Thesis for the Degree of Ph.D.

THE INFLUENCE OF SUBSTITUENTS ON THE FORMATION
OF SUBSTITUTED NAPHTHOLS FROM
BENZENE DERIVATIVES.

By

ALEXANDER GUTHRIE, B.Sc. (Edin.), A.I.C.

Directed and supervised by J. B. Shoesmith, D.Sc.

Chemistry Department,
University of Edinburgh. May, 1928.
INDEX.

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>Preparative</td>
<td>10</td>
</tr>
<tr>
<td>Experimental</td>
<td>64</td>
</tr>
<tr>
<td>Discussion of Results</td>
<td>84</td>
</tr>
<tr>
<td>Summary</td>
<td>96</td>
</tr>
</tbody>
</table>
INTRODUCTION.

Towards the latter part of the last century it was realised that substitution in the benzene nucleus was no longer a matter of mere speculation but that there appeared to be some connection between the position taken up by the substituent and the type of atom already present in the nucleus.

There is a well-defined group of substituted benzenoid derivatives which on further substitution give a preponderating quantity of ortho- or para-di-derivatives, and another group which give meta-compounds. For example, when phenol is allowed to react with nitric acid the compounds produced are o- and p-nitrophenol, which means that in phenol the positions ortho- and para- to the hydroxyl group are more reactive than the meta; whilst with nitrobenzene it is the meta-position which is more reactive than the ortho or para. A large amount of information as to the presence of reactive positions in the substituted benzenoid derivatives has been obtained in recent years (J.C.S. Ann. Reports, 1925 and onwards) but those observations have in the main been confined to simple substitution in the benzene ring.

The question as to whether the regularities
observed in benzene substitution can be traced in the formation of polynuclear compounds from simple, substituted benzene derivatives has apparently not hitherto been considered. This is presumably because there are relatively few reactions of this type which are suitable for investigation. After a full consideration of the reactions which might be used for this purpose, the one selected was that which takes place when phenylisocrotonic acid and its nuclear-substituted derivatives are heated. (Fittig and Erdmann, Annalen, 1885, 227, 242), that is

\[
\text{phenylisocrotonic acid} \xrightarrow{\text{H_2O}} \text{\(\alpha\)-naphthol}
\]

during which \(\alpha\)-naphthol is formed.

The advantage of this reaction is its simplicity, since it merely involves the loss of a molecule of water by elimination of a hydrogen atom from the benzene nucleus with the hydroxyl of the carboxyl group, and takes place in the absence of dehydrating agents, the presence of which would complicate the reaction from a quantitative point of view. (Compare the synthesis of 9-hydroxyphenanthrene from o-benzylbenzoic acid (Ber., 1894, 27, 2789) and of phenylanthranol from triphenylmethane-o-carboxylic acid (Ber., 1880, 202, 54), both of which require the
presence of sulphuric acid.

A further advantage lies in the fact that compounds containing substituents in the benzene residue, which might bring about differences in reactivity in the position at which ring closure must take place, are obtainable. For example, if a compound such as m-methoxyphenylisocrotonic acid be compared with phenylisocrotonic acid, since in anisole itself the position para to the methoxyl group is known to be very reactive, the corresponding position in m-methoxyphenylisocrotonic acid at which ring closure takes place would be expected to be more reactive than the position at which the ring closes in phenylisocrotonic acid. This is apparent from a consideration of the formulae of the two compounds compared with the formulae of benzene and anisole where the sign * denotes the reactive positions.¹

![Diagram](image)

m-methoxyphenylisocrotonic acid

¹: Anisole is attacked very vigorously with fuming nitric acid (Annalen, 1850, 74, 299) and forms o- and p-nitroanisole (Ber., 1919, 52, 1476).
It may be pointed out at this juncture that one of the most unusual features in this type of reaction from the point of view of substitution in the benzene nucleus, is that the entering group (in this case the unattached end of the side-chain of the phenylisocrotonic acid) must in every case unite with one of two definite positions,—ortho to the attached end of the side-chain, whereas a substituent group in ordinary substitution has the choice of entering in the nucleus in any position, namely, in the position which is most reactive. It is shown later that in point of fact, the ring always closed in one direction, so that the vibration of the side-chain in the substituted phenylisocrotonic acids is very much more restricted than might generally be supposed.

It has already been indicated that the introduction of a methoxyl group into the meta-position to the side-chain in phenylisocrotonic acid might reasonably be expected to render the ortho-position, that is, the position of ring closure in naphthol formation, reactive. It follows therefore that the same group united with the ortho- or para nuclear carbon atoms would render the ortho-position less reactive than when placed in the meta-position, and that the ease of ring-closure in phenylisocrotonic acid and its derivatives should be a measure of the reactivity of the position of ring closure.
Although the phenylisocrotonic acids are ideal for the study of ring closure, a comparatively small amount of research has been devoted to their synthesis. It is well known that they may be prepared by heating the phenylparaconic acids. The reaction is shown in the equation

\[
\text{C}_6\text{H}_5\text{CH}^\cdot\text{CH}^\cdot\text{CH}^\cdot\text{CH}_2\text{C}^\cdot\text{O} \rightarrow \text{C}_6\text{H}_5\text{CH}^\cdot\text{CH}^\cdot\text{CH}_2^\cdot\text{CO}_2\text{H} + \text{CO}_2
\]

phenylparaconic acid phenylisocrotonic acid

The isocrotonic acid, however, is difficult to obtain in satisfactory yield in the pure state, and since the phenylparaconic acids are more easily attainable, it was decided to carry out investigations on these. There appeared to be no reasonable objection to estimating the degree of ring-closure by heating the paraconic acids, thereby converting them directly to the isocrotonic acids and thence to the naphthols, that is, without actually isolating the isocrotonic acid. One objection was foreseen however, namely, that it would be necessary in order to arrive at an accurate measure of the ring-closure to assume that every paraconic acid (2 g. by weight) gave rise to the same (equivalent) amount of isocrotonic acid. The weight of isocrotonic acid produced was determined in each case in order to test the validity of this assumption, and moreover it was considered advisable
to measure the amounts of other substances formed during the course of the reaction, the reason for which will be apparent from a study of the experimental section. Although the assumption that the conversion to isocrotonic acid might be the same in each case was not realised in fact, a method of calculation was arrived at which completely eliminated any error which would necessarily arise if this assumption were adhered to.

Due consideration having been given to the choice of substituents, the following series of phenylparaconic acids was decided upon: unsubstituted; p-methyl; the isomeric methoxy, bromo and nitrophenylparaconic acids. The list was extended to the naphthalene series, namely, to the \( \alpha \)- and \( \beta \)-naphthylparaconic acids.

The phenylparaconic acids were prepared in two ways:—by condensing the benzaldehydes (a) with equimolecular proportions of sodium succinate and acetic anhydride (Fittig and Jayne, Annalen, 1883, 216, 100), (b) with succinic anhydride and sodium acetate (Erdmann, Annalen, 1883, 247, 372) which are shown by the simplified equation

\[
\text{C}_6\text{H}_6\text{CHO} + \text{CH}_2\text{CO}_2\text{H} \rightarrow \text{C}_6\text{H}_5\text{CH} = \text{CH} = \text{CO}_2\text{H} \cdot \text{CH}_2\text{O} + \text{H}_2\text{O}
\]

\[
\text{CH}_2\text{CO}_2\text{H} \quad \text{phenylparaconic acid}
\]

Preliminary condensations at various temperatures were
carried out in each case with a view to arriving at the optimum yield of acid. In most cases, although the yields increased slightly at higher temperatures, the amount of tarry material formed, greatly overbalanced the advantages which accrued from an increase in the yield.

Only a trace of an acid, the amount of which was too small to obtain in the pure state, was obtained in the case of one of the o-methoxybenzaldehyde condensation mixtures. Attempts to prepare the p-methoxy-acid were fruitless, the chief reaction-product being tar, and when the observation was confirmed that p-nitrophenylparaconic acid, when heated, charred hopelessly (as had been observed by other investigators previous to this research for the o-, m- and p-nitro acids), researches in the nitro-series were abandoned. Numerous attempts were made to prepare p-tolylparaconic acid which terminated in the isolation of a few grams of white but impure acid. The significance of the term "white" is discussed below. The unsubstituted, m-methoxy, o-, m- and p-bromobenzaldehyde and the isomeric naphthaldehyde condensations were the only ones from which satisfactory amounts of acid could be obtained.

A considerable amount of investigation was necessary before standard conditions could be found
for obtaining consistent yields of the $\alpha$-naphthols (to within 2%) by heating the phenylparaconic acids. The quantitative experiments revealed a most unusual phenomenon. If the acid were yellow, or had the merest suggestion of a yellow tinge (although the melting-point in some cases had a range of not more than $0.5^\circ$), the yield of $\alpha$-naphthol was increased, in one case in particular, by four times the normal value. An example of this is given here: faintly yellow acid, m.p. 99° - 99.5°, yield of $\alpha$-naphthol 13.5%: pure white acid, m.p. 98° - 98.5°, yield of $\alpha$-naphthol 4.4%. The latter is really the more impure acid in the usual sense of the term. It was obvious, therefore, that the acids were only of value for the quantitative experiments, if they were pure white in colour. As will be seen later, a mechanical method was at last decided upon as being the most efficient for isolating the acids in a pure-white state, in good yield — a most difficult operation.

A good deal of attention has been paid to the preparation of aldehydes, always an urgent question in synthetic organic researches, and an attempt has been made, where convenient, to compare different methods of procedure. The oxidation of the substituted toluenes with manganese dioxide and sulphuric acid was disappointing but it was the means of
preparing a large quantity of p-bromobenzaldehyde.

It may be mentioned in passing that a surprisingly large number of compounds which are described in the literature were found to have been prepared in an impure state, as is evident from the low melting-points as compared with those described in these researches.

The substituted paraconic acids detailed below were isolated in a pure white state and were converted to the isocrotonic acids, thence to the naphthols by heating under standard conditions, when the following yields of naphthol were obtained:

- unsubstituted phenylparaconic acid, 7·5% ; m-methoxy-, 31%;
- o-bromo, 25%; m-bromo-, 48%; p-bromo- 5·6%;
- α-naphthylparaconic acid, 7·9%; β-naphthyl, 1·1%.

Those yields are consistent to within about 3% in the case of the highest value, to less than 1% in the lowest.
PREPARATIVE.

The yields are expressed in per cent of those expected by theory. In the case of the acids, the yields are those of the pure-white acid. Temperatures, except for those termed "uncorrected", were taken from standard thermometers.

The Condensation Apparatus.

A special apparatus was fitted up for the condensation of the aldehydes with succinic acid. The temperatures of the condensations were above 100° and since the methods of condensation were compared, it was necessary to keep the temperature constant during the 6 hours heating. An oil-bath thermostat was found to be inconvenient. The following apparatus after many modifications proved most satisfactory. The condensation vessel consisted of a strong 250 c.c. bolt-head flask (A), the rim of which was removed. Into this was fitted a rubber stopper, through which passed a water-condenser with calcium chloride tube attached. The neck of the flask fitted tightly by means of a cork into a hole bored through a round piece of hard asbestos board (B). Two other holes were provided, one for a water-condenser (C) and the other for a thermometer (D). The asbestos board
rested on the top of a large nickel crucible (E). A piece of split rubber tubing lying on the edge of the crucible acted as a vapour-tight joint. The crucible contained a concentrated solution of calcium chloride, the boiling solution of which maintained a constant temperature (to within 1°) by the refluxing of the water vapour. Temperatures up to 140° may be attained by varying the concentration of the calcium chloride. The crucible was protected by an asbestos shield. The condensations were carried on for 6 hours, and were terminated by means of an automatic time-switch which cut off the gas supply (Guthrie, J.S.C.I., 1928, 47, 202 T).
The Preparation of the Condensation Reagents.

**Succinic Anhydride.**

Powdered succinic acid (200 g.) was heated under reflux for 12 hours with 280 c.c. acetyl chloride (2 mols). The solution was cooled with stirring and the solid filtered off, washed with chloroform and dried in a soda-lime desiccator in vacuo. Yield, 77%; m.p., 119°-120°.

**Anhydrous Sodium Succinate.**

Sodium succinate formed by the neutralisation of succinic acid with sodium carbonate was dried by heating to 140°-150° for several days in an air-oven and finely powdered.

**Alcohol-Free Sodium Ethylate.**

Metallic sodium (700 g.) was added in small quantities at a time to chilled absolute alcohol (138 g.) contained in a flask fitted with a reflux condenser, and the reaction completed on the steam-bath. The solid compound was heated to about 130° in an air-oven until white in colour (2 hours) and cooled in vacuo.

**Acetic Anhydride.**

Ordinary anhydride was redistilled, b.p., 139°-140°.

**The Aldehydes.**

Since the condensations do not proceed satisfactorily in the presence of traces of water,
solid aldehydes were dried for at least four days over sulphuric acid in vacuo. Liquid aldehydes were distilled, the ethereal solutions having been previously dried over calcium chloride and preserved in well stoppered bottles in an atmosphere of carbon dioxide.

The Preparation of Phenyl Paraconic Acid.

Altogether 12 condensations were compared. Succinic anhydride gives rise to less decomposition products than sodium succinate. Benzaldehyde b.p., 117° (26.5 g.), succinic anhydride (20.5 g.) and sodium acetate (20.5 g.), were heated together at 110° for 7 hours. Unchanged aldehyde was steam-distilled off, the residue filtered through a wet filter and the filtrate acidified with concentrated hydrochloric acid. The acid was purified by a method of decantation described below. Yield, 30%.

The acid crystallises from water in stellate needles m.p. 99°-99.5° [m.p., 99°; Fittig (Annalen, 1889, 255, 142)]

The Purification of Crude Phenyl Paraconic Acid.

A careful investigation was made to determine the most efficient method of obtaining pure and perfectly colourless phenyl paraconic acid. After having steam-distilled off unchanged benzaldehyde from the condensation mixture, the latter was filtered hot through a wet filter and acidified. A brown
oil was thrown down which was followed by the precipitation of a crystalline solid consisting mainly of succinic acid. Considerable difficulty was at first experienced in obtaining with efficiency, a colourless crystalline acid from the brown solid which again liquefies on heating with water. The following methods of purification were carried out:

1. The crude acid was recrystallised from various solvents such as aqueous alcohol (33%, 50%), benzene, toluene, light petroleum of b.p., 40°-60°; 60°-80°; 80°-100°; 100°-120°; ligroin, carbon disulphide, ethyl acetate, etc., and various mixtures of solvents.

2. The acid was dissolved in ether, the ethereal solution extracted with aqueous sodium or ammonium carbonate and the separated alkaline layer acidified. The precipitated acid was filtered off, re-dissolved in ether and the process of extraction and isolation of the acid repeated.

3. The barium salt was washed with acetone, heated with sulphuric acid, filtered hot and the filtrate cooled.

4. The acid was boiled repeatedly with animal charcoal (which was treated beforehand with hot dilute hydrochloric acid).

5. The acid could not be made to sublime at 130° under reduced pressure.

The methods outlined above were found to be most unsatisfactory in that the yellow tinge was still
present. It is obvious from experiment 2 that the impurity is itself an acid. The following procedure, however, was found to be most efficient. Its success depends upon the fact that the brown impurity is least soluble in water than in any other solvent tried and can be removed by mechanical separation.

The acid was heated with water in a narrow beaker (see diagram) and the mixture allowed to cool whereupon oil was thrown down which carries with it some of the impurity.

The supernatant liquid was decanted into a beaker, the cooling and decantation process being repeated until a crystalline solid had appeared. At this stage, the mixture was re-heated and the decantation continued until finally the acid was deposited as a pure white solid.

Some brown solid was frequently formed on the surface of the liquid but was efficiently separated by flicking the surface of the liquid with a glass rod. Towards the end of the purification it was completely removed by skimming the surface with filter paper. A further quantity of acid was obtained by treating
the residues in the above-mentioned manner.

**An Attempt to Prepare o-Methoxyphenylparaconic Acid.**

---

**o-Methoxybenzaldehyde.**

The aldehyde was prepared by the method of Shoesmith and Connor (J.C.S., 1927, 2230). Salicylaldehyde (122 g.) was emulsified with 40 c.c. water in a flask under reflux by vigorous stirring, and potassium hydroxide (106 g. in 160 c.c. water) added alternately with methyl sulphate (177 g.). The addition was so regulated that the mixture was slightly yellow, the colour indicating the presence of the potassium compound. The mixture was extracted with ether and the ethereal layer shaken with sodium hydroxide sixteen times, when the last trace of hydroxy compound was removed. Yield, 60%; b.p. 108°-110° at 9 mm.

---

**o-Methoxyphenylparaconic Acid.**

None of the methoxyphenylparaconic acids have been so far prepared. Altogether, 8 condensation experiments were carried out. o-Methoxybenzaldehyde was heated with equimolecular proportions of succinic anhydride and sodium acetate, at temperatures varying from 110° to 120°, for 6 hours. The condensation mixture, which was very deep brown in colour, (in contrast to the corresponding m-condensation, see p. 18)
was steam distilled and filtered through a double wet filter. A brown syrup was precipitated on acidifying the filtrate. The acid was extracted with ether, the ethereal layer shaken with sodium carbonate and the acid re-precipitated from the separated alkaline layer. The syrup again appeared and could not be made to crystallise. No solid material could be obtained by leaving the syrup for several days on a porous tile.

When the aldehyde (13.6 g.) is mixed with sodium succinate (16.2 g.) and acetic anhydride (10.2 g.) there is an immediate rise in temperature and the mixture solidifies. Heated to 110°-116° for 6 hours, it becomes only slightly discoloured in strong contrast to the succinic anhydride condensation. The mixture was steam-distilled, when a small amount of white solid, m.p. 72°–74°, distilled over. The residue was filtered hot through a wet filter and acidified, whereby a large amount of solid was thrown down, succinic acid by appearance. The solid was extracted with ether from which no sign of an aromatic compound could be detected.

The tar residues left after the distillation were recrystallised twice from aqueous alcohol, from which was obtained a small amount of solid in stellate needles, m.p. 72°-75°. About 75% aldehyde was recovered from the condensations. There is no doubt, therefore, that this condensation takes place to a limited extent only.
m-Methoxybenzaldehyde.

The aldehyde was prepared by the method of Chakravarti, Haworth and Perkin (J.C.S., 1927, 2265). m-Hydroxybenzaldehyde (250 g.), methyl alcohol (750 c.c.) and caustic soda (85 g. in the minimum amount of water) were heated together on the steam-bath and 220 c.c. dimethyl sulphate (290 g.) added to maintain a brisk ebullition. More dimethyl sulphate (200 g.) was added and the mixture kept alkaline by the addition of 50% sodium hydroxide. After removal of dimethyl sulphate by distillation, the residue was diluted, extracted with ether and unchanged hydroxy compound removed from the ethereal solution with caustic soda solution. The bisulphite compound was formed, dissolved in water and the aldehyde liberated with caustic soda.

m-Methoxyphenylparaconic Acid.

Altogether, 6 condensations were examined. The yields of acid obtained from the sodium succinate and succinic anhydride methods were approximately equal, but the latter method has the advantage of giving rise to less tar. m-Methoxybenzaldehyde (27.2 g.), succinic anhydride (20.4 g.) and sodium acetate (16.4 g.) were heated together at 121° for 6 hours and the
and the mixture freed of aldehyde by steam distillation. The product was filtered hot through a wet filter, acidified and the solid filtered off. The crude acid, which deposited an oil on heating with water, was recrystallised from this solvent by the method of decantation already described. The acid crystallises out with unusual purity from 30% alcohol, in which it is, however, rather soluble. Yield, 26%; m.p. 141.1°-141.5°. It crystallises from water in stellate, curled, pointed leaflets. It is sparingly soluble in cold, readily soluble in hot water. Its constitution was proved by its conversion to 6-methoxy-1-naphthol.

$$\text{C}_{12}\text{H}_{18}\text{O}_5 \text{ requires } C, 61.02\% \text{; } H, 5.08\%.$$  

$$\text{Found } C, 61.28\% \text{; } H, 4.96\%.$$  

The Preparation of 6-Methoxy-1-Naphthol.

m-Methoxyphenylparaconic acid (7 g.) was heated at 200° for 30 minutes and at 280° for 15 minutes in a distillation flask etc., the procedure being analogous to that employed in the synthesis of 1-phenanthrol (q.v. p. 48). The reddish-brown oil which distilled over was dissolved in ether and the ethereal solution shaken with sodium carbonate. The separated ethereal layer was extracted with sodium hydroxide solution from which the 6-methoxy-1-naphthol was precipitated with carbon dioxide. It came down
as a black oil which solidified on standing to a sticky solid. On recrystallisation from 30% alcohol it melted at 77°-78·5°. The yield was exceedingly small and extensive charring had taken place during distillation.

The acid (6 g.) was heated this time in a bulb-tube at 190° - 210° for 35 minutes, and at 155° - 165° for 45 minutes, but not distilled. The vapour was condensed as before with a blast of air. The 6-methoxy-1-naphthol was isolated in the usual manner; the yield in this case being larger and obviously crystalline in appearance. It separated as a white solid after recrystallising from 30% alcohol, m.p. 83·9° - 84·5°.

N.B. The methoxy-naphthol obtained in the quantitative experiments melted at 83·5° - 84·2° after one recrystallisation from 30% alcohol. The naphthol is described in the literature as an oil, b.p. 185° at 12 mm. (D.R.P., 298,098; Chem. Zentr., 1921, II, 504).

The naphthol is very soluble in cold ether and chloroform, insoluble in cold, light petroleum. It crystallises from water (in which it is slightly unstable) in needles, and gives Molisch's test.

\[ C_{11}H_{10}O_2 \text{ requires } C, 75·9\%; H, 5·8\%. \]

Found C, 76·2%; H, 5·8%. 
Note on Molisch's Test.

Molisch's test was found to be a most suitable means for detecting minute quantities of the naphthols studied in this research. It was carried out as follows:

The naphthol was introduced into a 2" x 3/8" test-tube and dissolved in one drop of chloroform. The tube was one-third filled with a concentrated aqueous solution of glucose and the chloroform thoroughly emulsified by vigorous shaking. Concentrated sulphuric acid was added by means of a glass tube reaching to the bottom of the test-tube so as not to disturb the solution. If the drops of chloroform coalesced, the test, if negative, was repeated. The purple coloration always appeared, when positive, in less than a minute. It is not to be confused with a reddish coloration, due to the decomposition of the glucose, which sometimes appears after the mixture has been standing for some time.

An ATTEMPT to Prepare p-Methoxyphenylparaconic Acid.

1. Anisaldehyde (B.D.H.) was purified through the bisulphite compound. 100 g. crude anisaldehyde gave 78 g. pure aldehyde. The aldehyde was heated
at temperatures ranging from $100^\circ$ to $140^\circ$ with sodium succinate and with succinic anhydride, and although the mixtures turned brown, no paraconic acid could be obtained. Condensation did not take place in the presence of toluene. A survey of Fittig's researches disclosed his attempts to obtain this acid (Annalen, 1889, 225, 9). He has shown that the reaction proceeds to the formation of anisyl-isonaconic acid etc.

$$\text{MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO} + \text{CH}_2 \cdot \text{CO}_2\text{H} = \text{MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} + \text{CH}_2 \cdot \text{CO}_2\text{H} \quad \text{CO}_2 + \text{H}_2\text{O}$$

$$2\text{MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO} + \text{CH}_2 \cdot \text{CO}_2\text{H} \rightarrow \text{MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \rightarrow \text{MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH} \cdot \text{C} \cdot \text{CO}_2\text{H} \rightarrow \text{MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH}$$

Anisaldehyde (54 g.) did not condense to any appreciable extent with diethyl succinate (70 g.) and sodium ethylate (54 g.) in the presence of 160 c.c. boiling, sodium dried ether, a method which was hoped might lead to the formation of $p$-methoxyphenylitaconic and $p$-methoxyphenylaticonic acid, from which the $p$-methoxyphenylparaconic acid might be obtained (Annalen, 1890, 256, 76; 1903, 330, 292 etc.).
The Preparation of o-Bromophenylparaconic Acid.

**o-Bromotoluene.**

o-Bromotoluene was prepared as described for the para-compound in Organic Syntheses V 21. The preparation is analogous to that described on p. 35 for p-bromotoluene. b.p. 181° - 197°; yield, 60%. The distilled liquid was found to contain cresol. The latter was removed by shaking the ethereal solution with caustic soda solution, the yield thereby falling to 24%. Other investigators in these laboratories obtained the same yield. The experimental conditions were altered with a view to diminishing the hydrolysis of the unstable diazonium compound, (the para-isomeride is much more stable than the ortho-) by reducing the amount of water present to a minimum and instead of steam-distilling during the course of the Sandmeyer reaction, the temperature of the stirred mixture was allowed to rise to 15°. The yield of o-bromotoluene obtained by this method was negligibly small.

1. **o-Bromobenzaldehyde.**

The aldehyde was prepared by a modified method of Adams and Vollweiler (J. Amer. Chem. Soc., 1918, 40, 1737).
Bromine (136 g.), 2 molecules, was dropped, during the course of 2.5 hours, into gently boiling o-bromotoluene (73 g.) under reflux, and boiled for 24 hours with a suspension of calcium carbonate (100 g.) in 300 c.c. water, which was added through the condenser. The mixture was diluted and steam-distilled. The colourless oil which distilled over was extracted from the filtrate with ether. The ethereal solution was shaken with sodium bisulphite solution, and from the precipitated bisulphite compound the aldehyde was liberated and distilled under reduced pressure; b.p. 93.5° - 95.5° at 7.5 mm. Yield, 62%.

2. The Oxidation of o-Bromobenzyl Alcohol to o-Bromo-Benzaldehyde by Means of Nitrogen Tetroxide.

Cohen, Collvert and Harrison (J.C.S., 1829, 71, 1050, 1057) obtained a quantitative yield of o- and p- nitrobenzaldehyde by the oxidation of the corresponding alcohols with pure, dry, liquid nitrogen tetroxide in chloroform solution.

$$\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{OH} + \text{N}_2\text{O}_4 \rightarrow \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}_2\text{O}_4 \rightarrow \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO} + \text{N}_2\text{O}_3$$

During the preparation of o-bromobenzaldehyde, a white solid (28 g.), m.p. 77° - 78.5°, was obtained.
by evaporating to dryness the ethereal solution which was left after removal of aldehyde. This substance proved to be o-bromobenzyl alcohol, [m.p. 72° (Rec. trav. chim., 1924, 43, 372)], which was converted to aldehyde as follows. The alcohol (17 g.) dissolved in 75 c.c. chloroform, was mixed with pure, dry, liquid nitrogen tetroxide (12 g.) in a stoppered bottle, the stopper of which was tied down. After an hour's time the liquid turned green and milky. After 2½ days the liquid was removed and warmed gently on a steam-bath. Ether was added to the cooled mixture and the aldehyde isolated through the bisulphite compound. Yield, 32 - 36%.

3. o-Bromotoluene (70 g.) was heated with manganese dioxide (35 + 35 g.) and concentrated sulphuric acid (70 c.c.) in 67 c.c. water at 25° and 70°, by the method described below for the 4-aldehyde (p. 35). Although the suspension turned brown in colour immediately on admixing, no aldehyde bisulphite compound could be obtained.

---

**o-Bromophenylparaconic Acid.**

Altogether, 7 condensations were studied. The sodium succinate condensation mixtures were only
light brown in colour and the precipitated acid was less deeply coloured than that obtained by the succinic anhydride method. The amount of unchanged aldehyde which distilled over was, in most cases, very small. o-Bromobenzaldehyde (12.4 g.), sodium succinate (10.8 g.) and acetic anhydride (6.8 g.) were heated together at 116° for 6 hours. The aldehyde was steam-distilled off, the residue filtered hot through a wet filter and the filtrate acidified and cooled. The precipitated acid was recrystallised from water (by the decantation method). The acid, as described below, was only obtained after a considerable amount of research on its purification. It may be noted here that it is doubtful whether the impurity was, in this case, o-bromophenylisocrotonic acid (a well-known by-product formed during the Fittig condensations) since when the acid was boiled with carbon disulphide and filtered, the evaporated filtrate melted at 152.5° - 154.5°, and the residue at 152° - 155.5°. The pure white acid obtained by the decantation process was recrystallised again from water, then from 30% acetic acid. This acid separates out from water in minute stellate needles, m.p. 159° - 161.3°. The acid is described in the literature by Fuson (J. Amer. Chem. Soc., 1924, 46, 2779) as crystallising from water in white crystals, m.p. 133° - 135°. The acid obtained
above exhibited a definite crystalline form only after recrystallising from 30% acetic acid. The excessive discrepancy in the melting-point (26°) would lead one to conclude that the acids were differently constituted. The constitution of the acid is, however, proved below to be o-bromophenylparaconic acid by its conversion to 5-bromo-l-naphthol.

The acid is easily soluble in cold benzene and chloroform, and sparingly soluble in the petrol ethers, etc.

Recrystallised from a large quantity of water and cooled slowly, the acid separates out in beautiful rectangular plates. The acid, therefore, exhibits dimorphism.

5-Bromo-l-Naphthol.

The naphthol obtained from the quantitative experiments (p. 77) by heating o-bromophenylparaconic acid after recrystallising once from 30% alcohol, melted at 136·8° - 137°. \([\text{m.p. } 137° \text{ (Fuson, J. Amer. Chem. Soc., 1924, 46, 2779)}] \). It crystallises from water in long white needles and is slightly soluble in hot water, very soluble in ether, chloroform and benzene; sparingly soluble in petrol ether \((100° - 120°)\), very soluble in hot. Neutral ferric chloride gives an opalescence followed by a white precipitate on standing. It does not give
Molisch's test in contrast to the 6- and 7- bromo-l-naphthols.

The Preparation of m-Bromophenylparaconic Acid.

---

m-Bromotoluene.

The method employed was that described in Organic Syntheses VI 8.

\[
\begin{align*}
\text{CH}_3 & \text{HAc} \rightarrow \text{CH}_3 \text{NHAc} \\
\text{CH}_3 \text{Br} \rightarrow \text{CH}_3 \text{Br} + \text{EtOH} & \rightarrow \text{CH}_3 \text{Br} + \text{HCl} \\
\text{CH}_3 & \text{Br} \rightarrow \text{CH}_3 \text{NH}_2 \text{HCl} \\
\text{CH}_3 & \text{Br} \rightarrow \text{CH}_3 \text{NH}_2 \text{HCl} + \text{NaOH}
\end{align*}
\]

p-Toluidine (214 g.) was refluxed with 800 c.c. glacial acetic acid and the acetamino derivative brominated at 50° - 55° with bromine (325 g.). The bromo-compound was run into water, filtered off, carefully dried, then refluxed with 500 c.c. alcohol (R.S.) and 500 c.c. concentrated hydrochloric acid. The hydrochloride, suspended in water and stirred, was converted to the free amine (yield, 259 g.) with caustic soda (160 g. in 500 c.c. water). To the 3-bromo-4-aminotoluene was added 340 c.c. alcohol (R.S.)
and 210 c.c. concentrated sulphuric acid. The well-stirred mixture cooled to 0° was diazotised with sodium nitrite (155 g. in 270 c.c. water). The diazonium compound was decomposed with copper powder and the suspension steam-distilled. The ethereal solution of the oil which distilled over was washed in turn with caustic soda solution, concentrated sulphuric acid and sodium carbonate solution, dried with calcium chloride and distilled. Yield, 31%; b.p. 182° - 189°.

m-Bromobenzaldehyde.

Probably the best method mentioned in the literature for the preparation of m-bromobenzaldehyde is that described by Einhorn and Gernsheim. Its reliability, however, was called into question, since by this method samples were obtained as a liquid boiling between 215° - 230°. As is shown below, this observation was confirmed and that only the higher boiling-point fractions contain the aldehyde. It was considered a matter of importance, therefore, to attempt to prepare the aldehyde by applying the method of Adams and Vollweiler for the preparation of the aldehyde from m-bromotoluene.

1. Bromine (389 g.) was added to gently-boiling m-bromotoluene during the course of 4 hours, and hydrolysed by boiling for 8 hours with calcium
carbonate (200 g.) and 600 c.c. water under reflux. The mixture was steam distilled and the distillate extracted with ether. The aldehyde was isolated from its ethereal solution through the bisulphite compound and distilled. Yield, 16%; b.p. 234°-237°. [b.p. 215° - 216°; (Einhorn and Gernsheim, Annalen, 1894, 284, 141)].

N.B. Some of the aldehyde was inadvertently converted to the acid by the Cannizzaro reaction during the formation of the aldehyde from the bisulphite compound with caustic soda, and this is in some measure accounts for the poor yield.

The liquid solidified quickly to a white solid, m.p. 21° - 22.3°; this melting-point is identical with the melting-point of the ortho-isomeride. The solid is undoubtedly an aldehyde, since it forms solid compounds with bisulphite solution and with p-nitrophenylhydrazine. That it is m-bromobenzaldehyde follows from the fact that on oxidation it gives m-bromobenzoic acid, m.p. 155.5° - 156.5°.

2. The aldehyde was prepared by the method of Einhorn and Gernsheim from m-nitrobenzaldehyde

\[ \text{CHO} \xrightarrow{\text{SnCl}_2 + \text{HCl}} \text{CHO} \xrightarrow{\text{NaNO}_2} \text{CHO} \xrightarrow{\text{CuBr}} \text{CHO} \]

The substance obtained was a liquid, boiling
over a range of \(12^\circ\). It was redistilled and two fractions collected; b.p. \(217^\circ - 225^\circ\), b.p. \(225^\circ - 233^\circ\). The residue left in the flask solidified immediately on cooling. The former fraction did not solidify by cooling in ice. The latter fraction solidified but again liquefied almost entirely at \(15^\circ\). Yield, 23%. This aldehyde was rejected in view of its wide range of boiling-point and semi-solid condition.

3. \(m\)-Bromotoluene was heated at \(70^\circ\) and \(90^\circ\) with manganese dioxide and sulphuric acid of various concentrations (60\% and upwards) but no aldehyde could be isolated. Any aldehyde formed was oxidised to \(m\)-bromobenzoic acid (yield, 3\% to 12\%).

\(m\)-Bromophenylparaconic Acid.

The sodium succinate condensation gives rise to a rather purer acid than that obtained by the succinic anhydride method. The acid is purer than the \(o\)-isomer in spite of the higher temperature of condensation. The amount of unchanged aldehyde recovered from the condensation was again small. \(m\)-Bromobenzaldehyde (12.4 g.), sodium succinate (10.8 g.) and acetic anhydride (6.8 g.) were heated together at \(124^\circ\) for 6 hours. The aldehyde was removed by steam distillation and the crude acid isolated as in the case
of the ortho-acid. The acid did not liquefy on heating with water in which it is considerably less soluble than the o- or p- isomers. It was purified by heating with water and filtering through a hot filter. Yield, 40%. The acid crystallises from water in small, colourless, stellate needles, m.p. 164.5° - 165°. Fuson (J. Amer. Chem. Soc., 1925, 47, 416) describes the acid as crystallising from water in yellow leaflets, m.p. 164° - 165°.

When the acid is recrystallised from a large quantity of water and cooled slowly, it separates out in large rectangular plates. It, therefore, exhibits dimorphism as does o-bromophenylparaconic acid.

6-Bromo-1-Naphthol.

The naphthol produced in the quantitative experiments (p. 78), after recrystallisation once from 30% alcohol, melted at 125.5° - 129°, and in another single recrystallisation melted at 127.5° - 129°. [m.p. 129° - 130° (Fuson, loc. cit.).]

N.B. The filtrate on standing, deposited a white solid which melted at about 85° - 89°, but the amount of material was too small to isolate in the pure state. It may therefore be considered (as a probability only) that a very small quantity of 8-bromo-1-naphthol (m.p. 60° - 61°) is formed by the
ring closing in the ortho-position to the bromine atom.

6-bromo-l-naphthol separates out from water in white needles. It is slightly soluble in water. Neutral ferric chloride gives a white precipitate which turns greyish-purple on standing for some hours. It gives Molisch's test.

The Preparation of p-Bromophenylparaconic Acid.

p-Bromotoluene.

A mixture of copper sulphate (252 g.), copper turnings (80 g.), concentrated sulphuric acid (120 g.), sodium bromide (616 g.) and 3 litres of water, was heated for 12 hours in a flask fitted with reflux condenser. p-Toluidine (428 g.) was dissolved in concentrated sulphuric acid (784 g.) and 4 litres of water, and the vigorously stirred solution diazotised with sodium nitrite (280 g.) in 544 c.c. water, the temperature being maintained at 0° by cooling in a freezing mixture. The cuprous bromide mixture was heated to boiling in a flask fitted up for steam distillation with tap-funnel added. The diazonium solution was added in small quantities at a time to the boiling mixture which was steam-distilled at the same time. The distillate was made alkaline with
sodium hydroxide and the heavy oil separated off. The alkaline layer was extracted with ether and the ethereal layer added to the oil. The solution was shaken in turn with concentrated sulphuric acid, water, aqueous sodium hydroxide and again with water, then dried over calcium chloride and distilled; b.p. 175° - 180°. Yield, 68%.

**p-Bromobenzaldehyde.**

1. There are relatively few methods described in the literature for the preparation of the bromo-substituted benzaldehydes. Of these probably the best method is the dibromination and hydrolysis in the side-chain of the bromotoluenes. It was considered of value to attempt to obtain a more direct and more convenient method, namely, that of the immediate oxidation of the bromotoluenes. It has been shown that toluene may be oxidised to benzaldehyde by means of manganese dioxide and sulphuric acid (65%), (Houben Weyl, II 7)

\[
\text{C}_6\text{H}_5\text{CH}_3 + 2\text{MnO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow \text{C}_6\text{H}_5\text{CHO} + 2\text{MnSO}_4 + 3\text{H}_2\text{O}
\]

Only a trace of p-bromobenzaldehyde was obtained by heating the equivalent mixture to 40° with vigorous stirring for 23 hours. The commercial manganese dioxide was replaced by activated manganese dioxide prepared by method (3) of Whitesell and Frazer, (J. Amer. Chem. Soc., 1923, 45, 2843), but the yield of aldehyde was actually less than before. By
increasing the temperature to 70° - 80° and heating for 12 hours the yield of aldehyde was raised - as also was the yield of p-bromobenzoic acid, a circumstance to be avoided. The yield of acid was reduced to less than half its former value, by adding the manganese dioxide in equal portions with an interval of about 6 hours between. The aldehyde was obtained in 16% yield in the following manner.

p-Bromotoluene (70 g.), manganese dioxide (25 g.) and sulphuric acid (75 c.c. in 57 c.c. water) were heated to 70-80° for 6 hours with vigorous stirring under an air condenser. Another 25 g. dioxide were added and the process continued for a further 6 hours. The suspension was diluted, extracted with ether in a large separating funnel, the ethereal layer shaken with sodium carbonate solution and the aldehyde isolated through the bisulphite compound in the usual manner.

From 130 g. of p-bromotoluene, (the unchanged material being recovered after each experiment and oxidised again) about 150 g. of the aldehyde bisulphite compound was finally isolated.

2. Bromine (450 g.) was dropped into gently-boiling p-bromotoluene (232 g.) and hydrolysed with a mixture of calcium carbonate (220 g.) and 690 c.c. water. An additional amount of chalk (220 g.) was added.
Owing to an unavoidable accident the yield of aldehyde was poor.

The bisulphite compound (310 g.) obtained from experiments 1 and 2 was decomposed in aqueous solution with caustic soda, the precipitated aldehyde filtered off, washed with water and dried in vacuo over sulphuric acid. Yield, 122 g; m.p. 55.8° - 57.8°. [m.p. 56° - 57° (J. Amer. Chem. Soc., 1918, 40, 1737)].

p-Bromophenylparaconic Acid.

The condensation products obtained by the sodium succinate and succinic anhydride methods were closely similar. p-Bromobenzaldehyde (64 g.), succinic anhydride (34 g.) and sodium succinate (28 g.) were heated together at 140° until the reaction set in, then the mixture was heated at 124° for 6 hours. The product was steam-distilled, filtered hot through a wet filter, diluted and extracted with ether, thereby cleaning the solution very efficiently. The latter procedure was not satisfactory in all cases, since in the working up of some condensations (for example, with α-naphthaldehyde) a good deal of acid was lost in the ethereal extract.

The solution was heated to remove traces of ether and acidified. The isolated acid was re-crystallised from water by the decantation method.
The tendency of the para-acid to remain suspended in the liquid state is very much more pronounced than in the case of the ortho-isomeride, and consequently more difficult to obtain perfectly pure. Once this stage was reached, however, it was not difficult to obtain an acid of good melting-point. Yield, 23%; m.p. 140° - 140.5° [m.p. 140° - 140.5° (Fuson, J.A.C.S., 1925, 47, 516)]. The acid crystallises from water in white, stellate needles.

Fuson (loc. cit.) describes the acid as crystallising from water in "colourless crystals".

7-Bromo-l-Naphthol.

The naphthol obtained in the quantitative experiments (p. 78) by heating p-bromophenylparaconic acid, recrystallised once from 30% alcohol, melted at 106.7° - 107.3° [m.p. 105.5° - 106.5° (Fuson, loc. cit.)]. The naphthol crystallises from water in very long needles. It is very soluble in ether, chloroform and benzene; sparingly soluble in cold, and very soluble in hot, light petroleum (b.p. 100° - 120°). Neutral ferric chloride gives an opalescence which turns rapidly pale lilac in colour (after a few minutes) and a lilac precipitate is deposited on standing. It gives Molisch's test.
The Preparation of \( p \)-Tolylparaconic Acid.

\( p \)-Tolylnitrile.

The nitrile was prepared by the method described in *Organic Syntheses IV* 68.

\[
\begin{align*}
\text{CH}_3 & \quad \text{HCl} \quad + \quad \text{NaNO}_2 \\
\text{CH}_3 & \quad \text{NHCN} \quad + \quad \text{NaOH} \\
\text{CH}_3 & \quad \text{CN} 
\end{align*}
\]

A solution of sodium bisulphite (160 g.) and sodium hydroxide (86 g.) in 2 litres of water, was added to copper sulphate (625 g.) and sodium chloride (163 g.) dissolved in 1 litre of water. The suspension was cooled and the precipitate washed by decantation, then suspended in 1 litre of water. To this suspension was added slowly and with stirring, a solution of potassium cyanide (433 g.) in 500 c.c. water. The solution was cooled to 0\(^\circ\) and 1 litre of benzene added.

\( p \)-Toluidine (214 g.) was converted to the hydrochloride by adding 400 c.c. concentrated hydrochloric acid (3.0, 1.18) in 100 c.c. water. Sodium nitrite (140 g.) dissolved in 400 c.c. water was added slowly to the hydrochloride solution with stirring at 0\(^\circ\). The diazotised solution which was neutralised with anhydrous sodium carbonate (100 g.) was added to the sodium cupro-cyanide kept at 0\(^\circ\) and
agitated briskly with a centrifugal stirrer. When all the diazotised solution had been added the temperature was kept at 0° for thirty minutes and allowed to rise to 20° during a period of 3 hours. The mixture was stirred for a further two hours and the temperature raised to 50° without stirring. The mixture was allowed to cool to room temperature and the aqueous layer siphoned off from the benzene layer. The latter was steam-distilled. The pale yellow solid, which distilled over after the benzene, was filtered off and dried in vacuo over sulphuric acid. Yield, 73%; m.p. 25° - 27°.

p-Tolylaldehyde.

The nitrile was reduced and hydrolysed to aldehyde by the method of Stephen (J., 1925, 127, 1874). A mixture of stannous chloride (148 g.) dried by heating "fused stannous chloride" at 160° and 300 c.c. and 300 c.c. ether (717) was saturated at 0° with dry hydrochloric acid gas, p-tolylnitrile (50 g.) added, and the stream of acid passed in during a period of 2 to 3 hours. The solid was filtered off, washed with ether (717) and steam distilled. The oil which distilled over was extracted with ether, the aldehyde purified through the bisulphite compound
and distilled. Yield, 33%; b.p. 90° - 92° at 8 mm. (uncorrected).

**p-Tolylparaconic Acid.**

Altogether 12 condensations were carried out at temperatures ranging from 105° to 120° by both methods. The acid, although white, was impure. The condensation appears to proceed best with large quantities of aldehyde (about 50 g.). The mixture is heated at 140° until the reaction sets in, then at 120° for 6 hours. The small quantity of pure acid which was finally obtained crystallised from water in white plates, m.p. 140° - 141°. It is slightly soluble in hot ether; somewhat more soluble in cold chloroform, very soluble in hot; somewhat soluble in hot benzene. Its constitution was proved by its conversion to 7-methyl-1-naphthol.

C_{12}H_{14}O_4 requires C, 65.43%; H, 5.45%.

Found C, 65.21%; H, 5.68%.

**7-Methyl-1-Naphthol.**

Impure p-tolylparaconic acid (1 g.) was heated at 200° for 20 minutes then at 320° for 15 minutes and at 330°, when a yellow oil distilled over. The procedure and isolation of the naphthol was analogous to that employed in the synthesis of 1-phenanthrol (q.v. p. 48). 7-methyl-1-naphthol
crystallises from water in white needles, m.p. 108°-108.5° \[m.p. 109° \text{ (Ber., 1923, 56, 625); 107° -108° (Rec. trav. Chim., 1925, 44, 360)} \].

Neutral ferric chloride produces an opalescence which turns rapidly faint pink in colour. A lilac precipitate is deposited on standing for 1 hour. It gives Molisch's test but underneath the purple layer there appeared a much deeper band of green coloured liquid. Of all the naphthols studied during this research, the 7-methyl-1-naphthol is the only one which forms a double coloration in the Molisch's test.

Note:— The sodium carbonate extract obtained during the isolation of the naphthol was acidified and the solid filtered off. The solid was recrystallised from water from which it separates in white rhombic plates, m.p. 114° (uncorrected). This acid is in all probability p-tolylphenylisocrotonic acid.

The Preparation of p-Nitrophenylparaconic Acid.

p-Nitrobenzaldehyde condenses with succinic acid only with great difficulty [Salomonson (Ber. 1885, 18, 2154)]. Erdmann (Ber., 1885, 18, 2741) prepared the acid in good yield by the nitration of phenylparaconic acid. The latter method was therefore adopted.
Phenylparaconic acid (12 g.) was nitrated by adding the acid to an excess of fuming nitric acid in small quantities at a time. The mixture was well stirred and kept below -5°. The solution was kept for 1 hour and poured into ice when a greyish semi-solid mass was precipitated. The mother-liquor was decanted off and diluted with water. Pure white acid was obtained immediately from this. The crude acid was purified by the decantation method. Yield, 56%. The acid crystallised from water in long, stellate, pointed plates, m.p. 154.5° - 155°. (Quoted m.p., 154°, 163°).

The Heating of p-Nitrophenylparaconic Acid.

The properties exhibited by the p-nitro acid (and the o- and p-isomers) on heating are most unusual. Erdmann (Berl, 1885, 18, 2741) and Salomonson (Ber., 1885, 18, 2153; Recueil, 1887, 6, 6) tried repeatedly to obtain the naphthols by heating the acids but without success. Salomonson attributes this to two facts - (a) that the nitrophenyl isocrotonic acids are not formed and hence the naphthol cannot be synthesised, (b) that the acid chars at 230° - 250°. That the isocrotonic acid is not formed at all would appear doubtful since the loss of carbon dioxide at 200° has been noted by
Erdmann and also in these researches, although it may be granted that carbon dioxide is evolved only in small quantities below 210°.

p-Nitrophenylparaconic acid (2 g.) was heated at 180°. The loss of carbon dioxide was negligible at this temperature. The colour of the acid darkened considerably by raising the temperature to 205°. At 215° the evolution of carbon dioxide was rapid, but the acid became viscous and almost black in colour. At 220° the experiment was abandoned. After cooling, the acid was quite black and friable and had been converted completely into resin. The observations of Erdmann and Salomonson having been confirmed for the para-acid, it was considered unprofitable to consider a study of the other nitro-acids.

**The Preparation of α-Naphthylparaconic Acid.**
**α-Naphthaldehyde.**

1. **α**-bromonaphthalene (98 g.) was dissolved in 350 c.c. sodium-dried ether and magnesium turnings (12 g.) added. The reaction set in after the addition of a crystal of iodine. After the reaction had ceased, ethyl-orthoformate (70 g.) was run into the boiling solution under reflux in small quantities at a time and the solution boiled for 12 hours. Stirring was found unnecessary. The mixture was cooled to 0° and decomposed by ice. The minimum amount of hydrochloric acid was added (sufficient to dissolve all solid material) and the ethereal acetal layer separated and washed with water. The acetal was isolated and hydrolysed by heating for 20 minutes with 5 N hydrochloric acid. It was observed that the acetal turns black during the hydrolysis even although the mixture be carefully warmed on the steam-bath at the start. The solution was extracted with ether, the ethereal layer washed with sodium carbonate and shaken with bisulphite solution. A further quantity of aldehyde was obtained by heating the residue obtained from the evaporated ethereal solution, with 5 N acid for 30 minutes. The aldehyde was liberated from the bisulphite compound and distilled.

Yield, 39%; b.p. 173° - 174° (uncorrected) at 35 mm.
\[ \alpha - \text{Naphthaldehyde-}p\text{-nitrophenylhydrazone.} \]

The phenylhydrazone was prepared by the method described on p. 61 for the \( \beta \)-compound. It crystallises from acetic acid in scarlet needles, m.p. 241° - 243° [m.p. 234°, (Stephen, J.C.S., 1925, 127, 1874)]. It does not exhibit the change in colour that takes place with the \( \beta \)-compound when heated alone or heated with glacial acetic acid etc., but gives a deep magenta colour with concentrated alcohol potassium hydroxide which is unchanged on heating. Its alcohol solution shows the following reversible colour reaction,

\[
\text{Yellow} \xrightarrow{\text{NaOH}} \text{deep red.}
\]

and gives a deep magenta colour with concentrated alcoholic potash which is unchanged on heating.

2. The aldehyde was also prepared by the catalytic reduction of \( \alpha \)-naphthoylchloride [Rosemund. (Ber., 1918, 51, 591)].

\[ \alpha - \text{Naphthoylchloride.} \]

\( \alpha \)-Naphthoic acid (47 g.) was heated with thionyl chloride (108 g.) under reflux for 5 hours on the steam-bath. The mixture was cooled and the acid chloride filtered off and desiccated in vacuo over
soda-lime. Yield, 33%; m.p. 22°; b.p. 158° at 12 mm.

α-naphthoyl chloride is described in the literature as an oil, b.p. 297.5° (Zentr., 1905, (1), 542).

α-naphthoyl chloride (7 g.) was dissolved in 20 c.c. xylene, active palladinised barium sulphate (1 g.) added and the suspension heated to 170°. A current of dry hydrogen was passed in (see diagram) until the evolution of hydrochloric acid had ceased (about 8 hours). The catalyst was filtered off, washed with ether and the filtrate shaken with bisulphite solution and the aldehyde liberated. Yield, 33%; b.p. 158° at 12 mm.

It is noteworthy that in the absence of solvent during this reduction, the side-chain was completely removed and naphthalene produced in quantity. The residue on sublimation gave a white solid which condensed in leaflets, m.p. 78° - 80°.
\[ \alpha \]-methylnaphthalene was heated with manganese dioxide and 65% sulphuric acid at 130°. The mixture turned brown in colour but no aldehyde bisulphite compound could be obtained.

**\[ \alpha \]-Naphthylparaconic Acid.**

\[ \alpha \]-Naphthaldehyde (65 g.), succinic anhydride (4.2 g.) and sodium acetate (34 g.) were heated together at 140° until reaction set in and at 122° for 6 hours. A higher temperature as usual causes formation of tarry by-products which renders subsequent purification of the paraconic acid difficult. Excess of \[ \alpha \]-naphthaldehyde was removed in a current of steam and the residue filtered hot, cooled, extracted with ether and acidified. In some cases a considerable amount of liquid tar was produced after condensation and the acid was extracted from this with hot water. The precipitated acid was recrystallised from water and filtered hot. It resembles the \[ \beta \]-acid in not forming an oil during crystallisation from water. The acid was now recrystallised from 30% alcohol from which it separates in white rectangular prisms, m.p. 169°. Carbon dioxide was evolved at the melting-point.

\[
\text{C}_15\text{H}_{12}\text{O}_4 \quad \text{requires} \quad \text{C}, \; 70.3\%; \quad \text{H}, \; 4.7\%.
\]

\[
\text{Found} \quad \text{C}, \; 70.2\%; \quad \text{H}, \; 4.7\%.
\]
The Synthesis of 1-Phenanthrol.

1-Phenanthrol is the only one of the five theoretically possible monohydroxy derivatives of phenanthrene not described in the literature.

α-Naphthylparaconic acid (2 g.) was heated in a distillation flask immersed in a metal bath at 180° - 200° until evolution of carbon dioxide had ceased (30 minutes). The temperature of the bath was then raised rapidly to about 340° and distillation of the vapour prevented by impinging a blast of cold air on the neck of the flask. After 15 to 20 minutes the temperature was raised and distillation allowed to proceed. The red oil which distilled over solidified, and was dissolved in ether; the ethereal solution was extracted with sodium carbonate to remove carboxylic acid and then with aqueous sodium hydroxide. The latter extract was saturated with carbon dioxide, the precipitate extracted with ether and the ether evaporated. The 1-Phenanthrol so obtained crystallised from light petroleum (b.p. 100° - 120°) in colourless, prismatic needles. It crystallised from water in prismatic needles, m.p. 156°. Yield, 5%.

\[ C_{14}H_{10}O \text{ requires } C, 86.6\% \text{; } H, 5.2\% \]
\[ \text{Found } C, 85.9\% \text{; } H, 5.2\%. \]

By using crude α-naphthylparaconic acid, the yield of 1-phenanthrol was raised to about 15%. As subsequent considerations show, there can be little doubt that the reaction which takes place is as
It is considered highly improbable that the ring should close in the \( \alpha' \)-carbon position; if it did, this would imply the presence of a 7-membered ring which, according to Baeyer's theory, is an unstable one.

The Properties and Derivatives of 1-Phenanthrol.

1-Phenanthrol is insoluble in water, very soluble in methyl alcohol and benzene; easily soluble in ligroin and very soluble in hot ligroin. With caustic soda and chloroform it gives a green coloration in hot dilute solution (Lustgarten's test for naphthols) and a prussian-blue coloration in concentrated solution. It does not give Holisch's test. A dirty olive-green precipitate is formed by heating gently a dilute alcoholic solution with neutral ferric chloride. Cold concentrated
sulphuric acid produces a yellow coloration which on heating turns orange to red and finally, almost colourless. With phenyldiazoniumchloride, a red dye is formed which darkens considerably during the addition of excess reagent. With p-nitrophenyldiazoniumchloride various tints, varying from red to purple, were obtained, but an excess of the reagent resulted in the immediate formation of a red precipitate.

The Picrate of 1-Phenanthrol.

A solution of 1-phenanthrol (0.06 g.) in methyl alcohol was added to 1.5 molecules picric acid (0.106 g.) in methyl alcohol. The precipitate was filtered off and recrystallised from the same solvent from which it was deposited in orange-red feathery needles, m.p. 181° - 181.5°.

1-Methoxyphenanthrene.

1-Phenanthrol (0.8 g.) was dissolved in 8 c.c. methyl alcohol. 4 c.c. of a 10% methyl-alcoholic potassium hydroxide and 3 c.c. of a 13% solution of methyl sulphate in methyl alcohol were added and the solution heated on the steam-bath for 1 hour. It was diluted with water, extracted with ether and the ethereal layer washed with aqueous sodium hydroxide to remove unchanged phenanthalen.
1-methoxyphenanthrene left on evaporation was recrystallised from absolute methyl alcohol. Yield, 50\%.

It separates from this solvent in colourless prismatic needles, m.p. 105°. \( [\text{m.p. 105° - 106°;} \]

Pschorr, Wolfes and Buckow (Ber., 1900, 33, 170).

The Picrate of 1-Methoxyphenanthrene.
The picrate was formed in methyl alcoholic solution as described for the picrate of 1-phenanthrol. It crystallised from methyl alcohol in orange, stellate needles, m.p. 150° - 150.5°. \( [\text{m.p. 153°, Pschorr, Wolfes and Buckow}] \).

The Acetate of 1-Phenanthrol.
1-Phenanthrol (0.07 g.) was added to ice (1.5 mols.) acetic anhydride and the mixture heated. The solution was cooled and shaken five times with aqueous sodium hydroxide, the ethereal layer isolated and evaporated to dryness. The residue was re-crystallised from light petrolatum (60° - 80°) from which it separated in prismatic needles, m.p. 134.5° - 134.8°.

A search of the literature revealed that there is a remarkable resemblance between 9-phenanthrol and 1-phenanthrol and their derivatives, as is seen from the following table.
1-Phenanthrol | 9-Phenanthrol

<table>
<thead>
<tr>
<th>Property</th>
<th>1-Phenanthrol</th>
<th>9-Phenanthrol</th>
</tr>
</thead>
<tbody>
<tr>
<td>m.p.</td>
<td>156°</td>
<td>152°; 152° - 153°; 148° - 149°.</td>
</tr>
<tr>
<td>Stable in air</td>
<td></td>
<td>Unstable in air.</td>
</tr>
<tr>
<td>Insoluble in water; easily soluble in ligroin, very soluble in hot ligroin.</td>
<td></td>
<td>Insoluble in water; slightly soluble in ligroin, easily soluble in hot ligroin.</td>
</tr>
<tr>
<td>NaOH + CHCl₃ → blue coloration.</td>
<td></td>
<td>NaOH + CHCl₃ → blue coloration.</td>
</tr>
<tr>
<td>Cold concentrated H₂SO₄ → yellow coloration.</td>
<td></td>
<td>Cold concentrated H₂SO₄ → orange-red coloration.</td>
</tr>
<tr>
<td>Methyl ether:</td>
<td>m.p. 105°, needles from MeOH.</td>
<td>m.p. 96° - 97°, needles from MeOH.</td>
</tr>
<tr>
<td>Picrate:</td>
<td>m.p. 182°, needles.</td>
<td>m.p. 183°, 185°, needles from MeOH.</td>
</tr>
<tr>
<td>Acetate:</td>
<td>m.p. 134.5° - 134.8°, needles from MeOH.</td>
<td>m.p. 77°, 77° - 78°, needles from MeOH.</td>
</tr>
</tbody>
</table>

It would seem not altogether improbable that tautomerism from the 1- to the 9- position might have taken place during the course of the distillation.

The question as to whether tautomerism does actually take place or not, is of considerable importance with regard to the special relationship of the benzene nuclei in naphthalene, and the question arises...
as to whether the 1:5 positions in naphthalene are closer together in space than the 1:8 positions. (Fuson, J. Amer. Chem. Soc., 1924, 46, 2779). Fuson chose the Erdmann ring-closure for the synthesis of 5-bromo-1-naphthol from o-bromophenylparaconic acid, on the grounds that the synthesis is a normal one, that is, that tautomerism does not take place during the distillation at 250° - 300°. The whole significance of his conclusions depends on the question of the possibility of tautomerism of the hydroxyl group. If tautomerism did take place during the synthesis of 1-phenanthrol, doubt might be legitimately thrown on his assumption. It was considered desirable, therefore, to synthesise the methyl ether of 1-phenanthrol by another method which precludes any possibility of tautomerism, and observe whether the melting-point of the mixed ethers was lower than that of the so-called 1-methoxyphenanthrene.

The Synthesis of 1-Methoxyphenanthrene.

The synthesis employed was that of Pschorr, Wolfes and Buckow (Ber., 1900, 33, 170) and is shown in the following scheme
o-Methoxybenzaldehyde.

The aldehyde used was obtained by the methylation of o-hydroxybenzaldehyde (p. 16).

o-Methoxybenzyl Alcohol.

o-Methoxybenzaldehyde (102 g.) was dissolved, and no more, in an approximately 12% solution of
potassium hydroxide in methyl alcohol, methyl alcohol (135 g.) added, and the solution kept for 3 days at room temperature. Water was added and the alcohol distilled off, leaving an oil which was dissolved in ether. The solution was washed with aqueous sodium hydroxide, then with water, and the ether distilled off. Yield, 19 g; b.p. 235° - 237° (uncorrected).

o-Methoxybenzylchloride.

The alcohol was dissolved in benzene and dry hydrochloric acid gas passed in for 2 hours. The benzene layer was separated off, washed and dried with calcium chloride. The benzyl chloride was isolated from the ethereal solution, but not distilled.

o-Methoxybenzynitrile.

The oil was dissolved in alcohol (152 g.) and water potassium cyanide (8.6 g.) in 10.5 c.c./added. After heating for two hours on the steam-bath, water was added, the mixture extracted with ether, and most of the alcohol distilled off.

o-Methoxyphenylacetic Acid.

The alcoholic solution was diluted with 18 c.c. water and 15% alcoholic potassium hydroxide (107 g.) added. The mixture was heated at 100° for 4 hours and an equal volume of water added. The acid was extracted with ether, the ethereal layer shaken with
aqueous sodium carbonate and the alkaline layer acidified with hydrochloric acid. The acid was re-

drystallised from very dilute alcohol. Yield, 6.5 g.; m.p. 119° - 121° (quoted m.p. 124°). The acid was

converted to its sodium salt by adding sodium carbonate (3.5 g.) in aqueous solution until neutral.
The solution was evaporated to dryness and the salt dried at 120°.

(α-)-o-Methoxyphenyl-o-Nitrocinnamic Acid.

The sodium salt was heated for 23 hours at 100° with o-nitrobenzaldehyde (6.4 g.) and 33 c.c. acetic anhydride. The mixture was diluted, warmed and allowed to cool, whereupon a bright, reddish-brown precipitate was thrown down. The solid material was filtered off and recrystallised from 30% alcohol. Yield, 10 g.; m.p. 210° - 214°.

(α-)-o-Methoxyphenyl-o-Aminocinnamic Acid.

The acid was dissolved in ether and extracted with 80 c.c. ammonia. The ammoniacal layer was run slowly into a mixture consisting of ferrous sulphate (80 g.) in 240 c.c. water, and 200 c.c. concentrated ammonia heated to boiling. The residue was filtered off, the filtrate acidified slightly with concentrated hydrochloric acid, a further 2 c.c. acid added, and the amino-acid filtered off.
**1-Methoxyphenanthrene-10-Carboxylic Acid.**

The amino-acid was dissolved in 260 c.c. sulphuric acid (S.G. 1.19) and 260 c.c. water added. The acid was diazotised with 5 N sodium nitrite solution and decomposed with 1½ molecules dry copper powder prepared by Gattermann's method (Ber., 1890, 23, 1219). The acid was neutralised with sodium hydroxide solution, the copper powder filtered off, and the acid precipitated with hydrochloric acid.

**1-Methoxyphenanthrene.**

The dry carboxylic acid was distilled under reduced pressure and the distillate extracted with warm petrol ether (60° - 80°). The extract was filtered from the appreciable quantity of insoluble material and cooled, when needles, m.p. 173° - 174° (uncorrected), were deposited and separated off. The solid residue was again extracted with petrol ether. This, when evaporated to dryness, yielded crystals which were recrystallised from methyl alcohol, from which a white solid separated in prismatic needles, m.p. 103° (uncorrected). No mention is made by Pschorr, Wolfes and Buckow of the solid, m.p. 173° - 174°. The quantity obtained was too small for further investigation.

The methyl ether was mixed with the methyl ether prepared by the Erdmann ring-closure. The
melting-point of the mixed ethers was 103° - 104° (uncorrected).

It follows, therefore, that the Erdmann ring-closure is a normal reaction, the hydroxyl group remaining in the 1-position during distillation at a temperature as high as 340°.

The Preparation of β-Naphthylparaconic Acid.

The acid was prepared by the following series of reactions:

1. A mixture of anhydrous stannous chloride (95 g.) and 300 c.c. ether (717) was saturated with dry hydrochloric acid gas at 0° and β-Naphthonitrile (50 g.), dissolved in 300 c.c. ether (717), run into the mixture, and this in turn saturated with the gas. The mixture turned greyish in colour almost immediately, and several hours later a brown precipitate appeared. The solid was filtered off, hydrolysed in hot water, and the aldehyde steam-distilled. The distilled
product was warmed with light petroleum, the solution filtered and shaken with bisulphite solution.

Stannous chloride (95 g.) was added to the filtrate from the reduction product in the last experiment and $\beta$-naphthonitrile (50 g.) converted to the aldehyde. The bisulphite compound was dissolved in water and the aldehyde liberated with aqueous sodium hydroxide. The aldehyde was filtered off, washed with very dilute acid, and finally with water, and dried for several days in vacuo over sulphuric acid. Yield, 36%; m.p. 60° - 60.5°.

In two previous experiments the finely-divided nitrile was added in the solid state to the stannous chloride mixture, when the following colour changes took place: - olive green $\rightarrow$ brilliant green $\rightarrow$ yellow green $\rightarrow$ canary yellow. This solid on hydrolysis did not give rise to any aldehyde. Nickel foil was added, in another experiment, but it did not have any catalytic reduction effect.

$\beta$-Naphthoylchloride.

$\beta$-Naphthoic acid (47 g.) was heated with thionyl chloride (108 g.) on the steam bath under reflux for 5 hours. The mixture was cooled, the solid filtered off and dried in vacuo over soda-lime. It was recrystallised from light petroleum (40° - 60°) from which it separated in white needles, m.p. 50.8° - 51.3°.
It is described in the literature as a solid, m.p. 43° (Annalen, 1876, 120, 317); 40° (J., 1906, 89, 123).

It was considered necessary to analyse the acid chloride in view of the discrepancy in melting-point which is large for such a low temperature.

0.2717 g. of the acid chloride was heated on the steam-bath for 15 minutes with 10 c.c. 10% alcoholic potassium hydroxide. 5 c.c. concentrated nitric acid (A.R.) was added, followed by 25 c.c. 0.0988 N silver nitrate. The silver halide was filtered off and the filtrate titrated with N/10 ammonium thiocyanate. C.104 N thiocyanate required was 10.21 c.c.

\[ C_{11}H_7OCl \text{ requires } C1,18.6\% \]
\[ \text{Found: } C1,18.4\% . \]

2. β-naphthoyl chloride (5 g.) was dissolved in 20 c.c. xylene, and active palladised barium sulphate (1 g.) added. The suspension was heated to 180° and a current of dry hydrogen passed in until the evolution of hydrochloric acid. The catalyst was filtered off, the filtrate shaken with bisulphite solution, and the aldehyde liberated from the separated bisulphite compound. Yield, 90%; m.p. 60° - 60.5°.

This method is perhaps less convenient than method 1, but the yield is better and the aldehyde is more readily obtained in a pure state. It will be
noticed that the yield of $\alpha$-naphthaldehyde is very much lower than in the case of the $\beta$-compound, a circumstance which is due no doubt to steric hindrance.

$\beta$-Naphthaldehyde-$p$-nitrophenylhydrazone.

A solution of $p$-nitrophenylhydrazine in acetic acid was added to $\beta$-naphthaldehyde dissolved in hot acetic acid and the mixture heated. A scarlet precipitate was formed which after cooling was filtered off, m.p. 241° - 242°, which happens to be identical with the $\alpha$-isomeride. When concentrated alcoholic potassium hydroxide is added to its alcoholic solution, a purple-red colour is produced which is unchanged on heating. When the scarlet solid was recrystallised from glacial acetic acid, it separated out on cooling in yellow leaflets, m.p. 241° - 242°. The red compound turns yellow in colour when heated in the melting-point tube (135° - 145°). When the glacial acetic acid solution is diluted, the red compound is precipitated. The colour change of red to yellow is also brought about when the red compound is warmed with alcohol, chloroform or benzene.

It appears obvious from these experiments that the red $\beta$-phenylhydrazone is much less stable than the red $\alpha$-isomeride described on p. 45, and that the red compound is an unstable modification of the yellow.

In alcoholic solution the following reversible
colour reaction is exhibited:

\[
\begin{align*}
\text{deep red } & \xrightarrow{\text{HCl}} \text{ yellow} \\
& \xrightarrow{\text{NaOH}}
\end{align*}
\]

Chattaway and Clemo (J.C.S., 1923, 123, 3041) consider that the most probable explanation of the deepening in colour when alkali is added to an alcoholic solution of the p-nitrobenzaldehydephenylhydrazone is that the hydrogen atom of the imino group wanders to the nitro-group, which is accompanied by the development of the quininoid structure in the molecule.

Further research would be required to determine the relationship between the differently coloured substances in the solid state and with those produced in the reversible alkali-acid reactions.

\[\beta\text{-Naphthylparaconic Acid.}\]

\[\beta\text{-Naphthaldehyde (35.5 g.), succinic anhydride (36 g.) and sodium acetate (28 g.) were heated together at 140° until reaction set in, after which the heating was continued at 121° for 6 hours. The mixture was steam-distilled and the residue filtered hot. The filtrate was acidified and cooled, \]
the precipitated acid filtered off and dissolved in water in which it is sparingly soluble. The acid did not come down as an oil. The solution was filtered hot, the filtrate cooled and the white crystalline solid which separated out filtered off, m.p. 172° - 173° m.p. 167° - 170°, Ludewig (Annalen, 1911, 379, 351). The acid evolves carbon dioxide at the melting-point and crystallises from water in hexagonal plates.
EXPERIMENTAL.

The Distillation of Phenylparaconic Acid.

The purpose of the distillation experiments was, for the most part, to find a method for estimating accurately the yield of \( \alpha \)-naphthols obtained during distillation of the phenylparaconic acids under standard conditions. These conditions could not apparently be repeated with sufficient accuracy and the method of distillation was consequently abandoned.

Fittig and Erdmann (Annalen, 1885, 227, 242) obtained \( \alpha \)-naphthol in a yield of 15\%. The experiments described in brief below, demonstrate how a development in the technique of obtaining the naphthols in high yields was reached in those researches. See Table I.

The \( \alpha \)-naphthol and phenylisocrotonic acid were isolated and estimated by the method described on p. 71.

In a preliminary experiment phenylparaconic acid was heated in a 10 c.c. distillation flask immersed in a metal bath at 180° until the evolution of carbon dioxide had ceased and consequently, the formation of phenylisocrotonic acid completed. The
temperature was then allowed to rise slowly to 360° during a period of two hours, during which, distillation proceeded gradually. No \( \alpha \)-naphthol could be detected in any of the fractions.

At about 160° - 170° a colourless oil distilled. Its boiling-point, as determined by Siwoloboff's method, (Ber., 1886, 19, 795), was 160° (uncorrected). The liquid was therefore \( \alpha \)-phenylpropylene (b.p. 165°, Annalen, 1874, 172, 130), which was formed presumably as shown by the equation

\[
\begin{align*}
\text{CH}_3\text{C} & \text{H} \quad \text{CH} \quad \text{CO}_2\text{H} \\
\text{O} & \text{C} \quad \text{C} \\
\text{H}_2 & \text{H}
\end{align*}
\]

An analogous reaction takes place when \( \alpha \)-methylphenylparaconic acid (Annalen, 1882, 216, 125) and \( \beta \)-methylphenylparaconic acid (Annalen, 1889, 255, 274) are distilled, the hydrocarbons formed in this case being phenylbutylene.

\text{TABLE I.}
TABLE I.

Distillation of Phenylparaconic Acid.

<table>
<thead>
<tr>
<th>Number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of acid taken (g.)</td>
<td>5</td>
<td>5</td>
<td>4.5</td>
<td>5</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Yield of (\alpha)-naphthol (g.)</td>
<td>0.1</td>
<td>0.3</td>
<td>0.5</td>
<td>0.7</td>
<td>0.85</td>
<td>2.0</td>
</tr>
<tr>
<td>Yield of (\alpha)-naphthol (%)</td>
<td>2.9</td>
<td>8.6</td>
<td>15.9</td>
<td>20.0</td>
<td>24.3</td>
<td>28.2</td>
</tr>
<tr>
<td>Yield of phenylisocrotonic acid (g.)</td>
<td>1.9</td>
<td>1.7</td>
<td>1.0</td>
<td>0.55</td>
<td>-</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Note: The yields of the \(\alpha\)-naphthols in Tables I to IX are given in per cent of that expected by theory.

Experiment 1. (see Table I.). The temperature in this experiment was raised quickly to 360° and since there was an appreciable yield of \(\alpha\)-naphthol, it was concluded that the temperature at which ring closure takes place with ease (subsequently found to be above 210°) should be reached as soon as possible, otherwise carbon dioxide is detached from the end of the chain, rendering void the possibility of the formation of \(\alpha\)-naphthol.

Experiment 2. On the other hand, if the distillation is allowed to proceed too rapidly it is obvious that the phenylisocrotonic acid produced during the first stages of the reaction will have
little or no opportunity of reacting so as to form $\alpha$-naphthol, since it will distil over unchanged.
The temperature, therefore, was kept at 280° (at which the phenylisocrotonic did not distil) for one minute before raising it to 360°.

**Experiment 3.** The temperature was maintained at 280° - 300° for 5 minutes.

**Experiment 4.** The temperature was maintained at 280° - 300° for 10 minutes.

**Experiment 5.** The temperature was maintained at 280° - 300° for 15 minutes. A blast of cold air was impinged on the neck of the flask. This had the effect of condensing the vapour so that it dropped back into the hot bulb. This effect could be maintained at the given temperature for any length of time.

**Experiment 6.** With 10 g. of acid, the condensing effect of the air-blast was insufficient. A flask with a much longer neck was used, the vapour in this case being kept down with ease at 290° - 295° for 20 minutes.
The \( \alpha \)-naphthol was obtained as a faint yellow solid, m.p., 91°, and the phenylisocrotonic acid, after recrystallisation from water, as a white substance, m.p., 84° - 84·5° [m.p., 36° (Annalen, 1882, 216, 101)].

The Quantitative Estimation of the Amount of Naphthol Formed by Heating the Various Phenylparaconic Acids at a Constant Temperature.

The following factors had to be taken into consideration before deciding upon the most suitable temperature at which the phenylparaconic acids might be heated.

(a) Since \( \alpha \)-naphthol is formed from \text{phenylisocrotonic acid} the whole of the phenylparaconic must first of all be converted to the \text{isocrotonic acid}. The paraconic acid was therefore made to undergo a preliminary heating until the evolution of carbon dioxide had ceased. The temperature chosen was 180°.

(b) Since \( \alpha \)-naphthol only begins to be formed at 200° - 210° (see p. 83) the temperature at which the \text{isocrotonic acid} is to be converted to naphthol must be somewhat higher than this and if possible, such that all the substituted phenylparaconic acids give rise to determinable yield of the naphthols. The temperature of 240° was chosen as being the most suitable, at which there was, moreover, relatively little discoloration of the reaction mixture.
The heating of the paraconic acids was carried out in the apparatus shown below.

Along the axis of a boiling-tube A 2.2 cm × 20 cm. was placed a thermometer \( T_1 \), the bulb of which lay almost wholly in the cone situated at the end of the tube. The thermometer was surrounded by a glass cooling-coil B attached to an air blast. The thermometer and coil were kept rigidly in place by a 3-holed cork fitting into the mouth of the tube. A side-tube C
permitted of the escape of carbon dioxide. In the later experiments, nitrogen was introduced into the reaction-tube to prevent oxidation of the naphthol and was led in through a glass tube lying in C. The nitrogen was passed through an alkaline solution of pyrogallol, to remove the last traces of oxygen, then through a long tube packed with cotton-wool to remove any spray which might be carried into the reaction tube. The tube and thermometer T2 were immersed in a metal bath D, the temperature of which was regulated for 180° and 240° by an adjustable mercury thermo-regulator E. Below the bath was suspended a brass plate F which served to smooth out irregularities in the bunsen flames. The bath was protected by an asbestos cover and the bunsens by an asbestos shield. The thermo-regulator was removed from the bath on completion of the experiment so as to avoid fracture during the cooling of the metal. The cold air-coil served to condense any vapour which would otherwise be lost at the higher temperature (240°). A white solid was deposited on the lower part of the coil but was quickly washed down by the oil formed during the reaction.

Phenylparaconic acid (2 g.) was heated to 180° - 185° for 30 minutes, until effervescence had nearly ceased, then the temperature was raised to 240° - 245° for 7-5 minutes. The somewhat prolonged time of heating at the latter temperature was chosen
in order not only to obtain measurable yields of of \( \alpha \)-naphthol, but also to eliminate, as far as possible, any catalytic effects which would affect the yield more noticeably in a shorter than in a longer period. The reddish-brown oil was cooled and extracted with ether. The ethereal extract was shaken with a saturated solution of sodium carbonate-bicarbonate and the alkaline layer separated. The ethereal layer was shaken with 1.5 N sodium hydroxide and the separated alkaline layer saturated with carbon dioxide to precipitate naphthol. The suspension was warmed gently to remove traces of ether, cooled and filtered off in a tared Gooch crucible. It was washed thrice with a small amount of water, heated to 50° - 60° for two hours (at which temperature the loss of dry naphthol was negligible), dried in vacuo over sulphuric acid and weighed. The yields in per cent of those expected by theory were as follows: 14.3, 1.9, 7.3, 20.0 (from very impure acid), 1.1, 0.8, 6.9, 10.5. The values are obviously too divergent for quantitative purposes.

An entirely new method of determining the amount of \( \alpha \)-naphthol was resorted to, and the various other interfering factors sought out and eliminated in turn.

The following is a summary of the method
finally adopted for the estimation of the various products of reaction:

```
Ethereal solution of reaction oil
  Na₂CO₃

Ethereal layer
  NaOH

Aqueous layer
  HCl

phenylisocrotonic acid
```

The oil from the reaction was dissolved in 20 c.c. ether and shaken with 5 + 5 c.c. sodium carbonate-bicarbonate solution* (that is, the extraction was repeated, using altogether 10 c.c. alkali). The alkaline layer was acidified with 10 c.c. concentrated hydrochloric acid and the precipitated acid extracted with 7 + 5 + 5 c.c. ether → "ACID". The ethereal layer was shaken with 5 + 5 c.c. 1.5 M sodium hydroxide; ethereal layer → "RESIDUE". The alkaline layer was saturated with carbon dioxide

* Sodium bicarbonate was added to the sodium carbonate solution in order to ensure that no α-naphthol might be extracted at this stage.
passed through aqueous sodium bicarbonate (2-3 hours) and the precipitated naphthol extracted with 5+5+5 c.c. ether. Ethereal layer → "NAPHTHOL". The liquid which remained was acidified with 10 c.c. concentrated hydrochloric acid and extracted with 7 + 5 c.c. ether → "HO-ACID". The ethereal solutions ("acid", "residue", etc.) were evaporated and dried in vacuo over sulphuric acid. The acid and residue were dried for 24 hours before weighing.

The accuracy of the above method for estimating the amount of α-naphthol produced was tested as follows: α-naphthol (0.2 g.) was dissolved in 20 c.c. ether and the ethereal solution treated exactly as above. It was found that 0.199 g. naphthol was recovered.

Note:— It would appear from Fittig's researches on the substituted butyrolactones that the lactone ring is only opened by hot sodium hydroxide (Annalen, 1882, 216, 103). The accurate experiments carried out in the present researches seem to show, however, that in cold alkali, an equilibrium is set up as shown by the equation,

\[
\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}^\cdot 0 \xrightarrow{\text{H}_2\text{O}} \text{C}_6\text{H}_5\cdot\text{CHOH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}
\]

It is difficult to see how the substance can be anything else but γ-phenyl-γ-hydroxybutyric acid. In this connection it may be remarked that quantitative
Lactone fission experiments have been carried out by Sircar (J., 1927, 1257) where it is assumed from Fittig's researches (Ber., 1890, 23, 91) that the lactone ring is stable to cold alkali. Moreover, it may be concluded from those considerations and from the researches of Fittig and his collaborators that the substance termed "residue" is $\gamma$-phenyl-$\gamma$-butyrolactone. The so-called "acid" was proved to be phenylisocrotonic acid.

**TABLE II.**

Heating of Phenylparaconic Acid.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Time (mins.)</th>
<th>Colour</th>
<th>$\text{H}_2\text{O}$ added (c.c.)</th>
<th>Naphthol (g.)</th>
<th>Acid (g.)</th>
<th>Residue (g.)</th>
<th>HO-Acid (g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td></td>
<td>0.13</td>
<td>9.5</td>
<td>0.87</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td></td>
<td>0.14</td>
<td>10.0</td>
<td>0.89</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td></td>
<td>0.19</td>
<td>13.5</td>
<td>0.76</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>Y</td>
<td>0.35</td>
<td>24.8</td>
<td>0.56</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>Y</td>
<td>0.20</td>
<td>14.1</td>
<td>0.68</td>
<td>0.33</td>
<td>0.12</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>Y</td>
<td>0.21</td>
<td>14.6</td>
<td>0.69</td>
<td>0.39</td>
<td>0.10</td>
</tr>
<tr>
<td>6a</td>
<td>3</td>
<td>W</td>
<td>0.09</td>
<td>6.2</td>
<td>1.02</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>6</td>
<td>W</td>
<td>0.05</td>
<td>3.5</td>
<td>1.06</td>
<td>0.15</td>
<td>0.06</td>
</tr>
<tr>
<td>8</td>
<td>6</td>
<td>W</td>
<td>0.04</td>
<td>2.6</td>
<td>0.89</td>
<td>0.25</td>
<td>0.07</td>
</tr>
<tr>
<td>9</td>
<td>5</td>
<td>W</td>
<td>0.013</td>
<td>2.2</td>
<td>1.17</td>
<td>0.16</td>
<td>0.05</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>W</td>
<td>0.15</td>
<td>4.6</td>
<td>1.09</td>
<td>0.18</td>
<td>0.05</td>
</tr>
<tr>
<td>11</td>
<td>5</td>
<td>W</td>
<td>0.06</td>
<td>4.4</td>
<td>1.07</td>
<td>0.18</td>
<td>0.06</td>
</tr>
<tr>
<td>12</td>
<td>7</td>
<td>W</td>
<td>0.04</td>
<td>2.5</td>
<td>1.21</td>
<td>0.21</td>
<td>0.03</td>
</tr>
<tr>
<td>13</td>
<td>5</td>
<td>W</td>
<td>0.06</td>
<td>4.1</td>
<td>1.16</td>
<td>0.22</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Average yields (7 - 13) 0.05 3.4 1.09 0.19 0.05

*Y indicates that the acid was very faintly yellow (or definitely yellow).
+W signifies that the acid was pure white.

The average yields for all the acids are summarised in Table IX.
The Effect of Purity on the Yield of \( \alpha \)-Naphthol.

It will be seen from Table II (experiments 1 - 6a) that difficulty was met with in attempting to obtain consistent results. It was suspected after experiment 4 that if the acid were yellow in colour, abnormally high yields of naphthol might be expected (see p. 71, where a qualitative yield of 20% was obtained). A comparison of experiments 4 to 6 with experiments 7 to 13 (see also Table III) shows that there is no doubt whatever that a powerful catalyst is present when the acid is tinged yellow. The yield, moreover, was independent of the melting-points of the acid (provided it was pure white). The melting-points were as follows: - in exp. 11, 98° - 98.5°; in 7 and 8, 99° - 99.5°; in 12 and 13, 99.6° - 99°, and so on. Fittig and Erdmann (Annalen, 1885, 227, 242) have shown in a qualitative manner that if the impure acid is distilled (when not carefully dried and in large quantities at a time) that the naphthol is formed in higher yield than when the acid is impure (and distilled in the dry state and in smaller quantity).

The Effect of Superheating.

The figures under the heading "Time" indicate the time taken for the temperature to rise from 180° - 240°. The result of experiment 4 compared with 5, and that of 6a compared with the later values
show that the discrepancies were due to super-heating. The temperature was raised in the experiments which follow, during a period of not less than 5 minutes.

The Effect of Water.

In view of the observations of Fittig and Erdmann (loc. cit.), experiments were undertaken to determine whether water present in traces or in quantity had a catalytic effect on the closing of the ring. Fittig (Annalen, 1889, 255, 142) confirmed the work of Jayne that phenylparaconic acid has the formula $C_{11}H_{16}O_4\cdot\frac{3}{4}H_2O$. This unusual formula is shown, moreover, in the case of the six stereoisomers of phenylparaconic acid (Fittig and Jayne, Annalen, 330, 352).

Two samples of acid which had been purified with particular care were dried in a sealed vessel for one month over phosphorus pentoxide. The inside of the reaction-tube was dried by a blast of hot air, a boat containing the pentoxide introduced and the tube allowed to cool with calcium chloride tube attached. (exp. 7, 8).

To one of those dried acids was added 0.13 c.c. water (exp. 9). To a sample of acid dried in vacuo over sulphuric acid was added 0.15 c.c. water (exp. 10).

It may be concluded, therefore, that water present in traces or in quantities amounting to 3% of the acid, has no catalytic effect on the closing of
the ring, within the limits of experimental error.

Experiments 1 - 11 were carried out in air; 12 and 13 in an atmosphere of nitrogen as were all subsequent estimations.

The results of heating the substituted phenylparaconic acids are summarised in the following tables.

**TABLE III.**

The Heating of m-Methoxyphenylparaconic Acid.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Time (mins.)</th>
<th>Colour</th>
<th>Naphthol (g.)</th>
<th>Acid Residue (g.)</th>
<th>HO-Acid (g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>W</td>
<td>0.23</td>
<td>0.33</td>
<td>0.93</td>
</tr>
<tr>
<td>2</td>
<td>13</td>
<td>W</td>
<td>0.21</td>
<td>0.98</td>
<td>0.38</td>
</tr>
<tr>
<td>3</td>
<td>11</td>
<td>Y</td>
<td>0.34</td>
<td>0.74</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Mean yields (1-2) 0.22 15.1 0.93 0.36 0.04

**TABLE IV.**

The Heating of o-Bromophenylparaconic Acid.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Time (mins.)</th>
<th>Colour</th>
<th>Naphthol (g.)</th>
<th>Acid Residue (g.)</th>
<th>HO-Acid (g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>W</td>
<td>0.60</td>
<td>0.45</td>
<td>0.50</td>
</tr>
<tr>
<td>2</td>
<td>13</td>
<td>W</td>
<td>0.63</td>
<td>0.40</td>
<td>0.54</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>W</td>
<td>0.61</td>
<td>0.43</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Average yields 0.61 39.2 0.43 0.52 0.02
TABLE V.

The Heating of m-Bromophenylparaconic Acid.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Time (mins.)</th>
<th>Colour</th>
<th>Naphthol (g.)</th>
<th>Acid (%)</th>
<th>Residue (g.)</th>
<th>HO-Acid (g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13</td>
<td>W</td>
<td>0.32</td>
<td>20.6</td>
<td>0.73</td>
<td>0.36</td>
</tr>
<tr>
<td>2</td>
<td>13</td>
<td>W</td>
<td>0.41</td>
<td>26.3</td>
<td>0.78</td>
<td>0.45</td>
</tr>
<tr>
<td>3</td>
<td>13</td>
<td>W</td>
<td>0.38</td>
<td>24.5</td>
<td>0.84</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Average Yields 0.37 23.8 0.78 0.41 0.04

Note: The evolution of carbon dioxide at 180°-185° was rather slow so that the temperature was raised to 185° - 190°.

TABLE VI.

The Heating of p-Bromophenylparaconic Acid.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Time (mins.)</th>
<th>Colour</th>
<th>Naphthol (g.)</th>
<th>Acid (%)</th>
<th>Residue (g.)</th>
<th>HO-Acid (g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>W</td>
<td>0.04</td>
<td>2.6</td>
<td>1.39</td>
<td>0.18</td>
</tr>
<tr>
<td>2</td>
<td>16</td>
<td>W</td>
<td>0.06</td>
<td>3.5</td>
<td>1.32</td>
<td>0.20</td>
</tr>
<tr>
<td>3</td>
<td>14</td>
<td>W</td>
<td>0.04</td>
<td>2.4</td>
<td>1.39</td>
<td>0.23</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>W</td>
<td>0.04</td>
<td>2.4</td>
<td>1.33</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Average Yields 0.05 2.7 1.36 0.21 0.03
TABLE VII.
The Heating of $\alpha$-Naphthylparaconic Acid.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Time</th>
<th>Colour</th>
<th>Naphthol Acid Residue (g.)</th>
<th>HO-Acid (g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16</td>
<td>W</td>
<td>0.06</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.18</td>
<td>0.40</td>
</tr>
<tr>
<td>2</td>
<td>16</td>
<td>W</td>
<td>0.06</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.14</td>
<td>0.42</td>
</tr>
<tr>
<td>Mean Yields</td>
<td></td>
<td></td>
<td>0.06</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.16</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.05</td>
<td></td>
</tr>
</tbody>
</table>

TABLE VIII.
The Heating of $\beta$-Naphthylparaconic Acid.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Time</th>
<th>Colour</th>
<th>Naphthol Acid Residue (g.)</th>
<th>HO-Acid (g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14</td>
<td>W</td>
<td>0.01</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.15</td>
<td>0.33</td>
</tr>
<tr>
<td>2</td>
<td>14</td>
<td>W</td>
<td>0.01</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.13</td>
<td>0.47</td>
</tr>
<tr>
<td>Mean Yields</td>
<td></td>
<td></td>
<td>0.01</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.17</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.02</td>
<td></td>
</tr>
</tbody>
</table>

Note: $\beta$-Naphthylisocrotonic acid is sparingly soluble in ether so that the usual method of extraction had to be altered. The reaction product was removed from the tube with boiling ether and the suspension filtered through a tared Gooch crucible. The filtrate was treated with sodium carbonate and sodium hydroxide solution in the usual manner except that the precipitated isocrotonic acid was filtered off through the crucible (instead of extracting with ether).
TABLE IX.
Average Yields.

<table>
<thead>
<tr>
<th>Name of Acid</th>
<th>Naphthol (g.)</th>
<th>Acid (%</th>
<th>Residue (g.)</th>
<th>HO-Acid (g.)</th>
<th>Total Solid (g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsubstituted</td>
<td>0.05</td>
<td>3.4</td>
<td>1.09</td>
<td>0.19</td>
<td>0.05</td>
</tr>
<tr>
<td>m-methoxy-</td>
<td>0.22</td>
<td>15.1</td>
<td>0.96</td>
<td>0.36</td>
<td>0.04</td>
</tr>
<tr>
<td>o-bromo-</td>
<td>0.61</td>
<td>39.2</td>
<td>0.43</td>
<td>0.52</td>
<td>0.02</td>
</tr>
<tr>
<td>m-bromo-</td>
<td>0.37</td>
<td>23.8</td>
<td>0.78</td>
<td>0.41</td>
<td>0.04</td>
</tr>
<tr>
<td>p-bromo-</td>
<td>0.05</td>
<td>2.7</td>
<td>1.36</td>
<td>0.21</td>
<td>0.03</td>
</tr>
<tr>
<td>α-naphthyl-</td>
<td>0.06</td>
<td>4.0</td>
<td>1.16</td>
<td>0.41</td>
<td>0.05</td>
</tr>
<tr>
<td>β-naphthyl-</td>
<td>0.01</td>
<td>0.6</td>
<td>1.17</td>
<td>0.40</td>
<td>0.02</td>
</tr>
</tbody>
</table>

TABLE X.
Absolute Yields.

<table>
<thead>
<tr>
<th>Name of Acid</th>
<th>$A_{\frac{N+13}{N}}$</th>
<th>Total weight of acid</th>
<th>Absolute yield of naphthol(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsubstituted</td>
<td>0.06</td>
<td>1.15</td>
<td>7.5</td>
</tr>
<tr>
<td>m-methoxy-</td>
<td>0.24</td>
<td>1.20</td>
<td>31</td>
</tr>
<tr>
<td>o-bromo-</td>
<td>0.66</td>
<td>1.09</td>
<td>85</td>
</tr>
<tr>
<td>m-bromo-</td>
<td>0.40</td>
<td>1.18</td>
<td>48</td>
</tr>
<tr>
<td>p-bromo-</td>
<td>0.05</td>
<td>1.41</td>
<td>5.6</td>
</tr>
<tr>
<td>α-naphthyl-</td>
<td>0.07</td>
<td>1.23</td>
<td>7.9</td>
</tr>
<tr>
<td>β-naphthyl-</td>
<td>0.01</td>
<td>1.18</td>
<td>1.1</td>
</tr>
</tbody>
</table>
The Corrected Yields of the $\alpha$-Naphthols.

The yields of the naphthols in Table IX (as in Tables I to VIII) are expressed in per cent of those expected by theory. Now, it has been stated in the experimental section that when phenylparaconic acid is heated, phenylisocrotonic acid and $\gamma$-phenyl-$\gamma$-butyrolactone are produced. It has been shown, moreover, that phenylpropylene is formed during the distillation of the acid. Two substances are therefore produced which do not play any role in the formation of the naphthol. It will now be shown that the naphthol yields given in Table IX do not represent a true percentage of the formation of the naphthols. It will be recalled that in reality it is not the phenylparaconic but the phenylisocrotonic acids which produce the naphthols. The results in Table IX would still stand for the purposes of comparison, provided and provided only - that the amounts of phenylpropylene and butyrolactone were the same in each case.

Neglecting the phenylpropylene for the moment, the results show that the amount of lactone ("residue") is not even approximately the same in each case. It is therefore necessary to calculate the amount of isocrotonic acid in each case and derive thereafter the yield of naphthol from those values.

In order to make certain that no water was left in the various materials isolated during treatment of the reaction product, the ethereal solutions of those
substances were dried in vacuo for 24 hours. Now the vapour pressure of phenylpropylene (b.p. 160°) cannot be far removed from that of xylene (b.p. 140°) (from the Ramsay-Young rule), which evaporates rapidly in vacuo, so that it is to be expected that the phenylpropylene would volatilise completely during the drying process. The difference in weight between the total amount of solid material and acid that of the paraconic/(2 g.) would give the amount of phenylpropylene formed during the reaction (For the weight of total solid material, see Table IX). By a somewhat involved and approximate calculation from those data the actual weight of isocrotonic acid which has been available for the formation of naphthol can be arrived at. The weight of phenylisocrotonic acid, however, can be rapidly and accurately calculated in a different manner:— It is equal to the observed weight of acid plus that which alone gave rise to the α-naphthol.

As is obvious, all side-reactions are eliminated in this calculation. If \( N \) represents the molecular weight of the \( \alpha \)-naphthols, 18 being the molecular weight of water, then during the formation of \( N \) g. naphthol, 18 g. water will be produced. Now, if \( A \) g. naphthol are formed in the reaction, the amount of water produced will be \( \frac{18 \times A}{N} \). The weight of naphthol plus water is equal to \( A + \frac{18 \times A}{N} \) or \( A\left(\frac{N + 18}{N}\right) \).
which is equal to the weight of acid concerned in the formation of the naphthol. This weight of acid added to the observed weight gives the total weight of acid.

N.B. This is not to be confused with isocrotonic acid which is formed at the start of the experiment, some of which is decomposed to phenylpropylene.

The corrected or absolute yields (Table X) were obtained by multiplying the values given in Table IX by the ratio

$$\frac{2 \times \text{M.W. of the paraconic acid}}{\text{calculated weight of acid \times M.W. of the isocrotonic acid}}$$

The Minimum Temperature of Naphthol Formation.

Molisch's test was used for detecting the first traces of $\alpha$-naphthol produced by heating samples (1g.) of the acid for 75 minutes at progressively lower temperatures. The naphthol was extracted and precipitated in the usual manner with carbon dioxide. It was extracted with chloroform and the solution evaporated to one drop and $\alpha$-naphthol tested for as described on p. 21. It was discovered that this test could be used to detect 0.1 mg., but no less, $\alpha$-naphthol and that this quantity of naphthol was formed during the experiment carried out at $200^\circ$-$210^\circ$ which therefore represents the minimum temperature at which $\alpha$-naphthol is formed by heating phenylparaconic acid (1 g.) for 75 minutes.
DISCUSSION OF RESULTS.

In reviewing the results obtained it may be concluded that the effect on ring-closure of a substituent in the nucleus of the phenylisocrotonic acid is marked. The most unlooked-for fact which has arisen is that the bromine atom has a much stronger effect than the methoxyl group. This is unexpected, since the influence that the methoxyl attached to a benzene nucleus has on further substitution is very much stronger (in the position at which ring-closure takes place) than has the bromine atom.

The first question to be discussed is the mechanism underlying the closing of the ring. This may be regarded as due (a) to the tendency of the reacting carbon atom in the nucleus to attract the carbon atom of the carboxyl group in the side chain, or (b) to the tendency of the hydrogen atom in the nucleus to attract the hydroxyl of the carboxyl group, followed by the loss of a molecule of water in both cases.

The simplest parallel to consider in this connection is the coupling of the compound, phenyl-diazoniumchloride with phenol. According to the latest theories of Robinson (Chem. and Ind., 1925, 44, 456) the mechanism of this reaction takes place in accordance with the following scheme. The oxygen
atom in phenol is a source of electrons, one of which is displaced towards the \( \alpha \)-carbon atom, which gives rise to a concomitant displacement of the electrons in the nucleus. This results in the \( \beta \)- and \( \delta \)-carbon atoms becoming negatively charged at the moment of reaction, as depicted in the diagram.

![Diagram](image.png)

The negatively charged position attracts the positive ion \([C_6H_5N:N]^+\) of the benzene diazonium chloride, and the hydrogen atom in this position is eliminated in the combination with negative chlorine ion as hydrochloric acid. It will be seen in phenylisocrotonic acid for the same reasons, that the carbon atom para to the methoxyl group will be negatively charged at the moment of reaction and will unite with the carbon atom of the carboxyl group which is the positive end of a dipole.*

![Diagram](image.png)

*All the information at our disposal points to the fact that the influence of this dipole on the reacting position in the nucleus of phenylisocrotonic acid will not be very large.
It is interesting to note that the same reactivity of the position of ring-closure would be expected from the polarity theory of Lapworth (Mem. Manchester Phil. Soc., 1920, 64, (2) 1; J., 1922, 121, 416). This theory postulates reactive positions in the molecule which are induced by the presence of a "key atom" denoted by a dot to its polar sign. The positions in the nucleus are regarded as being alternatively polarised, as is indicated in the following diagram where it will be noted that the carbon atom in para position to the methoxyl group is induced negatively, and that the carboxyl group in the side-chain induced positively by the negative $O^-$, thus,

According to either theory a reactive hydrogen atom is expelled from the para-position to unite with the negative hydroxyl group and be eliminated as water.

The induced reactivity of the terminal carbon atom of the side-chain by the methoxyl group in the nucleus would be negligible, as shown by the researches of Shoesmith and Connor (J. 1927, 1768) on the $\beta$-tolylethyl bromides.
Thus, reasons can be advanced why \( m \)-methoxy-phenylisocrotonic acid gives a comparatively high yield of methoxynaphthol.

The reactivity of the position of ring-closure not, in the above compound may, however, be due wholly to the same causes as those which are responsible for the preponderating amount of the para-isomeride obtained in simple substitution, since the order of ease with which the ring is closed in the bromo-isocrotonic acids is \( o \succ m \succ p \). Ring-closure takes place in the position ortho to the side-chain and therefore in the ortho-, meta- and para-bromo acid in position meta \( (m_1 \) in diagram), para \( (p) \) and meta \( (m_2) \) to the bromine atom, as illustrated in the diagram.

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{m}_1 & \quad \text{p} \\
\text{Br} & \quad \text{m}_2
\end{align*}
\]

The second and third of this series are seen to be readily explicable if the only influence was an alternating one, since the para-position to the bromine atom is more reactive than the meta. From the first and second cases, however, the meta-position \( (m_1) \) appears to be more reactive than the para \( (p) \). Hence the differences cannot be due solely to an alternating
influence.

If the enhanced reactivity of these positions does not arise in virtue of alternating effects, we have to consider whether the differences are due to a general influence. By general influence is meant the reactivity of the substituted acids as a whole compared with that of the unsubstituted. The general influence of a bromine atom is well portrayed in the hydrolysis of the bromobenzylbromides (Shoemith and Slater, J., 1926, 214) from which it is obvious that the effect of the presence of a bromine atom in the nucleus is to damp down the reactivity of the molecule as a whole. This is in direct opposition to the present results, since the yield of bromonaphthols from the meta and para acids was greater than \( \alpha \)-naphthol from the unsubstituted acid. Hence the general influence cannot be regarded as the cause of the differences in the yields of the bromonaphthols. In addition to the two influences already considered, namely alternating and general, there remains the third of those postulated as responsible for the reactivity of any atom in an organic molecule (Lapworth and Shoemith, J., 1922, 121, 139), namely, steric influence.

**The Steric Influence.**

The effect of steric influence will now be considered in all its aspects.
From data dealing with the hydrolysis of ortho-substituted esters; substitution in the ortho-position in the benzene residue; ionisation of ortho-substituted benzoic acids and so on, it has been supposed that an atom or group in the ortho-position to a substituent has a protective or repellent effect on the latter against attacking molecules. In m-bromophenylisocrotonic acid, during ring-closure, since the carbon atom of the carboxyl group attempts to unite with the nucleus in the ortho-position to the bromine atom, the carboxyl group must be regarded as the attacking molecule or substituent. It is to be expected, therefore, that there will be a tendency for the carboxyl group to be repelled away from the bromine atom towards the para position. During the reaction the side-chain is free to vibrate in all directions in the case of the unsubstituted acid. These vibrations will result in the carboxyl group coming into contact with the nucleus in the ortho-position to the side-chain. A bromine atom present in the meta-position will restrict the range of vibration of the side-chain to some extent by its repulsion of the carboxyl group, which strives to enter the nucleus between the bromine atom and the side-chain. Since the range of vibration of the carboxyl group has been diminished, the group will now attack
the position of ring-closure a greater number of times in a given period than before. Hence the yield of bromonaphthol will be enhanced with respect to the unsubstituted. The effect is represented pictorially in the following diagrams in which the lengths of the arrows represent the range over which the carboxyl group vibrates.

The same argument may be applied to explain the high yield from the m-methoxy acid as compared with the unsubstituted. It is important to note that the steric effect in the meta-substituted acids is exactly analogous to the effect met with in the hydrolysis of ortho-substituted esters.

A most convincing proof of this theory is to be found in the fact that the ring has not been observed to close in the position between the side-chain and the substituent in either the methoxy- or bromo-compounds, nor has it been observed in the case of the chloro-isomeride (Ber., 1888, 21, 3444; R.733: Annalen, 1888, 247, 372; 1893, 275, 255).
In the case of p-bromophenylisocrotonic acid, the bromine atom is so far removed from the side-chain that the conditions are not very much different from those existing in the unsubstituted acid. The yield of 7-bromo-l-naphthol is 5.6%; unsubstituted α-naphthol, 7.5%.

It is considered that there are two steric effects which govern the vibration of the side-chain in o-bromophenylisocrotonic acid, as the following argument will make clear. It was shown that the repellent effect of a bromine atom in the m-position was sufficiently powerful to exclude entirely the entrance of the carboxyl group into the position ortho to the bromine atom. It is only reasonable to expect, therefore, that this atom placed in the ortho-position to the side chain will drive the carboxyl group considerably nearer the position of ring-closure than before. This, regarded from a dynamic point of view, means that the range of vibration of the carboxyl group would be diminished, with a consequent increase in the number of attacks made on the position of ring-closure in a given time. This effect would perhaps be sufficient to explain the high yield of 5-bromo-l-naphthol (85%) as compared with 6-bromo-l-naphthol (48%).

There is yet another steric effect, however. The bromine atom would repel that part of the side-chain
which is immediately contiguous to the nucleus. In other words, the bromine atom strives to displace the side-chain in its attempt to extend its fields of force as it would towards any substituent such as an ester group. The displacement of the side-chain would reinforce the other steric effect with a resultant rise in the yield of naphthol, as depicted by the illustration (compare previous diagrams):

![Diagram](image)

The theory of steric influence appears to explain very successfully the varied yields of the naphthols obtained by ring-closure in o-, m- and p-bromo, m-methoxy- and unsubstituted phenylisocrotonic acids.

It may be pointed out in conclusion that the above considerations on the steric influences do not rule out the possibility that alternating influences may be present which would be overruled in the case of the o-bromo acid and enhanced in the case of the meta by the steric influence of the bromine atom.

The most striking result which has arisen from a study of the naphthylisocrotonic acids is the very low yields of phenanthrol obtained. These are almost
comparable with the yield of $\alpha$-naphthol obtained from phenylisocrotonic acid.

The theories which have been advanced to explain the reactivity of the $\alpha$ positions in naphthalene are limited. Of these may be mentioned the hypothesis of Thiele, Bamberger and Willstätter.

It has been shown by Shoesmith and Rubli (J., 1927, 3098) that an iodine atom in the $\beta$-position in naphthalene is very much more rapidly removed than when in the $\alpha$-position, by the action of hydriodic acid at 100°. Several other reactions are known which indicate that the $\beta$-position is more reactive than the $\alpha$ at elevated temperatures.

No theory has so far been advanced to explain satisfactorily the greater reactivity during substitution of the $\beta$-position at high temperatures, at which the present researches were carried out.

Both $\alpha$- and $\beta$-naphthylisocrotonic acids should give hydroxynaphthalene compounds by attack of the reactive $\beta$-positions, but the $\beta$-acid gives no such compound (no 1-anthranol) and the $\alpha$-isomeride gives a low yield of phenanthrol only. Thus the theory of reactivity of the $\beta$-carbon atoms as the cause of ring-closure does not adequately explain the observed facts.

Applying the theory of steric influence, the unsubstituted benzene nucleus may be regarded as a
substituent in the ortho-position to the side-chain in \( \alpha \)-naphthylisocrotonic acid, with this restriction, that the \( \alpha' \)-carbon atom (which is fixed in this nucleus) cannot be so free to vibrate as it would if it were present as a free group (say CH\(_3\)) and hence the tendency of its fields of force to displace that part of the side-chain contiguous to the nucleus would be less than an ortho-substituted phenyl-paraconic acid with a consequent decrease in the yield of phenanthrol. The steric hypothesis explains why the \( \alpha \)-acid gives a higher yield of phenanthrol than the \( \beta \)-but the theory fails to explain why the yield of 1-phenanthrol is only negligibly higher than the yield of \( \alpha \)-naphthol (7.5\%). Moreover, the theory is inadmissible from the point of view that it does not explain the direction in which the ring closes. It may be noted in this connection that a case is known where the ring closes in the \( \beta \)-carbon atom—namely, when 2-tetralyl-\( \gamma \)-n-butyric acid is heated with sulphuric acid
After a review of the data obtained from the \( \alpha \)-and \( \beta \)-naphthylisocrotonic acids one is struck by the remarkable and rather unexpected similarity between the ease of ring-closure in the \( \alpha \)-acid and phenylisocrotonic acid. In the benzene series the ring in the three substituted meta-acids always closes in the direction of least resistance and yet we find that in the \( \beta \)-naphthyl acid, the side-chain definitely refuses to become attached to the \( \beta_2 \)-position and migrates towards the \( \alpha \)-position which is not only less reactive but would seem to be shielded in some measure by the other benzene nucleus. The problem of reactivity and the effect of substituents in the naphthalene molecule has always been an exceedingly intricate one and the difficulties met with in attempting to explain its properties is further borne out by the results of this research. In conclusion, no theory is sufficiently comprehensive to explain ring-closure adequately in the naphthalene series.
SUMMARY.

Substituted paraconic acids in the benzene and naphthalene series were prepared in a pure-white state. These were converted to the α-naphthols by heating under standard conditions and the yields of the naphthols compared with a view to determining the effects of substituents on the ring-closure.

Whilst the theory of steric influence satisfactorily predicts the effect of substituents on the ease of ring-closure in the benzene series, no postulate per se is sufficient to explain in entirety the observed facts arising from ring-closure of the compounds in the benzene and naphthalene series studied in these researches.
The tap is well oiled and worked until it turns freely, slackening the screw if necessary. A thread is tapped on one end of the tubing and the gas tap screwed on to make a gas-tight joint. Two holes are drilled in the gas tap (about 1.7 cm. apart, to coincide with the holes in the alarm winder) and in the winder, if not already punched out. The tap and winder are now bolted together, face to face, and in such a way as to make their axial plane perpendicular to the plane of the winder and tap, otherwise the clock will be displaced when the alarm rings. The alarm is wound up not more than one or two turns more than are required just to turn off the gas tap. The tubing is clamped firmly in a horizontal position, and after attaching rubber tubing to either end, the apparatus is ready for use.

The alarm is set at the time required and the gas tap turned until it is on the "on" position. When the time expires the alarm winder will rotate until it is held by the tap in the "off" position, when the gas will be automatically cut out. Provided that the brass tubing be fixed rigidly, the clock will not require any further fixture to keep it in place.

The above apparatus has been in use now for about six months and has given complete satisfaction. It has also been used for switching off an electric current, and can obviously be applied in other directions.

AN AUTOMATIC TIME SWITCH FOR PROLONGED HEATING ETC.

BY ALEX. GUTHRIE, B.SC., A.I.C.

For an apparatus which has to be left heating for not more than 12 hrs., the following device will be found useful. It is claimed to combine efficiency with extreme simplicity and economy.

All that is required is a cheap alarm clock, preferably with two holes already punched out of the alarm winder, an ordinary household gas tap, and a piece of brass tubing, say 25 by 1.3 cm.
CCCVII.—The Synthesis of 1-Phenanthrol.

By JOHN BALDWIN SHOESMITH and ALEXANDER GUTHRIE.

1-Phenanthrol (II) is the only one of the five theoretically possible monohydroxy-derivatives of phenanthrene not described in the literature. It has been obtained by heating α-naphthylparaconic acid (I), loss of carbon dioxide and ring closure with elimination of water taking place as follows:

\[
\begin{align*}
\text{(I.)} & \quad \text{(II.)} \\
\text{CH:COOH} & \quad \text{OH} \\
\text{CH} & \quad \text{CH}_2 \\
\text{O:CO} & \quad + \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]

α-Naphthaldehyde was prepared (a) in a yield of 33% by the catalytic reduction of α-naphthoyl chloride, m. p. 22°, b. p. 158°/12 mm., by Rosenmund’s method (Ber., 1918, 51, 591)—it is noteworthy that in absence of solvent during this reduction the side chain was completely removed and naphthalene produced in quantity—and (b) in a yield of 25% by the action of ethyl orthoformate in ethereal solution on magnesium naphthyl bromide in the usual manner. The second is the more convenient method although the yield is somewhat smaller. By both methods the aldehyde was obtained as an oil, b. p. 173—174°/35 mm.; p-nitrophenylhydrazone, scarlet needles from acetic acid, m. p. 233—235°.

α-Naphthylparaconic Acid.—α-Naphthaldehyde (7.5 g.), succinic anhydride (5 g.), and anhydrous sodium acetate (6 g.) were heated together under reflux for 6 hours at 122° (a higher temperature causes formation of tarry by-products which render the subsequent purification of the acid difficult); excess of α-naphthaldehyde was
removed from the reaction product in a current of steam, and the residue filtered hot, cooled, extracted with ether, and acidified. The precipitated \( \alpha \)-naphthylparaconic acid (2 g.) was recrystallised from aqueous alcohol (water 2 parts, alcohol 1 part) from which it separated in well-defined, white, rectangular prisms, m. p. 169\(^\circ\) (evolution of carbon dioxide) (Found: C, 70.2; H, 4.7. \( \text{C}_{15}\text{H}_{12}\text{O}_4 \) requires C, 70.3; H, 4.7\%).

1-Phenanthrol: \( \alpha \)-Naphthylparaconic acid was heated in a distillation flask immersed in a metal-bath at 180—200\(^\circ\) until evolution of carbon dioxide had ceased (30 minutes). The temperature of the bath was then rapidly raised to about 340\(^\circ\) and distillation of the vapour prevented by impinging a blast of cold air on the neck of the flask. After 15—20 minutes the temperature was raised again and distillation allowed to proceed. The red oil which distilled over solidified and was dissolved in ether; the ethereal solution was extracted with sodium carbonate to remove carboxylic acids and then with aqueous sodium hydroxide. The latter extract was saturated with carbon dioxide, the precipitate extracted with ether, and the ether evaporated; the 1-phenanthrol so obtained was crystallised from light petroleum, separating as colourless, prismatic needles, m. p. 156\(^\circ\) (Found: C, 85.9; H, 5.2. \( \text{C}_{14}\text{H}_{10}\text{O} \) requires C, 86.6; H, 5.2\%); yield, 5\%.

In another experiment crude \( \alpha \)-naphthylparaconic acid was used, and the yield of 1-phenanthrol increased to about 15\%; this observation is similar to that of Fittig and Erdmann (Annalen, 1885, 227, 242), who found that crude phenylparaconic acid gives a better yield of \( \alpha \)-naphthol than does the pure acid.

1-Phenanthrol is stable in air and in solution (contrast the 9-isomeride, which is very unstable, Japp and Findlay, J., 1897, 71, 1115). It resembles \( \alpha \)-naphthol in giving a deep blue coloration on warming with chloroform in alkaline solution, but differs in giving no coloration with glucose solution and concentrated sulphuric acid (compare Molisch's test for carbohydrates). It dissolves in concentrated sulphuric acid with a yellow colour, the solution slowly becoming red and finally colourless when heated. Its alkaline solution gives dyes with diazotised aniline, etc. The picrate crystallises in orange-red, feathery needles, m. p. 182\(^\circ\), from methyl alcohol.

In order to characterise the compound further it was methylated as follows. To 1-phenanthrol (0.8 g.) dissolved in 8 c.c. of methyl alcohol, 4 c.c. of 10\% methyl-alcoholic potassium hydroxide and 8 c.c. of a 13\% solution of methyl sulphate in methyl alcohol were added, and the solution was heated on the steam-bath for 1 hour, after which it was diluted with water, extracted with ether, th
ethereal solution extracted with alkali to remove unchanged phenanthrol, and the 1-methoxyphenanthrene left on evaporation was recrystallised from methyl alcohol; yield, 50%. The colourless prismatic needles had m. p. 105°, and were found to be identical in all respects with a sample of 1-methoxyphenanthrene prepared by the method described by Pschorr, Wolfes, and Buckow (Ber., 1900, 33, 170).

The authors wish to acknowledge the grant of a Carnegie Teaching Fellowship to one of them (J. B. S.) during the tenure of which the investigation was carried out.

EDINBURGH UNIVERSITY.  

[Received, June 28th, 1928.]