td>127.2, 123.7</td>
</tr>
<tr>
<td>85</td>
<td>160.5</td>
<td>49.4</td>
<td>86.5</td>
<td>148.0, 135.5</td>
<td>127.4, 123.8</td>
</tr>
<tr>
<td>87</td>
<td>161.3</td>
<td>46.4</td>
<td>87.2</td>
<td>148.0, 135.4</td>
<td>127.4, 123.8</td>
</tr>
</tbody>
</table>

3.1.2 Reaction of p-Nitrobenzohydroximoyl Chloride with cis-1,4-Polyisoprene and cis-1,4-Polybutadiene

Having established that p-nitrobenzonitrile oxide will undergo 1,3-dipolar cycloaddition reactions with di- and tri-substituted alkenes, its reaction with PIP and PBD were investigated under similar conditions.

A solution of PBD and (82), at a molar ratio of diene units to (82) of 10:1, was heated under reflux in xylene. The progress of the reaction was monitored by withdrawing samples with time and examining these using i.r. spectroscopy and elemental analysis. The latter method provided a convenient way of determining both the reflux time required and the degree of modification which had occurred. This was achieved by examining the percentage nitrogen in each sample; PBD contains no nitrogen compared with 12.8% for the corresponding isoxazoline unit.
Examination of the i.r. spectra of these samples showed the presence of peaks at 1530 and 1340 cm\(^{-1}\), which were assigned to the nitro group. The size of these peaks, relative to the remainder of the spectrum, was seen to increase for 4-5 hours after which time no further change was observed.

The elemental analyses of the samples with time, given in Table 6, also indicate that the reaction was complete after 4-5 hours.

Table 6 Analytical data for the samples from the reaction of p-nitrobenzohydroximoyl chloride with PBD

<table>
<thead>
<tr>
<th>Reflux time (hours)</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>Total*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBD</td>
<td>88.35</td>
<td>11.23</td>
<td>0.00</td>
<td>99.58</td>
</tr>
<tr>
<td>1</td>
<td>87.25</td>
<td>11.09</td>
<td>0.40</td>
<td>99.34</td>
</tr>
<tr>
<td>2</td>
<td>84.04</td>
<td>10.28</td>
<td>1.06</td>
<td>98.01</td>
</tr>
<tr>
<td>3</td>
<td>83.88</td>
<td>10.12</td>
<td>1.80</td>
<td>98.86</td>
</tr>
<tr>
<td>4</td>
<td>82.48</td>
<td>9.79</td>
<td>2.57</td>
<td>99.24</td>
</tr>
<tr>
<td>5</td>
<td>81.18</td>
<td>9.56</td>
<td>2.96</td>
<td>98.77</td>
</tr>
<tr>
<td>6</td>
<td>80.90</td>
<td>9.56</td>
<td>2.88</td>
<td>98.28</td>
</tr>
<tr>
<td>12</td>
<td>81.18</td>
<td>9.59</td>
<td>2.99</td>
<td>98.57</td>
</tr>
</tbody>
</table>

* Total includes % oxygen which was calculated from the % nitrogen, assuming the nitrile oxide was added intact.
The reaction times obtained by these two techniques are in excellent agreement with each other and with the h.p.l.c. results for the model studies.

Experiments with PIP have similarly been examined. I.r. spectroscopy shows the appearance of the nitro peaks (1530 and 1340 cm\(^{-1}\)) with no change in their relative size observed after 4-6 hours. The end point determined from the elemental analyses (Table 7) gives a similar value for the reaction time; these are in good agreement with the value obtained from the model study.

Table 7 Analytical data of the samples from the reaction of p-nitrobenzohydroximoyl chloride with PIP

<table>
<thead>
<tr>
<th>Reflux time (hours)</th>
<th>% Nitrogen</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIP</td>
<td>0.00</td>
<td>99.6</td>
</tr>
<tr>
<td>1</td>
<td>0.87</td>
<td>99.3</td>
</tr>
<tr>
<td>2</td>
<td>1.80</td>
<td>99.3</td>
</tr>
<tr>
<td>3</td>
<td>2.20</td>
<td>99.7</td>
</tr>
<tr>
<td>4</td>
<td>2.46</td>
<td>99.1</td>
</tr>
<tr>
<td>6</td>
<td>2.56</td>
<td>98.8</td>
</tr>
<tr>
<td>36</td>
<td>2.48</td>
<td>99.3</td>
</tr>
</tbody>
</table>

The percentage of the alkene units modified, calculated from the % nitrogen, was established as 7.5 for both PBD and PIP. This corresponds to a 75% incorporation of the nitrile oxide in both cases.
Figure 7

A

B

C

D

$C_3$

$C_4$

$C_5$

$S_C$ (ppm)

150

100

50
The use of $^{13}$C n.m.r. spectroscopy to ascertain whether the nitrile oxides produced in these type of reactions were incorporated as isoxazoline rings has been discussed earlier (Section 3.1). In order to use this technique here a more highly modified sample of PIP was prepared using 1 mole of hydroximoyl chloride (82) per mole of polymer alkene units. Carrying out this reaction as described previously produced a polymer in which 40% of the alkene units had been modified. The proton resonance decoupled and off-resonance decoupled $^{13}$C n.m.r. spectra of this product are given in Figures 7C and 7B respectively. Figures 7A and 7D show the spectra of PIP and the model system (85) respectively.

The spectrum of the product (Figure 7C) has in addition to the peaks due to the starting polymer (PIP), others at 159.3-159.2, 148.1, 89.9 and 54.0 corresponding to the isoxazoline C₃ (160.6), Ar ring C (147.9), isoxazoline C₅ (86.5) and C₄ (49.0) of the model system (85). The peaks due to the other C and CH of the aryl rings are hidden by those of the unmodified alkene units. These assignments are confirmed by the off-resonance decoupled spectrum (Figure 7B) which shows that the peaks assigned to C₃ and C₅ have no hydrogens attached directly, appearing as singlets, while C₄ has one hydrogen attached and appears as a doublet as expected.

These spectra provide strong evidence for the incorporation of the nitrile oxide as isoxazoline rings.

Attempts to produce a similarly high degree of modification with PBD produced only crosslinked gels.
Reaction of hydroximoyl chloride (82) with PIP and PBD at a molar ratio of 1:5 were successful and these results together with those for other reactant ratios are summarized in Table 8.

Table 8  Variation of the degree of modification of PIP and PBD with changes in the initial molar ratio of diene units to p-nitrobenzohydroximoyl chloride

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Ratio of (82) to diene units</th>
<th>% of diene units converted to isoxazoline rings</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIP</td>
<td>1:10</td>
<td>7.5</td>
</tr>
<tr>
<td>PIP</td>
<td>1:5</td>
<td>12.0</td>
</tr>
<tr>
<td>PIP</td>
<td>1:1</td>
<td>40.0</td>
</tr>
<tr>
<td>PBD</td>
<td>1:10</td>
<td>7.5</td>
</tr>
<tr>
<td>PBD</td>
<td>1:5</td>
<td>12.0</td>
</tr>
<tr>
<td>PBD</td>
<td>1:1</td>
<td>-</td>
</tr>
</tbody>
</table>

In conclusion, these experiments indicate that it is possible to attach nitro groups to polydienes via the 1,3-dipolar cycloaddition of nitrile oxides, and that the proportion of the alkene units which are modified can be controlled.

3.1.3 Reduction of Polymer - Bound Nitro Groups

Having established that nitro groups can be introduced to PIP and PBD using p-nitrobenzonitrile oxide, a suitable method of reduction was required to give polymer-bound amine groups. The main criterion
influencing the choice of reducing agent was that the residual alkene units should be left intact. The choice of solvent was confined by the solubility of the nitro-polymer, which proved to be insoluble in water, methanol and ethanol. The method chosen was one using triirondodecacarbonyl and alkali in a two phase system. The proposed mechanism (Scheme 23) involves $\text{H Fe}_3(\text{CO})_{11}$ as the active species.

3.1.3a Reduction with Triirondodecacarbonyl

Before attempting the reduction of the polymer-bound nitro groups, test reactions were carried out on the model nitro-compounds (83), (85) and (87). In order to identify the products of the reaction of (83), the cycloadduct of p-nitrobenzonitrile oxide with cyclooctene, with $\text{Fe}_3(\text{CO})_{12}$ an authentic sample of the corresponding amino compound (89) was prepared under standard reaction conditions, the yield of the product was low (45%).

Treatment of (83) with $\text{Fe}_3(\text{CO})_{12}$ yielded the amino compound (89) in 61% yield; h.p.l.c. showed the presence of residual starting material and (89) only. Similar behaviour was found with (85), giving the corresponding amino compound (90) in 60% yield.

In order to ascertain whether the remaining alkene bonds in the nitro-containing polymer would undergo side-reactions during the reduction a test reaction was carried out on the isoxazoline (87), which incorporates both nitro and alkene groups. From this reaction mixture the amino compound (91), in which the residual alkene group remains intact, was isolated in 70% yield. H.p.l.c. analysis indicated that the alternative reduction products (83) and (89) had not been formed; 0.1% and 2.0% respectively would have been detected if present.
Figure 8

A

B

C

\[ \nu \text{ (cm}^{-1}) \]

3800 3500 3000 1800 1600 1400 1200
These results confirmed that triirondodecacarbonyl was a suitable reducing agent for nitro groups in the presence of alkene bonds.

This reduction technique was then applied to PIP in which 12% of the double bond units had been modified with hydroximoyl chloride (82). Isolation and purification of the product yielded a reddish-brown solid, the i.r. spectrum of which (Figure 8C) showed a marked decrease in the size of the nitro peaks at 1530 and 1340 cm⁻¹ (marked X) compared with the starting material (Figure 8B). In addition to this change, new peaks were observed at 3450, 3370 and 3220 cm⁻¹, consistent with the formation of polymer-bound amino groups.
No $^1\text{H}$ or $^{13}\text{C}$ n.m.r. absorptions were detected for the product in the ranges $S_H$ 0-10 ppm and $S_C$ 0-200 ppm. One possible explanation is the incorporation of a paramagnetic iron species in the polymer. These are known$^{132}$ to disrupt the detection of n.m.r. spectra by increasing the relaxation rate of the nuclei to a point where they are not registered. This hypothesis is supported by the elemental analysis of the product which showed the presence of 12.3 weight % iron.

The i.r. spectrum of the product obtained after treatment with a solution of Fe$_3$(CO)$_{12}$ for 3 hours did not show the presence of any iron-carbonyl bands. It is proposed that this was due to the displacement of the carbonyl groups during the reaction by either the alkene, amine or aromatic groups, all of which have been reported$^{132}$ to displace carbonyl groups. An example of this is the reaction of ironpenta-carbonyl with cis-1,4-polybutadiene$^{133}$ (Scheme 24).

Scheme 24

Repeating the reduction reaction with 12 hours stirring gave a product which showed the presence of iron-carbonyl bands, at 2220 cm$^{-1}$. This is thought to be due to the inability of the active groups left to displace all the carbonyl groups from the increasing number of
attached iron species. The exact form of this iron complex remains unknown, although it is unlikely to contain a neutral iron atom as these are not known\(^1\) to be paramagnetic. This is demonstrated by the fact that \(^1\)H n.m.r. have been recorded for the neutral iron species produced in Scheme 24.

Reduction of PIP and PBD in which 7.5% of the alkene units had been modified with (82) gave products with i.r. spectra similar to that shown in Figure 8C. Attempted reduction of 12% modified PBD and 40% modified PIP yielded only crosslinked gels.

In order to substantiate the claim that amine groups had been incorporated in these polymers, some characteristic reactions were carried out and the products examined by i.r. spectroscopy. The reactions selected were those with acid chlorides and isocyanates. As before, the model system was examined first to optimise the yields under conditions suitable for the polymer.

The reactions of model amine (89) with p-tolyl isocyanate and acetyl chloride were carried out by dissolving the reactants in toluene, warming to 50°C for 1 hour, and leaving to stand overnight. This gave adducts (92) and (93) in good yield.
Figure 9

A

NH₂

B

NH

C=O

C

NH

C=O

ν (cm⁻¹)

3800 3500 3000 2500 2000 1800 1600 1400 1200
The amine-containing polymer derived from 12% modified PIP was reacted with p-tolyl isocyanate and acetyl chloride under identical conditions and the i.r. spectra of the products are given in Figures 9C and 9B respectively.

The spectrum (Figure 9B) of the product formed by reaction with acetyl chloride shows the disappearance of the NH peaks together with the appearance of carbonyl (1690 and 1670 cm\(^{-1}\)) and NH (3300 and 1620 cm\(^{-1}\)) bands.

The spectrum (Figure 9C) of the product formed by reaction with p-tolyl isocyanate shows similar changes. The peaks produced, 1710 cm\(^{-1}\) (carbonyl), 3370 and 1610 cm\(^{-1}\) (NH) along with those of the previous
reaction and the model systems are summarized in Table 9.

Table 9: I.r. spectral data for urea and acetyl derivatives of polymer-bound and model amines (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>System</th>
<th>Amine NH(_2)</th>
<th>Acetyl derivative NH C=O</th>
<th>Urea derivative NH C=O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
<td>3450 3370 3220</td>
<td>3300 1620 1610</td>
<td>1670 1610 3220 1610</td>
</tr>
<tr>
<td>Model</td>
<td>3500 3400 3220</td>
<td>3365 1625 1615</td>
<td>1695 1670 1620 1620</td>
</tr>
</tbody>
</table>

The information displayed in Figure 9, in conjunction with the close correlation of the i.r. peaks from the polymer and model systems (Table 9), provides strong evidence for the formation of polymer-bound amino groups.

3.1.3b Reduction by Catalytic Hydrogenation

Catalytic hydrogenation of PBD and PIP has been reported\(^{134}\) to occur only at elevated temperatures and pressures. It was therefore anticipated that it may be possible to selectively hydrogenate the nitro groups of
the modified polymer at atmospheric pressure. However, hydrogenation of the model compound (87) over a palladium-charcoal catalyst gave a 70% yield of compound (89), in which both the nitro group and the alkene bond had been reduced.

These results suggest that, using this technique, as well as reducing the nitro groups the remaining isoprene units may be converted to the fully saturated analogue (Scheme 25).

**Scheme 25**

Hydrogenation of a solution of 12% modified PIP in toluene over a palladium-charcoal catalyst was attempted by the method used for the
model system. The i.r. spectrum of the polymer produced after 7 days showed a very small reduction in the relative size of the nitro peaks (ca 5%), accompanied by the appearance of very small amine peaks. There was no observable change in the $^1$H n.m.r. spectrum.

It would appear that the reduction of the polymer-bound nitro groups is occurring, but that the rate is too slow to be of use synthetically.

In both the hydrogenation experiment above and the reduction with $\text{Fe}_3(\text{CO})_{12}$ the presence of the residual polymeric alkene bonds has had a detrimental effect on the reaction. A method exists in the literature for the removal of these groups using p-toluene-sulphonyl hydrazide (TsH) (Scheme 26). This would produce a product with a fully saturated backbone.

Scheme 26

\[ p-\text{C}_6\text{H}_4\text{SO}_2\text{NHNH}_2 \xrightarrow{\Delta} [\text{HN}==\text{NH}] \rightarrow \text{CH}==\text{CH} \]

The proposed reaction scheme involves modification of PIP with hydroximoyl chloride as before, removal of the residual alkene units with TsH and reduction of the nitro groups using $\text{H}_2/\text{Pd}$ or $\text{Fe}_3(\text{CO})_{12}$. 
Reaction of model system (87) with TsH, at a molar ratio of 1:4, gave (83) in 66% yield along with two by-products resulting from reduction of the nitro group, together with unreacted starting material (30%).

This indicates that as well as removing the double bonds from the polymer this method reduces some of the nitro groups.

Reaction of TsH with 12% and 40% modified PIP, at a molar ratio of alkene bonds to TsH of 1:4, yielded a product, the $^1$H n.m.r. spectrum of which showed no absorptions in the region assigned to the alkene bonds (5.1-4.5 ppm). The i.r. spectrum of this polymer had a small absorption in the region characteristic of amines although the
size of this peak was much smaller than would be expected from the corresponding decrease in the nitro peaks. This may be due to the formation of other products by partial reduction of the nitro group.

Attempted hydrogenation of this product over a palladium-charcoal catalyst for 7 days yielded a polymer, the i.r. spectrum of which showed very little change from that of the starting material. The reason why only a small proportion of the nitro groups were reduced by this method remains unclear.

Reduction of the saturated polymer derived from 12% modified PIP with Fe$_3$(CO)$_{12}$ produced a product, the i.r. spectrum of which showed the presence of large amine peaks and the almost complete disappearance of the nitro peaks. No. n.m.r. spectra could be obtained, this was probably due to the incorporation of a paramagnetic iron species as before. This suggests that the alkene bonds, present in the earlier reductions on the unsaturated polymer with Fe$_3$(CO)$_{12}$, were not entirely responsible for the incorporation of this iron complex.

In conclusion, these experiments demonstrate that it is possible to attach nitro groups to PIP and PBD via 1,3-dipolar cycloaddition with p-nitrobenzonitrile oxide and that these may subsequently be reduced to give polymer-bound amino groups. The presence of these groups has been demonstrated by spectroscopic techniques and through their characteristic reactions with p-tolyl isocyanate and acetyl chloride.
3.2 Modification of Acrylonitrile Copolymers with
p-Nitrobenzonitrile Oxide

To test the possibility of modifying the pendant nitrile groups of acrylonitrile copolymers with nitrile oxides, the reaction of p-nitrobenzoxydiazole chloride with a suitable model was attempted. 2-Methylpropionitrile was selected as it was similar to the nitrile unit in copolymers of acrylonitrile. The reaction was carried out by refluxing a solution of the hydroximoyl chloride (82) and the nitrile in xylene at a molar ratio of 1:10. The progress of the reaction was monitored by observing the disappearance of (82) by h.p.l.c. After complete consumption of (82) had occurred (4 hours) the reaction mixture was worked up giving the 1,2,4-oxadiazole (94) in 45% (h.p.l.c.) yield.

\[
\begin{align*}
\text{p-ON} \text{C}_6 \text{H}_4 \text{C} = \text{N} \text{OH} & \xrightarrow{\Delta} \left[ \text{p-ON} \text{C}_6 \text{H}_4 \text{C} = \text{N} - \text{O} \right] \\
(82) & \\
\xrightarrow{(\text{CH}_3)_2 \text{CHC}=\text{N}} \\
\text{p-ON} \text{C}_6 \text{H}_4 \text{N} \backslash \text{CH}_{(\text{CH}_3)_2} & \\
(94)
\end{align*}
\]

The absence of the other regioisomer, the 1,2,5-oxadiazole, together with the low yield of cycloaduct compared with the
analogous reaction with cyclooctene can be explained by frontier molecular orbital theory.

Calculations have shown$^3$ that the HOMO and LUMO energy levels of nitriles are lower than those for alkenes. As the reactions of nitrile oxides are LUMO controlled with respect to the 1,3-dipole, the energy gained in the transition state during the reaction with alkenes is greater than that for the reaction with nitriles. This would lead to lower yields of oxadiazole, as is observed experimentally.

The greater orbital coefficients are known$^3$ to be on the carbon atom in the LUMO of nitrile oxides and on the nitrogen atom in the HOMO of nitriles. Thus the formation of the 1,2,4-oxadiazole by the interaction of the orbitals with the largest atomic coefficients is in agreement with the experimental results.

Although the yield of (94) was lower than that for the corresponding reaction with cyclooctene and 1-methylcyclohexene (89 and 52%), it was considered to be sufficiently large to make polymer modification worthwhile.

Copolymers of acrylonitrile were chosen in preference to polyacrylonitrile itself as they are less polar and hence more soluble in common organic solvents. The copolymers used were those with styrene and vinylidene chloride, containing 20 weight % and 25 weight % of acrylonitrile respectively. Their solubility in xylene, the solvent used for the model study, was low although they were known to be readily soluble in γ-butyrolactone. For this reason the model experiment was repeated in this solvent at 130°C and the oxadiazole (94) was isolated in 20% yield (cf 20% isolated in xylene under similar conditions).
3.2.1 Reaction of p-Nitrobenzohydroximoyl Chloride with Acrylonitrile/Styrene Copolymer

The reaction of p-nitrobenzohydroximoyl chloride (82) with acrylonitrile/styrene copolymer was carried out, as with the model experiments, by dissolving the polymer in γ-butyrolactone, adding the hydroximoyl chloride, and heating at 130°C. Due to the low yield of cycloadduct formed with 2-methylpropionitrile compared with that of cyclooctene, a molar ratio of (82) to polymer nitrile units of 4:10 was used. The reaction was monitored by withdrawing samples with time and examining these using i.r. spectroscopy and elemental analysis. The appearance of nitro peaks (1530 and 1340 cm⁻¹) was observed and the size of these relative to the rest of the spectrum was seen to increase for 5-6 hours, at which time the reaction was stopped. The elemental analyses of these samples with time are given in Table 10.
Table 10  Modification of acrylonitrile/styrene copolymer with p-nitrobenzohydroximoyl chloride

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>85.6</td>
<td>7.2</td>
<td>6.7</td>
</tr>
<tr>
<td>0.25</td>
<td>83.3</td>
<td>7.0</td>
<td>7.1</td>
</tr>
<tr>
<td>0.67</td>
<td>83.1</td>
<td>7.1</td>
<td>7.1</td>
</tr>
<tr>
<td>1.0</td>
<td>81.5</td>
<td>7.1</td>
<td>8.0</td>
</tr>
<tr>
<td>2.0</td>
<td>81.5</td>
<td>7.0</td>
<td>8.0</td>
</tr>
<tr>
<td>3.0</td>
<td>81.2</td>
<td>6.6</td>
<td>8.1</td>
</tr>
<tr>
<td>4.0</td>
<td>79.5</td>
<td>6.8</td>
<td>8.4</td>
</tr>
<tr>
<td>5.0</td>
<td>79.3</td>
<td>6.7</td>
<td>8.3</td>
</tr>
<tr>
<td>6.0</td>
<td>79.3</td>
<td>6.6</td>
<td>8.4</td>
</tr>
<tr>
<td>12.0</td>
<td>79.9</td>
<td>6.4</td>
<td>8.4</td>
</tr>
</tbody>
</table>

Table 10 indicates that there was no significant change in the composition of the product after 3-4 hours i.e. the reaction was complete. These reaction times obtained by i.r. spectroscopy and elemental analysis are in good agreement with each other and with the model experiment. From the elemental analysis of the product it was calculated that 8% of the nitrile units had been converted to oxadiazole rings. This constitutes a 20% yield based on the hydroximoyl chloride consumed.
In order to prove that the reaction had produced oxadiazole rings with $^{13}\text{C}$ n.m.r. spectroscopy a more highly modified sample was prepared using 10 moles of hydroximoyl chloride per mole of nitrile. The elemental analysis of the polymer produced indicated that 30% of the nitrile units had been modified. The $^{13}\text{C}$ n.m.r. spectrum of this product (Figure 10B) along with those of the acrylonitrile/styrene copolymer (Figure 10A) and the model oxadiazole (94) (Figure 10C) are given opposite.

Figure 10B shows, in addition to the peaks of the starting copolymer, others at 182.6, 165.8, 149.1, 132.1 and 125.4 which correspond to the oxadiazole C$_5$ (184.7), oxadiazole C$_3$ (166.5), O$_2$NC$_6$H$_4$ ring C's (149.2, 132.8) and O$_2$NC$_6$H$_4$ ring CH's (123.9) of the model (94) (Figure 10C). This provides strong evidence for the incorporation of the nitrile oxides as oxadiazole rings.

3.2.2 Reaction of p-Nitrobenzohydroximoyl Chloride with Acrylonitrile/Vinylidene Chloride Copolymer

Acrylonitrile/vinylidene chloride copolymer was modified in the same way as the acrylonitrile/styrene copolymer at two different initial molar ratios of (82) to nitrile viz 0.25:1 and 10:1.

Modification at 0.25:1 yielded a product in which 10% of the nitrile units had been converted to oxadiazole rings. The reaction was monitored by observing the changes in the i.r. spectra of the product with time. No further increase in the size of the nitro peaks (1530 and 1340 cm$^{-1}$) with respect to the rest of the spectrum was seen after 5-6 hours.
Figure 11

A

\[
\begin{align*}
  &\text{CH}_2-\text{CH} \end{align*}
\]

\[
\begin{align*}
  &\text{CH}_2-\text{CCl}_2
\end{align*}
\]

\[
\begin{align*}
  &\text{N} \equiv \text{C}
\end{align*}
\]

B

\[
\begin{align*}
  &\text{CH}_2-\text{CH} \end{align*}
\]

\[
\begin{align*}
  &\text{CH}_2-\text{CH} \end{align*}
\]

\[
\begin{align*}
  &\text{CH}_2-\text{CCl}_2
\end{align*}
\]

\[
\begin{align*}
  &\text{N} \equiv \text{C}
\end{align*}
\]

\[
\begin{align*}
  &\text{N} \equiv \text{N}
\end{align*}
\]

\[
\begin{align*}
  &\text{p-O}_2\text{N-CH}_3
\end{align*}
\]

\[
\begin{align*}
  &\text{N} \equiv \text{O}
\end{align*}
\]

\[
\begin{align*}
  &\text{N} \equiv \text{N}
\end{align*}
\]

\[
\begin{align*}
  &\text{CH(CH}_3)_2
\end{align*}
\]

\[
\begin{align*}
  &\text{p-O}_2\text{N-CH}_6
\end{align*}
\]

\[
\begin{align*}
  &\text{N} \equiv \text{O}
\end{align*}
\]

\[
\begin{align*}
  &\text{N} \equiv \text{N}
\end{align*}
\]

\[
\begin{align*}
  &\text{CH(CH}_3)_2
\end{align*}
\]

\[
\begin{align*}
  &\text{C}_5
\end{align*}
\]

\[
\begin{align*}
  &\text{C}_3
\end{align*}
\]

\[
\begin{align*}
  &\text{Ar C}
\end{align*}
\]

\[
\begin{align*}
  &\text{Ar C}
\end{align*}
\]

\[
\begin{align*}
  &\text{Ar C}
\end{align*}
\]

180 160 140 120 100 80 60 40 20 0
Treatment at a molar ratio of 10:1 resulted in a product in which 50% of the nitrile units had been modified. The $^{13}$C n.m.r. spectrum of the starting copolymer (Figure 11A), the product (Figure 11B) and the model oxadiazole (94) (Figure 11C) are shown opposite.

Figure 11B shows, in addition to the peaks of the starting copolymer, others at 182.0, 166.6, 149.3, 131.8, 128.5 and 124.6 corresponding to the oxadiazole C$_5$ (184.7), oxadiazole C$_3$ (166.5), O$_2$NC$_6$H$_4$ ring C's (149.2, 132.8) and O$_2$NC$_6$H$_4$ ring CH's (128.2, 123.9) of the model oxadiazole (94) (Figure 11C). Again this provides strong support for the incorporation of nitrile oxides as oxadiazole rings.

These experiments indicate that despite the low reported reactivity of aliphatic nitriles towards nitrile oxides it is possible to modify nitrile containing polymers by 1,3-dipolar cycloaddition reactions.
3.3 **Preparation and Reaction of Polymer-Bound Nitrile Sulphides**

At the outset of this project, only one example of a polymer-bound 1,3-dipole had been reported\textsuperscript{119}. Thermolysis of the polymer formed by copolymerisation of isoprene with a vinyl substituted tetrazole (95) yielded a crosslinked product (96). This reaction has been rationalised\textsuperscript{119} in terms of the generation of a nitrile imine, formed by loss of nitrogen from the tetrazole ring, which undergoes a 1,3-dipolar cycloaddition reaction with a residual alkene unit (Scheme 28).

**Scheme 28**

\[
\begin{align*}
\text{CH}_2=\text{CH} & \quad \text{H}_3\text{C}\text{C}-\text{CH} \\
\text{N}=\text{N} & \quad \text{Ph} \\
\end{align*}
\]
During the course of the present work similar reactions involving azides have also been reported. The aim of the present research was to incorporate a nitrile sulphide precursor into a polymer and examine its reactions. Of the precursors available, 1,3,4-oxathiazol-2-ones were chosen due to their ease of preparation and their tendency to give good yields of cycloadducts. The strategy was to produce the poly (1,3,4-oxathiazol-2-one) by polymerising or copolymerising 1,3,4-oxathiazol-2-ones containing pendant alkene groups. From the known chemistry of 1,3,4-oxathiazol-2-ones it was anticipated that thermolysis of the poly(1,3,4-oxathiazol-2-ones) in the presence of a suitable dipolarophile, ethyl cyanoformate (ECF) or dimethyl acetylenedicarboxylate (DMAD), would lead to the corresponding poly (1,2,4-thiadiazoles) and poly (isothiazoles). Similar products may be attainable by prior 1,3-dipolar cycloaddition of the 5-alkenyl-1,3,4-oxathiazol-2-ones with these dipolarophiles and subsequent polymerisation. Both routes are exemplified in Scheme 29.
Isolation of products with similar spectroscopic properties, eg $^{13}$C n.m.r. spectra, by these two pathways should provide strong support for the formation of polymer-bound nitrile sulphides.

Rationalisation of the $^{13}$C n.m.r. spectra of these polymers would be simplified if a model system containing a fully saturated substituent were prepared, as this would give the position of the heterocyclic ring carbons. The compounds chosen for this were 5-isopropyl-1,3,4-oxathiazol-2-one and its ECF and DMAD cycloadducts.

3.3.1 Synthesis of 5-Isopropyl-1,3,4-oxathiazol-2-one

5-Isopropyl-1,3,4-oxathiazol-2-one (34b) was prepared by the general method described in the literature$^{127}$ from 2-methylpropionamide and chlorocarbonylsulphenyl chloride (Scheme 30).

This involved dissolving the reactants in chloroform and heating under reflux until h.p.l.c. indicated no further increase in the size of the peak due to the oxathiazolone and HCl evolution had ceased. The product, 5-isopropyl-1,3,4-oxathiazol-2-one (34b), was isolated by chromatography and distillation in 30% yield.

Scheme 30

\[
\begin{align*}
(CH)_2CHCONH_2 + ClSCl &\xrightarrow{H^+} (CH)_2CHCONH_2 + ClSCl \\
(CH)_3CHCONH_2 &\xrightarrow{H^+} (CH)_3CHCONH_2
\end{align*}
\]
3.3.2 Thermolysis of 5-Isopropyl-1,3,4-oxathiazol-2-one in the presence of Ethyl Cyanoformate and Dimethyl Acetylenedicarboxylate

Thermolysis was carried out by the method described in the literature\textsuperscript{136} i.e. dissolving the oxathiazolone and the ECF or DMAD, at a molar ratio of 1:10, in xylene and heating under reflux. When no oxathiazolone could be detected by h.p.l.c., heating was stopped and the products were isolated by chromatography and distillation. This gave the ethyl 3-isopropyl-1,2,4-thiadiazole-5-carboxylate (97b) and the dimethyl 3-isopropylisothiazole-4,5-dicarboxylate (36b) in 62\% and 64\% yields respectively.

\[
\begin{align*}
\text{(CH}_3\text{)}_2\text{CH} & \xrightarrow{\Delta} \text{(CH}_3\text{)}_2\text{CH} \\
 \text{N} & \quad \text{N} \\
\text{O} & \quad \text{CO}_2\text{Et}
\end{align*}
\]

(97b)

\[
\begin{align*}
\text{(CH}_3\text{)}_2\text{CH} & \xrightarrow{\Delta} \text{(CH}_3\text{)}_2\text{CH} \\
 \text{N} & \quad \text{N} \\
\text{C}_2\text{Me} & \quad \text{CO}_2\text{Me}
\end{align*}
\]

(36b)

3.3.3 Synthesis of 1,3,4-Oxathiazol-2-ones containing a Pendant Alkene group

The only previous report of the synthesis of an alkenyl-1,3,4-oxathiazol-2-one concerned the prop-1-enyl derivative (34c), which had been prepared from crotonamide and chlorocarbonylsulphenyl chloride in 48\% yield\textsuperscript{128}. 
Repeating this reaction under the conditions used for 5-isopropyl-1,3,4-oxathiazol-2-one (34b) gave (34c) in 22% yield. Encouraged by this result, several other 5-alkenyl-1,3,4-oxathiazol-2-ones were prepared in this way. These were 5-vinyl-1,3,4-oxathiazol-2-one (34d), 5-isopropenyl-1,3,4-oxathiazol-2-one (34e) and 5-styryl-1,3,4-oxathiazol-2-one (34f). The yields were 22%, 18% and 42% respectively.

\[
\begin{align*}
34d, & \quad R = \text{CH} = \text{CH} - \\
34e, & \quad R = \text{CH} = \text{C(CH}_3\text{)} - \\
34f, & \quad R = \text{PhCH} = \text{CH} - 
\end{align*}
\]

In each case no other products were detected and the residual starting material (amide) was recovered in near quantitative yields. All the products (34b-f) were fully characterised by i.r., \textsuperscript{1}H n.m.r. and \textsuperscript{13}C n.m.r. spectroscopy. The mass spectra of these compounds show characteristic \textsuperscript{13}I nitrile and nitrile sulphide fragments.

3.3.4 **Thermolysis of 5-Alkenyl-1,3,4-oxathiazol-2-ones in the presence of Ethyl Cyanoformate and Dimethyl Acetylene-dicarboxylate**

The thermolyses were carried out by the procedure described for 5-isopropyl-1,3,4-oxathiazol-2-one (34b) and were found to give the corresponding 1,2,4-thiadiazoles and isothiazoles in the yields given in Table 11. No reaction could be carried out on 5-vinyl-1,3,4-oxathiazol-2-one as it was found to polymerise spontaneously on heating or on exposure to light.
Figure 12

Expansion of A from 130–180 ppm

A

\[
\text{CH}_3 - \text{CH} - \text{CH}_2 - N - S - \text{CO}_2\text{CH}_3
\]

B

$\delta_C$ (ppm)
Table 11  
Yields of isothiazoles and 1,2,4-thiadiazoles obtained by thermolysis of 5-alkenyl-1,3,4-oxathiazol-2-ones in the presence of ECF and DMAD

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Isothiazole (%)</th>
<th>1,2,4-Thiadiazole (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH_3 CH=CH-</td>
<td>68</td>
<td>64</td>
</tr>
<tr>
<td>PhCH=CH-</td>
<td>50</td>
<td>64</td>
</tr>
<tr>
<td>CH=CH(CH_3)-</td>
<td>34*</td>
<td>23</td>
</tr>
</tbody>
</table>

* 1:1 ratio of oxathiazolone:DMAD used

All the compounds prepared above were fully characterised by i.r., ^1H n.m.r., ^13C n.m.r. and mass spectroscopy, some aspects of which are discussed below.

Complete assignment of the ^13C n.m.r. peaks of the isothiazoles and 1,2,4-thiadiazoles was accomplished using fully coupled spectra. An example of this technique is the assignment of the peaks of dimethyl 3-isopropylisothiazole-4,5-dicarboxylate; the proton decoupled (Figure 12B) and fully proton coupled spectra (Figure 12A) of which are shown opposite.

The peaks at 52.6, 31.1 and 21.3 ppm are readily assigned to the carbons of the methyl group of the CO_2Me, the CH of the isopropyl group and the CH_3 of the isopropyl group respectively.

In the fully coupled spectrum peak X remains as a singlet indicating it is separated from protons by greater than 3 bonds and can be assigned to C_5. Peak Y appears as a doublet showing the presence of a CH group.
within two bonds; it is therefore assigned to C$_4$. The two carbonyl carbons are coupled with the protons of the ester methyl groups and appear as quadruplets centred at 164.2 and 159.4 ppm. The signal due to C$_3$ is split by the six methyl protons and the methine proton of the isopropyl substituent. These have different coupling constants giving a complex and poorly resolved multiplet viz Peak Z. By applying this technique to each compound all the spectra have been completely assigned.

The mass spectral breakdown patterns of the thiadiazoles were found to be similar to those reported in the literature i.e. loss of ECF and breakdown of the thiazirine produced to the corresponding nitrile and sulphur. The breakdown patterns of the isothiazoles were more complicated than those reported for simple isothiazoles with alkyl substituents in the 4 and 5 positions. Initial breakdown was by loss of OCH$_3$ and subsequent loss of CO and OCH$_3$, or by loss of sulphur.

3.3.5 Copolymerisation of 5-Alkenyl-1,3,4-oxathiazol-2-ones with Styrene and Methyl Methacrylate

Copolymerisations of alkenyloxathiazolones with methyl methacrylate (MMA) and styrene were carried out in preference to homopolymerisations as this was expected to give a better insight into the behaviour of the oxathiazolones during polymerisation. The kinetics of the copolymerisation were compared with those for the formation of polystyrene and poly(methyl methacrylate).

The copolymerisation of the isopropenyl oxathiazolone with MMA was carried out by dissolving the oxathiazolone, MMA and the initiator, azobisisobutyronitrile (AB1BN), in methyl ethyl ketone (MEK) and heating
under reflux (ca 80°C). The initial ratio of the oxathiazolone to MMA was 1:4 by weight and sufficient MEK was used to give a solution in which the combined monomers accounted for 20% of the weight. The amount of initiator used was 1% of the weight of the combined monomers. Alongside this reaction a homopolymerisation of MMA was run, again as a 20% solution in MEK using 1% initiator. Small samples (1 ml) of each reaction mixture were withdrawn with time. Each was precipitated, dried and weighed, and the percentage conversion to polymer evaluated. The results are given in Table 12

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>% conversion to poly (MMA)</th>
<th>% conversion to copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>23.6</td>
<td>2.4</td>
</tr>
<tr>
<td>1.0</td>
<td>41.8</td>
<td>2.9</td>
</tr>
<tr>
<td>1.5</td>
<td>58.2</td>
<td>4.6</td>
</tr>
<tr>
<td>2.0</td>
<td>68.9</td>
<td>7.9</td>
</tr>
<tr>
<td>2.5</td>
<td>73.9</td>
<td>10.8</td>
</tr>
<tr>
<td>3.0</td>
<td>69.6</td>
<td>11.1</td>
</tr>
<tr>
<td>3.5</td>
<td>73.3</td>
<td>11.6</td>
</tr>
<tr>
<td>4.0</td>
<td>79.7</td>
<td>11.3</td>
</tr>
<tr>
<td>8.0</td>
<td>81.1</td>
<td>12.8</td>
</tr>
</tbody>
</table>

It can be seen from these results that 81% by weight of the MMA in the homopolymerisation was converted to poly(methyl methacrylate) (PMMA)
and that 13% by weight of the combined monomers was converted to polymer during the copolymerisation of 5-isopropenyl-1,3,4-oxathiazol-2-one with MMA.

In order to improve the yield of the copolymer the concentration of the monomers was increased from 20% to 30% and 2% initiator was used. The greater concentration of monomers was expected to lead to a larger degree of polymerisation by increasing the rate of chain propagation relative to termination. In order to avoid an increase in the radical concentration which would lead to a shorter chain length due to radical coupling, the initiator was added in two parts, 1% at t=0 and 1% after 2 hours.

Repeating the reaction with these modifications produced a polymer in which 20% by weight of the combined monomers were incorporated. The number average molecular weight ($M_n$) of the copolymer produced from a 30% solution with 2% initiator was 3800 compared with 3700 for the 20% solution with 1% initiator. This indicates that the use of multiple additions had been successful in avoiding a reduction in the molecular weight.

The copolymerisation of 5-isopropenyl-1,3,4-oxathiazol-2-one with styrene and the homopolymerisation of styrene were attempted, as before, using a 30% solution with 2% initiator. The percentage conversion to polymer with time is shown in Table 13.
Table 13  Weight percentage conversion of styrene and a mixture of styrene and 5-isopropenyl-1,3,4-oxathiazol-2-one to polymer with time

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>% conversion to polystyrene</th>
<th>% conversion to copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.33</td>
<td>3.6</td>
<td>1.7</td>
</tr>
<tr>
<td>0.66</td>
<td>8.5</td>
<td>4.3</td>
</tr>
<tr>
<td>1.0</td>
<td>14.5</td>
<td>6.5</td>
</tr>
<tr>
<td>1.5</td>
<td>20.3</td>
<td>9.0</td>
</tr>
<tr>
<td>2.0</td>
<td>24.7</td>
<td>10.7</td>
</tr>
<tr>
<td>2.5</td>
<td>32.3</td>
<td>12.3</td>
</tr>
<tr>
<td>3.0</td>
<td>37.5</td>
<td>15.4</td>
</tr>
<tr>
<td>3.5</td>
<td>40.3</td>
<td>17.6</td>
</tr>
<tr>
<td>4.0</td>
<td>43.5</td>
<td>18.6</td>
</tr>
<tr>
<td>8.0</td>
<td>53.7</td>
<td>19.7</td>
</tr>
</tbody>
</table>

These results indicate that during the homopolymerisation 54% of the styrene was converted to polystyrene and that during the copolymerisation 20% by weight of the combined monomers, styrene and 5-isopropenyl-1,3,4-oxathiazol-2-one, were converted to polymer.

These experiments were repeated with 5-vinyl-1,3,4-oxathiazol-2-one with both styrene and MMA using a 30% solution and 2% initiator.

The results for polymers involving both oxathiazolones are summarised in Table 14.
Table 14  Weight percentage conversion to polymer of the reactions
of 5-vinyl and 5-isopropenyl-1,3,4-oxathiazol-2-ones with
styrene and MMA

<table>
<thead>
<tr>
<th>oxathiazolone substituent</th>
<th>copolymerant</th>
<th>% conversion to polymer</th>
<th>number average molecular weight ($\bar{M}_n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>isopropenyl</td>
<td>MMA</td>
<td>20.0</td>
<td>3800</td>
</tr>
<tr>
<td>isopropenyl</td>
<td>styrene</td>
<td>19.7</td>
<td>2900</td>
</tr>
<tr>
<td>vinyl</td>
<td>MMA</td>
<td>12.0</td>
<td>9600</td>
</tr>
<tr>
<td>vinyl</td>
<td>styrene</td>
<td>16.7</td>
<td>2900</td>
</tr>
</tbody>
</table>

The differing solubilities of the oxathiazolone containing copolymers with styrene (non-solvent, methanol) compared with those of polystyrene (non-solvent, hexane) provide strong support for the formation of a copolymer rather than a mixture of homopolymers. This evidence has been reinforced by the i.r. spectra of these copolymers which show a peak at 1750 cm$^{-1}$ similar to that found for 5-isopropyl-1,3,4-oxathiazol-2-one (34b). This cannot be seen for the copolymer with MMA due to the presence of a large carbonyl band from the MMA.

Definitive evidence for the incorporation of oxathiazolone rings has been obtained using $^{13}$C n.m.r. spectroscopy. The spectrum of the product formed by copolymerisation of 5-vinyl-1,3,4-oxathiazol-2-one (34d) with styrene(Figure 13B) along with those of polystyrene (Figure 13A) and 5-isopropyl-1,3,4-oxathiazol-2-one (34b) (Figure 13C) are shown opposite page 130.
Figure 13

A

\[ \text{[CH}_2\text{-CH]} \]

B

\[ \text{[CH}_2\text{-CH]} \text{[CH}_2\text{-CH]} \text{[CH}_2\text{-CH]} \text{[CH}_2\text{-CH]} \]

C

\[ \text{(CH}_3\text{)}_2\text{CH} \]

\[ \text{N=S=S=N} \]
Figure 13B shows, in addition to the peaks found for polystyrene, peaks at 173.3 and 162.9 ppm corresponding to those of the model (34b) at 173.7 (C₂) and 167.2 (C₃) ppm.

This information confirms that a copolymer incorporating the oxathiazolone unit has been formed. Similar evidence is also available for each of the other copolymers.

Closer examination of Figure 13B indicates that the peak assigned to the styrene ring carbon at 147 - 143 ppm is similar to a triplet of ratio 1:2:1. This has been reported to be characteristic of a random polymer rather than a block copolymer or a mixture of homopolymers.

Additional i.r. peaks at 2200 cm⁻¹ and ¹³C n.m.r. peaks at 120 - 125 ppm for all these products indicate the presence of a small amount of nitrile, presumably formed by the characteristic decomposition of the oxathiazolone rings.

The composition of the copolymers have been determined by examination of their elemental analyses (C, H, N and S) which are given in Table 15.

The number and weight average molecular weights (M̄ₙ and M̄ₜ) of the products were obtained using gel permeation chromatography with polystyrene internal standards. The results and the heterogeneity indices (M̄ₚ/M̄ₙ) are given in Table 15.
Table 15 Molar composition and molecular weights of the copolymers of 5-isopropenyl-1,3,4-oxathiazol-2-one (34e) and 5-vinyl-1,3,4-oxathiazol-2-one (34d) with styrene and MMA

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>% MMA</th>
<th>% (34)a</th>
<th>% nitrile b</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(34e)/MMA</td>
<td>58</td>
<td>39</td>
<td>3</td>
<td>1800</td>
<td>3800</td>
<td>2.1</td>
</tr>
<tr>
<td>(34e)/styrene</td>
<td>60</td>
<td>35</td>
<td>5</td>
<td>1900</td>
<td>2900</td>
<td>1.5</td>
</tr>
<tr>
<td>(34d)/MMA</td>
<td>84</td>
<td>11</td>
<td>5</td>
<td>6400</td>
<td>9600</td>
<td>1.5</td>
</tr>
<tr>
<td>(34d)/styrene</td>
<td>64</td>
<td>33</td>
<td>3</td>
<td>1900</td>
<td>2900</td>
<td>1.5</td>
</tr>
<tr>
<td>polystyrene</td>
<td></td>
<td></td>
<td></td>
<td>7400</td>
<td>14000</td>
<td>1.9</td>
</tr>
<tr>
<td>poly(MMA)</td>
<td></td>
<td></td>
<td></td>
<td>4200</td>
<td>19500</td>
<td>4.6</td>
</tr>
</tbody>
</table>

a - estimated error ± 2%
b - estimated error ± 4%

The striking feature of Table 15 is the relationship between the $M_w$ value and the percentage oxathiazolone in the copolymer. The vinyl oxathiazolone (34d)/MMA copolymer has $M_w$ and oxathiazolone incorporation values of 9600 and 10% respectively, whereas those for the others are 2900 - 3800 and 29 - 39%. This indicates that as the proportion of oxathiazolone in the copolymer increases the $M_w$ decreases. One possible explanation for these observations is that the rate of chain termination is greater for the radical centred on the oxathiazolone alkene group than that of MMA and styrene.
Table 15 also indicates that the ratio of oxathiazolone to MMA or styrene in the product is greater than the initial ratio. This indicates that the radicals centred on styrene and MMA and/or the oxathiazolone unit show a marked preference for reaction with an oxathiazolone unit.

3.3.6 Attempted Copolymerisation of 5-(Prop-1-enyl)-1,3,4-oxathiazol-2-one and 5-Styryl-1,3,4-oxathiazol-2-one with Methyl Methacrylate

These attempted copolymerisations were carried out as described in Section 3.3.5 with a 30% by weight solution of the combined monomers and 2% initiator. The kinetics appeared to be similar to those for the homopolymerisation of MMA as shown in Table 16.

Table 16 Weight percentage conversion of MMA and a mixture of MMA and 5-styryl-1,3,4-oxathiazol-2-one (34f) and 5-(prop-1-enyl)-1,3,4-oxathiazol-2-one (34c) to polymer with time

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>PMMA</th>
<th>MMA/(34c)</th>
<th>MMA/(34f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>21.1</td>
<td>25.2</td>
<td>25.6</td>
</tr>
<tr>
<td>1.0</td>
<td>41.1</td>
<td>-</td>
<td>42.9</td>
</tr>
<tr>
<td>1.5</td>
<td>-</td>
<td>50.3</td>
<td>-</td>
</tr>
<tr>
<td>2.0</td>
<td>68.3</td>
<td>-</td>
<td>63.5</td>
</tr>
<tr>
<td>5.0</td>
<td>91.0</td>
<td>89.1</td>
<td>91.3</td>
</tr>
</tbody>
</table>
The i.r. spectra of the resulting polymers were identical to that of PMMA, indicating that these oxathiazol-2-ones had not been incorporated and were only acting as diluents.

### 3.3.7 Copolymerisation of Ethyl 3-Isopropenyl-1,2,4-thiadiazole-5-carboxylate and Dimethyl 3-Isopropenylisothiazol-4,5-dicarboxylate with Styrene and Methyl Methacrylate

The copolymerisation of dimethyl 3-isopropenylisothiazole-4,5-dicarboxylate (36e) with MMA and styrene and ethyl 3-isopropenyl-1,2,4-thiadiazole-5-carboxylate (97e) with styrene were carried out as described in Section 3.3.5. The kinetics of the reactions were markedly different to those for the production of the corresponding homopolymer. The yields of polymer were MMA/(36e)(30%), styrene/(36e)(15%) and styrene/(97e)(15%).

The i.r. spectra of these products showed an absorption in the carbonyl region. This is consistent with the incorporation of the heterocyclic ring.

The $^{13}$C n.m.r. spectra of the copolymers of (36e) with MMA and styrene showed the presence of peaks in positions which are characteristic of the isothiazole ring by comparison with dimethyl 3-isopropylisothiazole-4,5-dicarboxylate (36b)(Table 17).

![Chemical structures](image_url)
Table 17  Comparison of the isothiazole ring carbon positions (ppm) of model and polymer-bound isothiazoles

<table>
<thead>
<tr>
<th>System</th>
<th>C₃</th>
<th>C=O</th>
<th>C=O</th>
<th>C₅</th>
<th>C₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>(36e)/MMA copolymer</td>
<td>174-172</td>
<td>165.9-165.6</td>
<td>159</td>
<td>154.9</td>
<td>133.5</td>
</tr>
<tr>
<td>(36e)/styrene copolymer</td>
<td>174-172</td>
<td>165-164</td>
<td>159-158</td>
<td>157-153</td>
<td>*</td>
</tr>
<tr>
<td>(36b)</td>
<td>174.5</td>
<td>164.2</td>
<td>159.4</td>
<td>155.4</td>
<td>131.5</td>
</tr>
</tbody>
</table>

* peak coincident with larger peak

The $^{13}$C n.m.r. spectrum of the product of the copolymerisation of (97e) and styrene shows, in addition to the peaks of styrene others at 184-182, 178-176.5 and 166-159 ppm corresponding to those of the model (97b) at 183.5 (C₅), 178.3 (C₃) and 158 (C=O) ppm.

These observations provide convincing evidence for the incorporation of the heterocyclic rings intact. The composition of these products has been determined from their elemental analyses (C, H, N and S) and are given in Table 18.

Table 18  Molar composition of isothiazole and thiadiazole containing copolymers

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>% MMA or styrene</th>
<th>% heterocyclea</th>
</tr>
</thead>
<tbody>
<tr>
<td>(36e)/MMA</td>
<td>88</td>
<td>12</td>
</tr>
<tr>
<td>(36e)/styrene</td>
<td>64</td>
<td>36</td>
</tr>
<tr>
<td>(97e)/styrene</td>
<td>85</td>
<td>15</td>
</tr>
</tbody>
</table>

a - estimated error ± 2%
3.3.8 Generation and Reactions of Polymer-Bound Nitrile Sulphides from Copolymers of 5-Vinyl-1,3,4-oxathiazol-2-one and 5-Isopropenyl-1,3,4-oxathiazol-2-one with Methyl Methacrylate and Styrene

As indicated in Section 1.3, the instability of nitrile sulphides is such that direct observation is not possible. The existence of this species has been implied from reactions in which their involvement explains the products obtained. In order to demonstrate that polymer-bound nitrile sulphides can be generated from these newly prepared oxathiazolone containing copolymers three typical reactions were attempted. These were: thermolysis in an inert solvent and in the presence of ECF and DMAD. The proposed reactions are summarised in Scheme 31.

Scheme 31

3.3.8a Thermolysis in an Inert Solvent

Thermolysis was achieved by refluxing a solution of the copolymer in xylene. The reactions were monitored by withdrawing samples with time
and observing the change in their i.r. spectra. These showed an increase in the nitrile peak at 2220 cm\(^{-1}\) and in the case of the styrene copolymers no carbonyl peaks, from the oxathiazolone rings, could be detected after 4 hours reflux. Determination of the end point for the copolymers with MMA was more difficult due to the presence of a large carbonyl peak from the MMA; in these cases heating was stopped when no further increase in the relative size of the nitrile peak was observed. The products were purified by multiple precipitations from chloroform into hexane.

The \(^{13}\)C n.m.r. spectra of the products showed no absorptions in the region characteristic of the oxathiazolone ring whilst there was an increase in the size of the peak due to nitrile. Using the method devised previously, the composition of the polymers were calculated from their elemental analyses (C, H, N and S), and the results obtained are shown in Table 19. A small amount of sulphur was detected in each case (1.2-3.1\%) and it has been assumed in these calculations that this has come from residual oxathiazolone rings.
Table 19  Comparison of the molar percentage composition of copolymers of 5-vinyl-1,3,4-oxathiazol-2-one (34d) and 5-isopropenyl-1,3,4-oxathiazol-2-one (34e) with MMA and styrene before and after thermolysis

<table>
<thead>
<tr>
<th>Polymer</th>
<th>% MMA or styrene</th>
<th>% oxathiazolone&lt;sup&gt;a&lt;/sup&gt;</th>
<th>% nitrile&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>(34e)/MMA</td>
<td>58</td>
<td>39</td>
<td>3</td>
</tr>
<tr>
<td>after thermolysis</td>
<td>65</td>
<td>8</td>
<td>27</td>
</tr>
<tr>
<td>(34e)/styrene</td>
<td>60</td>
<td>85</td>
<td>5</td>
</tr>
<tr>
<td>after thermolysis</td>
<td>55</td>
<td>3</td>
<td>42</td>
</tr>
<tr>
<td>(34d)/MMA</td>
<td>84</td>
<td>11</td>
<td>5</td>
</tr>
<tr>
<td>after thermolysis</td>
<td>88</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>(34d)/styrene</td>
<td>64</td>
<td>33</td>
<td>3</td>
</tr>
<tr>
<td>after thermolysis</td>
<td>63</td>
<td>7</td>
<td>30</td>
</tr>
</tbody>
</table>

<sup>a</sup> - estimated error ± 2%

<sup>b</sup> - estimated error ± 4%

As well as reflecting the change occurring in the copolymers, the data in Table 19 indicates that, within the experimental errors, the molar ratio of styrene or MMA to oxathiazolone plus nitrile remains constant during the reaction. This verifies that elemental analysis is a reliable technique for determining the composition of these copolymers.

These results are consistent with the formation of polymer-bound nitrile sulphides during the thermolysis of oxathiazolone containing polymers.
3.3.8b Thermolysis in the presence of Dimethyl Acetylenedicarboxylate and Ethyl Cyanoformate

These reactions were carried out by dissolving the oxathiazolone containing polymers in xylene, adding dimethyl acetylenedicarboxylate (DMAD) or ethyl cyanoformate (ECF) at a molar ratio of 1 : 10, and heating the solution under reflux. The reactions were monitored by withdrawing samples with time and observing the change in their i.r. spectra. The positions of the carbonyl peaks of the reaction products were not sufficiently different from those of the oxathiazolone containing polymers to allow an accurate determination of the end point of the reaction by this method. However, as the rate of decomposition of oxathiazolone rings is known to be independent of the presence or absence of dipolarophile\textsuperscript{73}, the reflux times obtained for the thermolysis in an inert solvent were used.

**Thermolysis in the presence of Dimethyl Acetylenedicarboxylate**

The reaction of each of the oxathiazolone containing polymers was carried out as detailed previously, monitoring with i.r. spectroscopy. This showed the expected changes i.e. an increase in the relative size
of the nitrile peaks, combined with the changes in the carbonyl region corresponding to those found for the model system (5-isopropyl-1,3,4-oxathiazol-2-one)(34b). The i.r. spectrum of the product from the thermolysis of the 5-isopropenyl-1,3,4-oxathiazol-2-one (34e)/MMA copolymer with DMAD was indistinguishable from that of the corresponding dimethyl 3-isopropenylisothiazole-4,5-dicarboxylate (36e)/MMA copolymer prepared previously.

In order to obtain further evidence for the formation of isothiazole rings by the reaction of polymer-bound nitrile sulphides with DMAD, $^{13}$C n.m.r. spectroscopy was employed. The $^{13}$C n.m.r. spectrum of the product of (34e)/MMA copolymer with DMAD (Figure 14 B) along with those of the starting copolymer (Figure 14 A), the model system (36b)(Figure 14 C) and the copolymer of (36e) with MMA (Figure 14 D) are shown opposite. Figure 14 B shows that during the thermolysis the peaks assigned to the oxathiazolone C$_3$ and C$_5$ ring carbons have disappeared. These were replaced by peaks at 174-172, 166.9, 159.0, 157-155 and 133.5 ppm corresponding to those of the model (36b) at 174.5 (C$_3$), 164.2, 159.4 (ester carbonyls), 155.4 (C$_5$) and 131.5 (C$_4$) ppm. The relationship between the spectra of the product and those of the (36e)/MMA copolymer is demonstrated in Table 20.
Table 20  
Comparison of the $^{13}$C n.m.r. data (ppm) of polymer-bound and model isothiazole rings

<table>
<thead>
<tr>
<th>System</th>
<th>$C_3$</th>
<th>$C=O$</th>
<th>$C=O$</th>
<th>$C_5$</th>
<th>$C_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(34e)/MMA copolymer after reflux in DMAD</td>
<td>174-172</td>
<td>165.6</td>
<td>159.0</td>
<td>157-155</td>
<td>133.5</td>
</tr>
<tr>
<td>(36b)</td>
<td>174.2</td>
<td>164.2</td>
<td>159.4</td>
<td>155.4</td>
<td>131.5</td>
</tr>
<tr>
<td>(36e)/MMA copolymer</td>
<td>174-172</td>
<td>165.9-165.6</td>
<td>159</td>
<td>154.9</td>
<td>133.5</td>
</tr>
</tbody>
</table>

The similarity of the peak positions of the reaction product of polymer (34e)/MMA with DMAD and those of the model system (36b), and the near superimposability with those of the copolymer of (36e) with MMA provide irrefutable evidence for the formation of the isothiazole ring during thermolysis.

The other oxathiazolone containing copolymers were found to behave similarly. The $^{13}$C n.m.r. data for the products are summarised in Table 21.
Table 21

Summary of the $^{13}$C n.m.r. data (ppm) for the polymers formed by the thermolysis of the copolymers of 5-vinyl-1,3,4-oxathiazol-2-one (34d) and 5-isopropenyl-1,3,4-oxathiazol-2-one (34e) with MMA and styrene in the presence of DMAD

<table>
<thead>
<tr>
<th>Starting copolymer</th>
<th>C$_3$</th>
<th>C=O</th>
<th>C=O</th>
<th>C$_5$</th>
<th>C$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(34e)/MMA</td>
<td>174-172</td>
<td>165.6</td>
<td>159.0</td>
<td>157-155</td>
<td>133.5</td>
</tr>
<tr>
<td>(34e)/styrene</td>
<td>174-172</td>
<td>165.2</td>
<td>158.9</td>
<td>157-154</td>
<td>134-132</td>
</tr>
<tr>
<td>(34d)/MMA</td>
<td>175-173</td>
<td>165-163</td>
<td>162-159</td>
<td>158-156</td>
<td>134-132</td>
</tr>
<tr>
<td>(34d)/styrene</td>
<td>171.6</td>
<td>162.6</td>
<td>159.0</td>
<td>157-154</td>
<td>132</td>
</tr>
</tbody>
</table>

It can be seen from Table 21 that the formation of isothiazole rings occurs for all the oxathiazolone containing copolymers, providing strong evidence for the intermediacy of a polymer-bound nitrile sulphide in each case.

Thermolysis in the presence of Ethyl Cyanoformate

These reactions were carried out using the technique described previously. The i.r. spectra of the products showed changes similar to those observed during thermolysis with DMAD. The spectrum of the product from the (34e)/styrene copolymer was indistinguishable from that of the copolymer of ethyl 3-isopropenyl-1,2,4-thiadiazole-5-carboxylate (97e) with styrene.
Further evidence for the formation of thiadiazole rings was obtained using $^{13}$C n.m.r. spectroscopy. The spectrum of the product from the thermolysis of the copolymer of (34e) and styrene (Figure 15B) along with those of the starting material (Figure 15 A), the model compound, ethyl 3-isopropyl-1,2,4-thiadiazole-5-carboxylate (97b) (Figure 15 C) and the copolymer of (97e) with styrene (Figure 15 D) are shown opposite.

Figure 15 B indicates that the peaks assigned to the C$_3$ and C$_5$ carbons of the oxathiazolone ring were removed during thermolysis. Simultaneously peaks appeared at 185-181, 179-176 and 158-157 ppm, corresponding to those of the model (97b) at 183.5 (thiadiazole C$_5$), 178.3 (thiadiazole C$_3$) and 158.4 (carbonyl carbon) ppm. An increase in the size of the nitrile peak (X) was also observed. With the notable exception of this nitrile peak, the spectrum of the product was identical to that of the copolymer of (97e) with styrene prepared previously. The positions of the relevant peaks along with those from the reactions of the other oxathiazolone containing copolymers are given in Table 22.
Table 22  
\begin{tabular}{lccc}
Polymer system & $C_5$ & $C_3$ & $C=O$ \\
\hline
(34e)/styrene copolymer + ECF & 185-181 & 179-176 & 158-157 \\
(34e)/MMA copolymer + ECF & 185-182 & * & 158.0 \\
(34d)/styrene copolymer + ECF & 182-179 & 179-176 & 158.1 \\
(34d)/MMA copolymer + ECF & * & * & 158.0 \\
(97e)/styrene copolymer & 184-182 & 178-176.5 & 161-159 \\
model compound (97b) & 183.5 & 178.3 & 158.4 \\
\end{tabular}

* coincident with larger peak - not visible

This data provides strong evidence for the formation of thiadiazole rings via polymer-bound nitrile sulphides for all these oxathiazolone containing copolymers.

The composition of both the isothiazole and thiadiazole containing polymers have been determined from their elemental analyses (C, H, N and S) and the results are given in Table 23. In order to complete these calculations it was necessary to assume that all the sulphur detected had originated from the isothiazole or thiadiazole rings.

Thermolysis of these copolymers in an inert solvent for identical times was shown (Section 3.3.8a) to lead to the decomposition of only 80 - 90% of the oxathiazolone rings. It must therefore be assumed that 10 - 20% of the oxathiazolones also remain after thermolysis in the presence of ECF and DMAD. This means that approximately 20 - 40% of the portion assigned to the isothiazole and thiadiazole rings may be due to oxathiazolone.
Table 23  Molar percentage composition of oxathiazolone containing copolymers and their products formed by thermolysis in an inert solvent and in the presence of ECF and DMAD

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>MMA or styrene</th>
<th>Heterocycle&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Nitrile&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>(34e)/MMA</td>
<td>58</td>
<td>39</td>
<td>3</td>
</tr>
<tr>
<td>thermolysis in an</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>inert solvent</td>
<td>65</td>
<td>8</td>
<td>27</td>
</tr>
<tr>
<td>thermolysis in DMAD</td>
<td>67</td>
<td>17</td>
<td>16</td>
</tr>
<tr>
<td>thermolysis in ECF</td>
<td>64</td>
<td>20</td>
<td>16</td>
</tr>
<tr>
<td>(34e)/styrene</td>
<td>60</td>
<td>35</td>
<td>5</td>
</tr>
<tr>
<td>thermolysis in an</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>inert solvent</td>
<td>55</td>
<td>3</td>
<td>42</td>
</tr>
<tr>
<td>thermolysis in DMAD</td>
<td>61</td>
<td>22</td>
<td>17</td>
</tr>
<tr>
<td>thermolysis in ECF</td>
<td>56</td>
<td>23</td>
<td>21</td>
</tr>
<tr>
<td>(34d)/MMA</td>
<td>84</td>
<td>11</td>
<td>5</td>
</tr>
<tr>
<td>thermolysis in an</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>inert solvent</td>
<td>88</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>thermolysis in DMAD</td>
<td>87</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>thermolysis in ECF</td>
<td>82</td>
<td>5</td>
<td>13</td>
</tr>
<tr>
<td>(34d)/styrene</td>
<td>64</td>
<td>33</td>
<td>3</td>
</tr>
<tr>
<td>thermolysis in an</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>inert solvent</td>
<td>63</td>
<td>7</td>
<td>30</td>
</tr>
<tr>
<td>thermolysis in DMAD</td>
<td>66</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>thermolysis in ECF</td>
<td>66</td>
<td>13</td>
<td>21</td>
</tr>
</tbody>
</table>

<sup>a</sup> estimated error ± 2%

<sup>b</sup> estimated error ± 4%
Table 23 indicates that during the thermolysis, approximately half the nitrile sulphides produced have undergone cycloaddition with DMAD or ECF, while the rest have decomposed to nitrile and sulphur. These findings are in fair agreement with the yields obtained from the investigation of the reactions of the model system (34b) which gave compounds (36b) and (97b) in 64% and 62% yields respectively.

It should also be noted that the ratio of MMA and styrene to the total of the other constituents remains constant, within experimental errors. This justifies the use of this method for calculating the composition of the polymers.

In conclusion, it has been shown that 5-alkenyl-1,3,4-oxathiazolones may be copolymerised with styrene and MMA and that subsequent thermolysis gives rise to polymer bound nitrile sulphides. The existence of these 1,3-dipoles has been demonstrated by their characteristic reactions with ethyl cyanoformate and dimethyl acetylenedicarboxylate to give the corresponding isothiazoles and thiadiazoles.
REFERENCES

21 G. Bianchi, C. De Micheli and R. Gandolfi,
"Double-bonded functional groups", Suppl. A,
29 A. Holm, J.J. Christiansen and C. Lohse,
J.C.S. Perkin I, 1979, 960.
30 R.K. Howe, T.A. Grumer, L.G. Carter, L.L. Black and
32 K.N. Houk, J. Sims, R.E. Duk Jr., R.W. Strozier and
34 J. Bastide, N. El. Ghandour and O. Henri-Rousseau,
1973, 2294.
36 J. Bastide, N. El. Ghandour and O. Henri-Rousseau,
Tet. Letts., 1972, 2979.
1972, 11, 838.
40 K. Bast, M. Christl, R. Huisgen, W. Mack and
41 M. Christl, R. Huisgen and R. Sustman, Chem. Ber.,
1973, 106, 3275.


77 J. Crosby, D.J. Greig, R.M. Paton and J.F. Ross, Unpublished observations.


80 German patent 1,132,108.


86 H. Gotthardt, Chem. Ber., 1972, 105, 188.
98 S.J. Hong, Daehan Hwahak Hwoejee, 1971, 15 (3), 121.
103 British Patent 1,073, 324.
104 S. Fujimoto, J. Polymer Sci., 1967, 5, 301.
107 British Patent 1,146,469.
British Patent 1,474,691.


Z. Rappoport "Handbook of tables for organic compound identification, CRC press, Ohio".


British Patent 1,079,348.


Modification of Acrylonitrile-Styrene and Acrylonitrile-Vinylidene Chloride Copolymers via 1,3-Dipolar Cycloaddition with 4-Nitrobenzonitrile Oxide

Introduction

It has recently been established (1) that nitrile oxides (RC≡N=O) will undergo 1,3-dipolar cycloaddition to the alkene double bonds in cis-1,4-polybutadiene and cis-1,4-polyisoprene thus introducing isoxazoline units. We now report that this technique may also be used to convert nitrile groups in acrylonitrile-styrene and acrylonitrile-vinylidene chloride copolymers into 1,2,4-oxadiazoles.

Results and Discussion

In view of the reported (2) low reactivity of aliphatic nitriles toward nitrile oxides we first examined the reaction of 4-nitrobenzonitrile oxide (1) with isobutyronitrile, which was selected as a model for the nitrile units in the polymers. 1 was generated in the presence of excess dipolarophile (1:10) by thermal dehydrochlorination (3) of 4-nitrobenzohydroximoyl chloride (2). Reaction for 4 h at 135-140°C in xylene afforded the 1,2,4-oxadiazole cycloadduct 3 (40%) (Scheme 1). The 13C-NMR spectrum (CDCl3) of the product has absorptions at 184.7 and 166.5 ppm, characteristic of the CN of the heterocyclic ring, in addition to peaks at 149.2 (C), 132.8 (C), 128.2 (2CH), and 123.9 (2CH) ppm, which are assigned to the 4-nitrophenyl substituent.

![Scheme 1](image)

Having established the ability of the nitrile oxide to undergo cycloaddition with such aliphatic nitriles, its reactions with the acrylonitrile copolymers were studied. Treatment of an acrylonitrile (40 mol %)-styrene (60%) copolymer with the hydroximoyl chloride (sufficient to give a 0.4:1 molar ratio of 2 to nitrile units) in γ-butyrolactone at 130°C for 4 h afforded a white solid. The presence in the product of units derived from 1 is evident from the infrared (IR) spectrum [film, νmax = 1525 and 1335 cm⁻¹ (NO₂)] and elemental analysis (8.4% N compared with 6.7% N in the original polymer). A residual peak at 2240 cm⁻¹ indicates that some of the cyano groups remain unreacted; from the nitrogen analysis the extent of the reaction was estimated as 30% (Scheme 2). By adjusting the reactant ratio the degree of modification could be varied. Thus, the proportion of nitrile groups reacted was found to increase from 30% for 0.4 mol of 2 per nitrile unit to 50% at 10:1. The 13C-NMR spectrum (Fig. 1)
Fig. 1. \(^{13}\)C-NMR spectrum (CD\(_3\)NO\(_2\), Me\(_4\)Si) of acrylonitrile-styrene copolymer modified (50\%) by 1. The peaks marked X are assigned to the carbons of the pendant oxadiazole and its 4-nitrophenyl substituent.

provides definitive evidence for the structure of the product. In addition to peaks at 141–147 (phenyl C), 129.8, 129.1 (phenyl CH), 123.0, 121.8 (C≡N), 34–37, and 26–29 (CH and CH\(_2\)) ppm, attributable to the styrene and unmodified acrylonitrile units, there are distinctive absorptions at 184.3 (C), 167.9 (C), 150.9 (C), 134.3 (C), and 125.4 (CH) ppm. In view of the similarity of these chemical shifts to those of the model compound (3) they are assigned to the carbons of the 1,2,4-oxadiazole ring and the C and CH of its 4-nitrophenyl substituent.

Similarly an acrylonitrile (31 mol \%)–vinylidene chloride (69\%) copolymer with 2 (1:10) gave a product with 50\% of the nitrile groups converted to oxadiazoles. The \(^{13}\)C-NMR spectrum (DMSO-d\(_6\)) shows peaks at 182.0 and 166.6 ppm for the oxadiazole carbons and at 149.3 (C), 131.9 (C), 128.5 (CH), and 124.6 (CH) ppm for its 4-nitrophenyl substituent similar to those in 3.

These results demonstrate that nitrile oxides are sufficiently reactive to undergo 1,3-dipolar cycloadditions with aliphatic nitriles, and that they may be used for the covalent modification of acrylonitrile-derived polymers.

Experimental

5-Isopropyl-3-(p-Nitrophenyl)-1,2,4-Oxadiazole (3)

This compound was formed from 4-nitrobenzohydroximoyl chloride (2)
(5.0 mmol) and isobutyronitrile (50.0 mmol) in refluxing xylene (100 mL) using the technique described by Sasaki and Yoshioka (3). After 4 h, 3 (2.0 mmol, 40%) was isolated as a white crystalline solid; mp 130°C (from toluene). Found: C, 56.7%; H, 4.7%; N, 17.8%. Calcd for C11H11N3O3: C, 56.6%; H, 4.8%; N, 18.0%.

Reaction of 4-Nitrobenzohydrazimoyl Chloride (2) with Acrylonitrile (40 mol %)-Styrene (60%) Copolymer

A solution of 2 (2.0 g, 10 mmol) and acrylonitrile-styrene copolymer (5.3 g, giving a 0.4:1 molar ratio of 2 to nitrile groups) in γ-butyrolactone (75 mL) was heated at 130°C for 4 h. Removal of the solvent by distillation under reduced pressure, precipitation of the residue into methanol (x3), and drying gave a white solid (5.4 g). Found: C, 79.9%; H, 6.4%; N, 8.4%. This corresponds to a product comprising 27% acrylonitrile, 60% styrene and 13% [3-(p-nitrophenyl)-1,2,4-oxadiazol-5-yl]ethylene units.

A repeat reaction using a 10:1 molar ratio of 2 to nitrile units afforded a product with C, 76.8%; H, 6.2%; N, 8.8%; corresponding to 20% acrylonitrile, 60% styrene, and 20% oxadiazolyl units.

Reaction of 4-Nitrobenzohydrazimoyl Chloride (2) with Acrylonitrile (31 mol %)-Vinylidene Chloride (69%)

Using the method described above and a 10:1 molar ratio of 2 to nitrile units yielded a product for which C, 38.2%; H, 2.7%; N, 7.7%; corresponding to 15% acrylonitrile, 69% vinylidene chloride, and 16% oxadiazolyl units.
References


R. Michael Paton
Ian Stobie

Department of Chemistry
University of Edinburgh
West Mains Road
Edinburgh EH9 3JJ
Scotland

Roy M. Mortier

Imperial Chemical Industries PLC
Organics Division
Blackley, Manchester M9 3DA
England

Received May 27, 1982
Accepted August 3, 1982