TO

MY PARENTS
SYNTHETIC STUDIES OF AROMATIC COMPOUNDS
CONTAINING SEVEN-MEMBERED RINGS

BY

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Within recent years much interest has centred on the subject of the fine structure and properties of the non-benzenoid aromatic compounds, particularly of those based on the seven-membered carbocyclic system, namely, azulene and tropone. Since there are already a number of reviews dealing with the chemistry of azulene, of tropone and its derivatives, and of non-benzenoid aromatic compounds generally (references to which appear in the bibliography), only a short account will be given here of the salient features of the study.

An aromatic compound may be defined as a cyclic compound, with a large resonance energy, in which all the ring atoms take part in a single conjugated system. Although benzene, which is the typical aromatic compound, may be formulated as a resonance hybrid of a number of canonical forms which include the classical Kekule cyclo-hexatriene formulae, it does not normally react to give addition products as do olefinic unsaturated compounds. Benzene undergoes mainly substitution reaction giving products which are still aromatic. The majority of such reactions proceed by expulsion of a proton from the ring by an electrophilic (or cationoid) reagent such as Br⁺, NO₂⁺ etc., but similar reactions are known where the
reagent is nucleophilic (anionoid) or a radical. Nucleophilic substitution of a hydrogen atom does not occur in benzene itself but the hydrolysis of chlorobenzene by alkali at high temperatures, in which the more electronegative chlorine atom is replaced by hydroxyl, is analogous. Even hydrogen may be replaced by a nucleophilic mechanism by inclusion in the benzene nucleus of a suitable group such as nitro- which causes activation towards nucleophilic reagents; thus, nitrobenzene reacts with potassium diphenylimide to give p-nitrotriphenylamine (Bergstrom, Granara and Erickson, J. Org. Chem., 1942, 7, 98).

It was pointed out by Bamberger, later put into electronic terms by Kaufmann and its importance stressed by Robinson that aromatic character in five- and six-membered rings appeared to depend on the presence of six dormant valencies, the "aromatic sextet" of Robinson. In 1937 Hückel presented a qualitative interpretation of some quantum mechanical calculations for a number of unsaturated and aromatic molecules using the molecular orbital (LCAO) method (Z. Elektrochem., 1937, 43, 752). These showed that for a planar cyclic molecule to be aromatic each ring atom must have a p-orbital available for \( \pi \)-bond formation, the p-orbitals so orientated that they can all overlap to form large \( \pi \)-orbitals, and there must be available \( (4n + 2) \) such p-orbitals, where \( n = 0, 1, 2, 3 \) etc. For benzene, \( n \) equals one. Six electrons are
available for $\pi$-bond formation and are accommodated by three symmetrical low energy orbitals which form rings of electron density above and below the carbon ring. The same is true for pyridine, of which the hetero-atom likewise contributes one $\pi$-electron. In pyrrol there are only five ring-atoms but the nitrogen atom can contribute both its free electrons so that again all three $\pi$-orbitals are filled. The $-\text{NH}$ group acquires thereby a partial positive charge and so acidity, while the methine groups acquire partial negative charges and therefore enhanced activity towards electrophilic reagents.

The immediate lower and higher analogues of benzene

\[
\begin{array}{c}
\text{I} \\
\text{II}
\end{array}
\]

are cyclobutadiene (I) and cyclooctatetraene (II) respectively and the possibility of these molecules possessing aromatic properties was long a subject for speculation. Although cyclobutadiene is still unknown, an attempt to prepare it by alkali treatment of the stable 1-bromocyclobutene yielding acetylene (Willstätter and von Schmaedel, Ber., 1905, 38, 1992) cyclooctatetraene, first prepared by Willstätter from a natural product, can now be obtained in quantity by the polymerisation of acetylene.
(see Craig, Chem. Rev., 1951, 49, 103). Cyclooctatetraene has a resonance energy of about 12 Cals./mol., c.f. 41 for benzene (Prosen, Johnson and Rossini, J. Amer. Chem. Soc., 1947, 69, 2068). While a number of its reactions lead to the formation of derivatives of ethylbenzene and xylene it is itself otherwise not noticeably aromatic. In its reaction with halogens, for example, it resembles any typical olefine. Furthermore, the ring is known to be non-planar. Planarity would require that the annular valency angles be 135°, c.f. 120° for benzene. The strain which would be produced is evidently greater than the resonance energy which would be gained by assuming a planar structure. Similar considerations of angular strain apply to cyclobutadiene.

Hückel pointed out that the bond angles of planar five- and seven-membered rings are sufficiently close to 120° to allow molecules containing them to be stabilised to almost the same extent as the corresponding six-membered compound. Thus the lower and higher members, the C₅H₅ anion (III) and the C₇H₇ cation (V), should form with benzene, C₆H₆ (IV), a triad possessing aromatic resonance energy and stability. Cyclopentadiene by losing a proton can give

III
IV
V
the cyclopentadienyl anion which has six π-electrons and the requisite symmetry for aromaticity. The anion, therefore, is greatly stabilised with respect to cyclopentadiene, i.e., the acidity of cyclopentadiene is greatly increased. The reaction of cyclopentadiene with alkali metals to form stable salts has been long known and the structural relationship to benzene well recognised. The remarkable stability and aromatic character of dicyclopentadienyliron "ferrocene" which vaporises without decomposition and readily undergoes electrophilic substitution, demonstrates the similarity in behaviour of the C\textsubscript{5}H\textsubscript{5} ring to that of the benzene ring (see, Pauson, Quart. Rev., 1955, 9, 391). Ferrocene has been shown by X-ray analysis to have the highly symmetrical structure VI (Eiland and Pepinsky, J. Amer. Chem. Soc., 1952, 74, 4971). Further evidence of

![VI](image)

![VIIa](image)

![VIIb](image)

the electron attracting nature of the five-membered ring is provided by the observed dipole moment of 1.44 D for the hydrocarbon dimethylfulvene in which contributing forms of the types VIIa and VIIb take part. Fulvene itself although unstable is the simplest hydrocarbon possessing colour (for a review see, Day, Chem. Rev., 1953, 53, 167).
It has been shown (Doering and Knox, J. Amer. Chem. Soc., 1954, 76, 3203) that the crystalline and ionising bromide \( C_7H_7Br \) obtained on distillation of dibromocycloheptatriene is cycloheptatrienylium bromide, i.e., the bromide of V. The degree of stabilisation of positive charge in this cation must be very large for the compound is soluble in water and reacts immediately with silver nitrate. Structures based on this cation were first postulated by Dewar (Nature, 1945, 155, 50) to account for the aromatic properties of the non-benzenoid compound

![Chemical structures](image)

VIII IXa IXb

stipitatic acid (VIII) which is a mould metabolite. The simplest compound of the type is tropone (IXa) which is a colourless liquid miscible with water and, having basic properties, forms a hydrochloride. Doering and Knox describe tropone otherwise as tropylium oxide (IXb) and in agreement with such a structure and representation tropone possesses a considerably higher dipole moment, 4.3 D, than is to be expected solely from carbonyl contributions to its magnitude (Di Giacomo and Smyth, J. Amer. Chem. Soc., 1952, 74, 4411). Due to polarisation of the carbonyl group tropone acquires some aromatic character and at the same time its carbonyl activity is largely

Although Roberts, Streitwieser and Regan (J. Amer. Chem. Soc., 1952, 74, 4579) concluded that the \((4n + 2)\) rule of Hückel is justified only by the simple molecular orbital treatment for monocyclic conjugated polyolefines (they pointed out, for example, that pyrene and fluoranthene are obvious exceptions), the bicyclic molecule azulene, each of the ten ring carbon atoms of which has a p-orbital suitably orientated for \(\pi\)-bond formation, otherwise satisfies the conditions for aromaticity. The resonance energy of azulene \((X)\) is less than that of the isomeric compound naphthalene, 46.8 compared with 71.2 Cals./mol. (Heilbronner and Wieland, Helv. Chem. Acta, 1947, 30, 953, c.f. Kovats, Günthard and Plattner, Helv. Chim. Acta, 1955, 38, 1912), the difference arising from distortion of the valency angles in azulene from 120°. Calculation by a molecular orbital method (Wheland, J. Amer. Chem. Soc., 1941, 63, 2025) also shows that azulene should be less stable than naphthalene.

\[ X_a \]

\[ X_b \]
Consideration of the most important canonical forms contributing to the azulene hybrid (Xa and Xb) shows that all bonds have approximately half double-bond character (as distinct from order), except the 9:10 bond, which has predominantly single-bond character. In benzene similarly all bonds have approximately half double-bond character due to equal contribution to the hybrid of the two more important Kekule forms. Consequently, the calculated bond lengths in azulene are all similar to those in benzene, except the 9:10 bond which is longer.

![Diagram](image)

Consideration of the Kekule structures alone, however, does not permit a satisfactory explanation of the light absorbing and basic properties of the hydrocarbon azulene. Approximate quantum mechanical calculations of polarisation energies and \( \pi \)-electron densities (Brown, Trans. Faraday Soc., 1948, 44, 984) both indicated that the 1- and 3-positions in the five-membered ring of azulene have a high electron density which is balanced by an attenuation of the \( \pi \)-electron densities in the seven-membered ring carbon atoms. The results of these calculations for \( \pi \)-electron densities and bond-orders are shown in XI and XII. Consequently, electrophilic substitution in azulene
should take place at carbon atoms (1) and (3), while nucleophilic substitution should occur in the 4-position. It is noticeable that there is a regular alternation of magnitude of $\pi$-electron density round the peripheral carbon atoms, i.e. excluding carbon atoms (9) and (10), and that the calculated bond orders are all close to the value 1.667 for benzene, except the 9:10 bond. This is in contrast to naphthalene for which the $\pi$-electron densities are all unity and in which the four $\alpha:\beta$ bonds are of predominantly higher order than the others in the molecule.

A consequence of the above charge separation is that azulene should possess a significant dipole moment. Calculated values are generally high, ranging up to 6D. Since experimental determination of the dipole moment by the optical solution method is hindered by the very great light absorbing power of azulene, Wheland and Mann (J. Chem. Phys., 1949, 17, 264) assumed the molecular refraction of azulene to be the same as that of naphthalene and obtained a value 1.0D which agreed with their particular calculated value. The validity of their assumption is questionable and an experimental determination of the dipole moment may yet vindicate the calculated higher values which would be expected from such a large charge separation.

It has been suggested by Anderson, Nelson and Tazuma (J. Amer. Chem. Soc., 1953, 75, 4980), and by Stafford and
Reid (Chem. and Ind., 1954, 277) that azulene in the ground state is best represented as a resonance hybrid of two types of canonical forms, (i) the classical covalent forms (Xa, Xb) and (ii) betaine structures (Xc) in which the cationic character is associated with the seven-

![Diagram](image)  

membered ring and the anionic character equally with the equivalent 1- and 3-positions in the five-membered ring. This formulation allows interpretation of the reactions of azulene and includes them within the class of anhydro-salts which often possess comparable colour, reactivity and basicity because of a highly dipolar character. One typical property of such a system is its ready polarisability. In appropriate circumstances an electron pair may be developed on either carbon (1) or carbon (3) and shared with an electrophilic group. The basicity of the azulenes manifests both this polarisibility and the stability of the polarised state once the electrons have been shared, i.e. it reflects the stability of the corresponding cyclopentadienylcycloheptatrienylium ion (XIII). The remarkable basic properties of azulene as well as of tropone can be explained by the resonance stabilisation of the cycloheptatrienylium ion. In
accordance with the formulation XIII salts of azulenes (R=H) possess a reactive methylene group which condenses with aldehydes to give unstable fulvene-like compounds (Stafford and Reid, ibid.).

The predictions of positions of substitution in azulene have been borne out by experiment. While earlier work emphasised the unsaturated character of azulene such that it appeared that azulene had no aromatic properties (see, Pommer, Angew. Chem., 1950, 62, 281) it has since been found using mild conditions and reagents that azulene is very susceptible to both electrophilic and nucleophilic substitution. Anderson, Nelson and Tazuma (ibid.) obtained 1-acetyl, 1-nitro and 1-halogenoazulenes by direct substitution and orientated them with respect to 1-methoxycarbonylazulene. Disubstitution occurs readily to give 1:3-disubstituted azulenes and diacetyl- and dihalogenoazulenes have been obtained. Anderson, Cowles, Tazuma and Nelson (J. Amer. Chem. Soc., 1955, 77, 6321) obtained 1-benzylazulene on Friedel-Crafts alkylation of azulene with benzylchloride. Quaiazulene has been sulphonated to give quaiazulyl-3-sulphonic acid (Treibs and Schroth, Annalen, 1954, 586, 202). Quaiazulene (XIV), moreover, reacts with acyl halides in the absence of Friedel-Crafts catalysts to give 3-acetyl- and 3-benzoylquaiazulene (XV), resembling in this respect the enol betaines which undergo acylation by elimination of a proton at the carbon atom which carries partial negative
charge (Galloway, Reid and Stafford, Chem. and Ind., 1954, 724).

\[
\begin{align*}
\text{XIV} & \quad R = \text{CH}_3^- \quad \text{and} \quad \text{C}_6\text{H}_5^- \\
\text{XV} & \quad \text{ } + \quad \text{HBr}
\end{align*}
\]

Experimental investigation of the nucleophilic substitution reactions of azulene indicates reaction at the 4-position, supporting the predictions. Azulene reacts with lithium alkyls and aryls to give 4-alkyl- and 4-aryldihydroazulenes (XVI) which on dehydrogenation afford the 4-substituted azulenes (XVII) (Hafner and Weldes, Angew, Chem., 1955, 302). The susceptibility of the 4-position to nucleophilic attack is shown also by the ease of ether exchange when 4-alkoxyazulenes carrying an activating ester group in the seven-membered ring are treated with potassium hydroxide in an alcoholic or aqueous solution (Stafford, Ward and Reid, Chem. and Ind., 1955, 1258, and see below).

Azulene is a violet-blue compound which has extensive absorption in the visible region of the spectrum as well as in the ultra-violet. In the ultra-violet region its
spectrum resembles that of naphthalene. Introduction into the azulene nucleus of alkyl substituents, i.e., -I or negative inductive groups which induce negative charges on adjacent atoms (see, Dewar, Electronic Theory of Organic Chemistry, p. 52), invariably produces a bathochromic displacement of the ultra-violet absorption spectrum. This effect is observed for substituted aromatic compounds generally. In the visible region, however, while substitution in the 1-, 3-, 5- and 7-positions causes bathochromic displacement of the spectra, substitution in the 2-, 4-, 6- and 8-positions causes hypsochromic displacement, and for each position of substitution the magnitude of the displacement is practically independent of the nature of the alkyl substituent. (The 1- and 3-, the 4- and 8-, and the 5- and 7-positions in the nucleus are pairs of equivalent positions). These two series of positions, as was pointed out above, are those of local high and low \( \pi \)-electron densities respectively in the peripheral carbon atoms. No steric interference with coplanarity which would prevent full resonance in the molecule may be claimed to explain the hypsochromic displacements in the visible spectra of the 2-, 4-, and 6-methylazulenes. Pullman, Mayot and Berthier (J. Chem. Phys., 1950, 18, 257) have given a molecular orbital treatment of the problem which relates the hypsochromic shift to the inductive effect of the alkyl group (c.f. Longuet-Higgins and Sowden, J., 1952,
Comparing corresponding bands in the visible absorption spectra of alkyl mono-substituted azulenes with those in the spectrum of azulene itself, the displacements (in $\mu\text{m}$) for each position of substitution are shown in XVIII.

\[ \text{XVIII} \]

Thus, for example, 1- and 5-methylazulenes, whose visible absorption spectra are moved to longer wave lengths, are pure blue compounds while 2-, 4- and 6-methylazulenes appear violet. For di- and polysubstituted azulenes the displacements are approximately additive and it is possible to estimate the positions of the absorption bands for such a compound and to predict its colour. Conversely, from the positions of the bands orientations can be assigned to substituents. It is noteworthy that the same alternation of effect with position of substitution is observed for ester groups, i.e. $+E$ substituents which can conjugate with the azulene nucleus and, having a high electron affinity, become themselves more negative leaving the adjacent part of the molecule more positive. The spectral displacements however are in the opposite directions to those caused by alkyl ($-I$) groups in the same positions. That is, 1-methoxycarbonyl- and 5-methoxycarbonyl azulene are violet.
DISCUSSION

THE REACTION OF PHENANTHRENE AND OF CYCLOPENTAD[def]-
PHENANTHRENE WITH DIAZOAETIC ESTER.

In view of the extent to which diazoacetic ester ring-
formation experiments figure throughout the following
work a description is given here of this application of
the reagent. Aliphatic diazo compounds such as
diazomethane and diazoacetic ester react with olefinic
compounds (I) under conditions in which thermal or
radiation energy is supplied with evolution of nitrogen
and formation of a cyclopropane derivative. Two mechanisms
are possible; formation of an intermediate pyrazoline (II)
which decomposes to give the cyclopropane derivative (III)
and nitrogen, or, elimination of nitrogen from the diazo
compound, followed by reaction of the radical formed (IV)
with the unsaturated molecule.

\[
RCH\cdot CHR' + N_2CHR'' \rightarrow R'N\equiv N\equiv NCH\cdot CHR'' + N_2 \quad \text{(II)}
\]

\[
R''CHN_2 \rightarrow R''CH\cdot + N_2 \quad \text{(III)}
\]

\[
RCH\cdot CHR' + R''CH\cdot \rightarrow RCH\cdot CHR' \quad \text{(IV)}
\]

The reaction of acetylene with diazomethane to give
pyrazol (V) (Pechman, Ber., 1898, 31, 2950) and of
butadiene with diazomethane to give vinylpyrazoline (VI)
(Müller and Roser, J. prakt. Chem., 1932, 133, 291), and
the fact that the pyrazoline ester VII on heating gives the cyclopropane ester VIII is evidence in support of the first mechanism for olefinic compounds (see Huisgen, Angew. Chem., 1955, 67, 448, 449 and c.f. p.461). Aliphatic diazo compounds react similarly with aromatic compounds, for example, benzene and its homologues, but under more forcing conditions, and this fact together with the variety of products obtained is indicative rather of the radical mode of reaction. The yield of adduct in such cases is generally not good, the aromatic starting material being recovered largely unchanged. With benzene and diazoacetic ester the primary product isolable is the ethyl ester of norcaradiene carboxylic acid (IX) which forms a tetrabromide

and which on permanganate oxidation gives trans-1:2:3-cyclopropanetricarboxylic acid (X) (Buchner and Braren, Ber., 1901, 34, 982). From this it was deduced that the configuration about the cyclopropane ring of IX is the trans configuration. At higher temperatures the norcaradiene
derivative from the reaction of benzene with diazoacetic ester undergoes rearrangement to give mainly the ethyl ester of a cycloheptatriene acid of the type XI (for recent work see Grundmann and Ottmann, Annalen, 1953, 582, 163). It is such rearrangement to a seven-membered ring which makes the use of aliphatic diazo compounds important for the synthesis of azulenes and of tropone derivatives. Buchner and his co-workers examined the mixtures from the reaction of alkylbenzenes with diazoacetic ester and established that reaction occurs preferentially at unsubstituted C:C bonds, and where norcaradiene derivatives are formed exclusively at such bonds.

No norcaradiene derivative containing a quaternary carbon atom has yet been isolated, and in the case of mesitylene (XII) which has no unsubstituted C:C bond the major product was a trimethylcycloheptatriene carboxylate (XIII) (Buchner and Schottenhammer, Ber., 1920, 53, 865).

There was no evidence of the formation of a norcaradiene derivative and, while they have usually been postulated as intermediates in such cases prior to rearrangement, it is possible that the seven-membered ring is formed directly from unstable transition complexes arising from forcing out of the plane of the ring by the reagent of substituents
at the attacked position, resistance leading to rupture of the C:C bond.

Reaction of naphthalene (Buchner and Hediger, Ber., 1903, 36, 3502) and of phenanthrene (Drake and Sweeney, J. Org. Chem., 1946, 11, 67) with diazoacetic ester gave the esters of the benz- and dibenznorcaradiene carboxylic acids XIV and XV, respectively, neither of which could be induced to rearrange. Both on oxidation gave the carboxyphenylcyclopropane-1:2-dicarboxylic acid XVI, showing that in XV the cyclopropane ring is less susceptible to oxidation than the aromatic nucleus. The carboxyphenylcyclopropane-1:2-dicarboxylic acid (XVI) failed to give an anhydride, indicating that the 1:2-carboxyl groups are trans to each other, and this was confirmed by the isolation of trans-cyclopropane-1:2:3-tricarboxylic acid (X) as the final oxidation product (Buchner and Hediger, ibid.). This proves, therefore, that in XIV and XV the configuration about the cyclopropane ring is also the trans configuration.

Drake and Sweeney (ibid.) and Cook, Dickson and Loudon (J., 1947, 746) have described as the hydrolysis product of the reaction between phenanthrene and diazoacetic ester an acid, m.p. 258°, whose systematic name is
trans-4b:5a-dihydro-5H-cyclopropa[def]phenanthrene-5-carboxylic acid (XV), and the latter authors described its methyl ester, m.p. 145°. Their work was repeated with a view to determining the ultraviolet and infra-red spectra of these compounds for comparison with the spectra of compounds obtained after similar reaction of cyclopenta[def]phenanthrene with diazoacetic ester. Phenanthrene was treated with diazoacetic ester under the conditions of Drake and Sweeney and the reaction mixture was separated by alkaline hydrolysis into an acidic fraction and a neutral fraction which was mostly unchanged phenanthrene. The acidic material was esterified with diazomethane and was chromatographed on an alumina column. The first eluates gave a small amount (about 3% of the total weight of ester mixture) of a crystalline methyl ester, m.p. 210°, isomeric with that of Cook, Dickson and Loudon, which on hydrolysis gave an acid, m.p. 248°, isomeric with that of both groups of workers. The possibility of polymorphism was eliminated on observing depression of melting points for mixtures of the ester and of the acid with samples of the authentic trans isomers supplied by Dr. Loudon. The bulk of the material chromatographed was obtained as a pale yellow glass and hydrolysis of part of this likewise gave only a viscous acidic oil or glass. Only after some time did each of these products deposit crystals, the ester m.p. 145°, the acid m.p. 261° (both from benzene),
FIGURE 1. (all spectra determined in ethanol)
identical with the samples which were supplied by Dr. Loudon. An alternative method of separation and purification of the products of reaction of phenanthrene with diazoacetic ester was developed which depends on the differential solubilities of the sodium salts of the two acids described. The sodium salt of the acid described by the previous workers is present in larger amount in the hydrolysis product and it was found to crystallise from concentrated aqueous solution without contamination by the salt of the other isomer which remains in solution. The second isomer was recovered by acidification of the mother liquors and was purified by esterification and chromatography, as described above. In this way yields of the pure acid, m.p. 261°, were obtained which were somewhat less than the yields of cruder acid reported by Drake and Sweeney. For experimental details see p. 50 et. seq.

That the new products from the reaction of phenanthrene with diazoacetic ester are stereoisomers of those previously described was shown by oxidative degradation of the acid, and by an examination of the ultra-violet and infra-red spectra of the acid, its methyl ester and its lithium aluminium hydride reduction product. Oxidation of the acid, m.p. 248°, isomeric with trans-4b:5a-dihydro-5H-cyclopropa[def]phenanthrene-5-carboxylic acid (XV), gave phenanthra-9:10-quinone in 85% yield, showing that
FIGURE 2. (spectra determined in ethanol)
addition of the ethoxycarbonylmethylene radical must have occurred at the 9:10 bond of the phenanthrene molecule, and leaving it intact. The only alternative to the norcaradiene structure XV is that of phenanthrene-9-acetic acid, which has m.p. 220° and whose methyl ester melts at 75° (Mosettig and van de Kamp, J. Amer. Chem. Soc., 1933, 55, 2998) and is therefore eliminated.

The ultra-violet spectra of the new acid, its methyl ester and its lithium aluminium hydride reduction product indicate a diphenyl nucleus (figures 1 and 2) and are very similar to those of their corresponding isomers. Furthermore, the infra-red spectra of the three new compounds each have a band at 1004 cm⁻¹ where it is known that many cyclopropane derivatives absorb.

Cis-trans isomerism about the cyclopropane ring is sufficient to account for the occurrence of two isomeric 4b:5a-dihydro-5H-cyclopropa[def]phenanthrene-5-carboxylic acids, although in the cases described above of benzene and naphthalene such pairs of isomers have not been isolated. It has been commonly supposed from the isolation of only the trans-1:2:3-cyclopropanetricarboxylic acid as the final oxidation product of norcaradiene derivatives that addition of the reagent occurs only in a trans manner. Since the major product of the reaction of phenanthrene with diazoacetic ester is trans-4b:5a-dihydro-5H-cyclopropa[def]phenanthrene-5-carboxylic ester, the second acid described here must have the cis configuration about
the cyclopropane ring and this difference might account satisfactorily for the disruption of the cyclopropane ring on oxidation. Because reaction in a cis manner of phenanthrene with diazoacetic ester (or the radical therefrom) is sterically more hindered, the cis product is present in the reaction mixture in much smaller amount than the trans product. The composition of the reaction mixture was unaffected either by heating for several hours at 200°, or by separation of the acids from neutral material after hydrolysis by sulphuric acid instead of by alkali. It is possible that chromatographic separation of the reaction products from other similar compounds, for example benzene and naphthalene, with diazoacetic ester may show the existence of similar isomer pairs.

When an aromatic compound contains a five-membered ring adjacent to a benzenoid ring which can undergo expansion to a seven-membered ring then a ready route is afforded to the synthesis of azulenic compounds. The method was first applied to the synthesis of azulenes by Pfau and Plattner (Helv. Chim. Acta, 1939, 22, 202) who reacted 2-isopropyl-4:7-dimethylindan (XVII) with diazoacetic ester.

\[
\text{XVII} \quad \text{XVIII} \quad \text{XIX} \quad \text{XX}
\]
The reaction product was saponified and the acid mixture obtained was dehydrogenated and decarboxylated by heating with palladium charcoal to give 2-isopropyl-4:8-dimethyl-azulene (XVIII), i.e. vetivazulene. When the product from the reaction of fluorene with diazoacetic ester was heated to 200°C rearrangement was followed by spontaneous dehydrogenation (only one mole of hydrogen need be lost) to give directly a benzazulene carboxylic ester (XIX) which on saponification and decarboxylation yielded 1:2-benzazulene (XX) (Treibs, Ber., 1948, 81, 38).

1:2-Benzazulene is the only azulene so far synthesised and studied (see also, Nunn and Rapson, J., 1949, 825) which possesses only one chemically recognisable position for the adoption of anionic character, so that similar systems in which the five-membered ring was more closely enveloped appeared to deserve study. Two structures were chosen for a preliminary investigation, cyclohepta-[bc]acenaphthylene (XXI) and cyclohepta[def]fluorene (XXII).

These are both capable of representation as cyclopolyolefines, but if all reasonable structures of both covalent and betaine types are written then important differences are observed.

Covalent structures for XXI are represented by XXIa
and XXIb in which, respectively, the classical naphthalene
and azulene forms all contribute, with the fixed bond-
structure indicated in the remaining part of the molecule,
thereby giving five reasonable covalent canonical forms.
The betaine structures are represented in part by XXIc, in
which the seven-membered ring donates an electron to
carbon atom (10), while the naphthalene portion may again
be written as varying in the usual way. For the compound
XXII there are only two purely covalent forms XXIIa and
XXIIb which are reasonable, and in neither of them is
the diphenyl or azulene structural type preserved. Both
require complete double-bond character for the central
bond. Betaine contributants are also limited to two
structures XXIIc and XXIID in which only positions 8 and 10
may act as electron sources. It is to be expected there-
fore that a hydrocarbon of structure XXI, cyclohepta[bc]-
acenaphthylene, would be typically azulenic, whereas one
of structure XXII, cyclohepta[def]fluorene, would be a
The hydrocarbon cyclohepta[bc]acenaphthylene was synthesised from γ-1-acenaphthenylbutyric acid (XXIII) which was prepared from 1-acenaphthenylacetic acid or preferably from β-1-acenaphthenylpropionic acid by the Arndt-Eistert reaction (Reid, Stafford and Ward, J., 1955, 1193). Ring closure by polyphosphoric acid (PPA) of the butyric acid gave 6:7:8:9-tetrahydro-6-oxocyclohepta-[bc]acenaphthene (XXIV) in excellent yield, which was best converted to the desired product by successive reduction with lithium aluminium hydride, dehydration of the resulting carbinol to 8:9-dihydrocyclohepta[bc]acenaphthene (XXV) and dehydrogenation with palladium charcoal. Alternatively, the compound XXIV was reduced by Clemmensen reduction to the hydrocarbon 6:7:8:9-tetrahydrocyclohepta-[bc]acenaphthene (XXVI) which was dehydrogenated over palladium charcoal to give again cyclohepta[bc]acenaphthylene. The success of this final dehydrogenation is in contrast to the experience of Gardner and Horton (J. Amer. Chem. Soc., 1952, 74, 657) who on heating 1:2:8:9:10:10a-
hexahydrocyclohepta[klm]benz[e]indene (XXVII) with

- XXVII
- XXVIII
- XXIX

palladium charcoal were unable to isolate any recognisable product. Their experimental conditions however were intended to cause dehydrogenation and rearrangement of XXVII to pyrene (XXVIII) and were not likely to permit survival of the azulene XXIX, were it in fact first formed.

Synthesis of cyclohepta[def]fluorene was attempted by the method of ring-expansion with diazoacetic ester used by Treibs to prepare 1:2-benzazulene (Ber., 1948, 81, 38). The method was applied to cyclopenta[def]phenanthrene (XXX) which was reacted with diazoacetic ester. From the analogous work on phenanthrene (see above) the product should have been a cyclopropane compound (XXXI)

- XXX
- XXXI
- XXXII
- XXXIII

arising by reaction at the 8:9 bond, which on rearrangement to the seven-membered ring compound XXXII and dehydrogenation should have given an ester derived from cyclohepta[def]fluorene, namely XXXIII. In fact two esters which were azulenic, i.e. deeply coloured and extractible
into phosphoric acid, were isolated and both on hydrolysis and decarboxylation yielded the isomer cyclohepta[bc]acenaphthylene. Their combined yield was about 40% based on the amount of starting hydrocarbon used up. Substantial attack must have occurred in ring A of cyclopenta[def]-phenanthrene and presumably on the 1:2 and 2:3 bonds in that ring to give two esters of the type XXXIV.

The material which was not extracted into phosphoric acid was separated by alkaline hydrolysis into a neutral fraction, mostly unchanged cyclopenta[def]phenanthrene, and a colourless homogeneous acid fraction in about 20% yield based on the amount of starting hydrocarbon used. In this compound a structure of the type XXXI or XXXII must be involved for (a), dehydrogenation experiments gave no evidence of the formation of derivatives of cyclohepta[bc]acenaphthylene, and (b), ultra-violet absorption spectra of the acid and its lithium aluminium hydride reduction product (figure 1) were in accord with a diphenyl formulation. The norcaradiene and cycloheptatriene structures, XXXI and XXXII respectively, were differentiated by a combination of oxidative degradation and infra-red spectroscopy studies.

If the structure were that of the norcaradiene acid
(XXXI), then in view of the relatively good yield in which it was obtained the configuration about the cyclopropane ring should be the trans configuration. By analogy with the work of Drake and Sweeney (ibid.), if the presence of a fluorene rather than a diphenyl structure had no effect on the stability of a cyclopropane ring then oxidation of a trans structure such as XXXI should lead to formation of a product retaining the cyclopropane ring. The acid, however, was readily oxidised to fluorenone-4:5-dicarboxylic acid (XXXV) and so must have the cycloheptatriene structure XXXII.

This was confirmed by infra-red spectroscopy and comparison with the infra-red spectra of the cis-4b:5a-dihydro-5H-cyclopropa[def]phenanthrene, or dibenznorcaradiene, derivatives described above. A fundamental difference occurs in the carbonyl absorption frequencies for the acid and ester derived from cyclopenta[def]phenanthrene and those from phenanthrene (Table 1.).

<table>
<thead>
<tr>
<th>IR spectra in KBr discs.</th>
<th>Carbonyl frequencies (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid from cyclopenta[def]phenanthrene</td>
<td>1671</td>
</tr>
<tr>
<td>Acid from phenanthrene (cis)</td>
<td>1722</td>
</tr>
<tr>
<td>Normal aliphatic acid</td>
<td>1715</td>
</tr>
</tbody>
</table>

A marked conjugation effect is shown by the cyclopentano compounds but not by those derived from phenanthrene,
indicating the presence in the former of the 8:9 double bond, i.e. indicating again a cycloheptatriene formulation. The acid, its ester and its lithium aluminium hydride reduction product derived from cyclopenta[def]phenanthrene had no band in the 1004 cm$^{-1}$ region of their infra-red spectra, such a band being indicative of the cyclopropane ring, but the acid and ester had bands at 843 and 847 cm$^{-1}$ respectively, which is the appropriate region for the C-H bonding vibration of a system $R_2C=CHR$. This band was missing in the infra-red spectrum of the lithium aluminium hydride reduction product, suggesting that reduction of the 8:9 double bond also had occurred but this was not confirmed by elementary analysis of the compound.

The facility with which the norcaradiene derivative XXXI undergoes rearrangement to a cycloheptatriene, if indeed it ever exists as other than a transitory reaction complex, is in strong contrast to the stability of the norcaradiene derivatives obtained from naphthalene, phenanthrene and a number of other polycyclic aromatic hydrocarbons. It is possible that in XXXI the methylene group causes some strain in the 8:9 bond of the original cyclopenta[def]phenanthrene molecule similar in effect to the strain caused by the methyl groups in mesitylene, which results in spontaneous rearrangement to the cycloheptatriene. Badger, Cook and Gibb (J., 1951, 3456) found
that anthracene (XXXVI), 1:2-benzanthracene (XXXVII) and pyrene reacted with diazoacetic ester at the bonds indicated to give the corresponding cyclopropane derivatives which were stable against rearrangement to cycloheptatrienes under conditions which led to rearrangement in similar derivatives from benzene and its homologues. Since the positions of addition in these molecules are not those normally attacked by electrophilic reagents and since the bonds indicated are those of highest order these results were interpreted as meaning that diazoacetic ester is a "double-bond reagent," i.e. a reagent which will indicate the bond of predominantly highest order in a molecule. Although reaction of pyrene with diazoacetic ester gave a second isomer of undetermined constitution, reaction occurred predominantly at the bond of highest order and so this case was not considered an exception. However, the reaction of cyclopenta[def]phenanthrene with diazoacetic ester gave a mixture containing three products in approximately equimolecular amounts and cannot readily be reconciled with the above hypothesis.

The Hammet function of a basic hydrocarbon may be defined as the concentration of sulphuric acid (w/w) which reduces by one half the concentration of hydrocarbon present in an equal volume of toluene or cyclohexane solution, or, alternatively, as the concentration of acid for which the distribution coefficient of the hydrocarbon is unity. The distribution coefficients for cyclohepta[bc]acenaphthylene between cyclohexane and a number of sulphuric acid solutions were determined and on plotting the logarithms of the distribution coefficients against the acid concentrations a straight line was obtained (see experimental section, p. 42). Interpolation to zero on the logarithm axis gave the Hammet function of the azulene hydrocarbon. The Hammet function for cyclohepta[bc]acenaphthylene is low, i.e. the basicity of the hydrocarbon is high, and is compared in Table 2 with those of azulene, 1:2-benzazulene and 5:6-benzazulene (W. Keller, Thesis, ETH, Zürich, 1952).

Table 2. Basicity of polycyclic azulenes (% H₂SO₄, w/w)

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Acid Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohepta[bc]acenaphthylene</td>
<td>44.2</td>
</tr>
<tr>
<td>1:2-Benzazulene</td>
<td>53.6</td>
</tr>
<tr>
<td>5:6-Benzazulene</td>
<td>61.7</td>
</tr>
<tr>
<td>Azulene</td>
<td>51.0</td>
</tr>
</tbody>
</table>

The basicity of a hydrocarbon reflects the equilibrium

\[
\text{Az} + \text{H}^+ \leftrightharpoons \text{AzH}^+ \quad (\text{Az} = \text{azulene})
\]

The forward reaction is favoured by a high polarisation in the ground state of the hydrocarbon, and the reverse
reaction is disfavoured by the stability of the resulting cation. In azulene and 5:6-benzazulene, there are two positions which are available for proton acceptance and they are, therefore, comparable compounds. The large difference in their basicities must arise from the influence of the condensed benzene ring on the initial degree of polarisation and/or the stability of the resulting cation. Both factors probably operate in the same direction, for in terms of resonance theory the more stable the cation the higher the contribution of polarised forms, i.e. the higher the degree of initial polarisation. Similarly, cyclohepta[bc]acenaphthylene and 1:2-benzazulene have each one site for the addition of a proton. The high basicity of the former indicates that there is a large degree of initial polarisation and that the derived cation is much more stable than that from 1:2-benzazulene. The close envelopment of the five-membered ring has thus enhanced in this case the azulenic character of the molecule because it has increased the polarisation already existing within the molecule.

For the compound cyclohepta[def]fluorene where such polarisation is limited and where cyclopolyolefinic structures are the principal contributing forms, difficulty has been experienced in a synthesis which is typical of those normally employed for azulenes. The stability of the dihydro ester derivative (XXXII) of cyclohepta[def]-fluorene to dehydrogenation indicates the energetic
disfavour of such a structure. It is, therefore, not the cyclopolyolefine contribution that is fundamental to azulene structure.

The compound XXXIX, cyclohepta[fg]acenaphthylene, has recently been synthesised by Boekelheide and Vick (J. Amer. Chem. Soc., 1956, 78, 653) and found to possess considerable aromatic character and stability.

![Diagrams](image)

Like azulene it possesses deep colour and readily undergoes nitration with cupric nitrate and acetic anhydride. It has been predicted (Pullman, Pullman, Berthier and Pontis, J. chim. phys., 1952, 49, 20) that electrophilic substitution should occur at the 7-position, i.e. in the five-membered ring as in azulene. It is therefore tempting to compare cyclohepta[fg]acenaphthylene to the hypothetical compound XL in which structures of the types XLa and XLb might be expected to take part and whose properties should consequently resemble those of azulene. While the properties of cyclohepta[fg]acenaphthylene do resemble those of azulene and while its absorption spectrum is very similar in general outline to that of its isomer cyclohepta-[bc]acenaphthylene, its properties and spectrum are also very similar to those of cyclohepta[de]naphthalene (XLI), as was predicted by Pullman et al. (ibid.). In
cyclohepta[de]naphthalene no polarisation of a five- and seven-membered ring system is possible and so it need not be that such polarisation already exists within the cyclohepta[fg]acenaphthylene molecule in the ground state. It would be interesting to know if cyclohepta[fg]acenaphthylene possesses basic properties comparable to the basicity of cyclohepta[bc]acenaphthylene.

The two isomeric cycloheptacenaphthylenes in common with pyrene and fluoranthenes each possess sixteen $\pi$-electrons and so provide further evidence of the inapplicability to polycyclic systems, particularly those containing peri-condensed rings, of the $(4n+2)$ rule of Hückel. Pyrene bears a close structural resemblance to both cyclohepta[bc]- and cyclohepta[fg]acenaphthylene but is otherwise not distinguished in its properties by deep colour or basicity.

The absorption spectrum of cyclohepta[bc]acenaphthylene (figure 3) conforms to a pattern common to the azulenes and many anhydro salts. The marked feature is that in neutral solvents the hydrocarbon has extensive absorption in the visible region. This is found in most compounds requiring a "betaine" type formulation and it is the visible band which is often abnormally affected by substitution and which is most dependent on the polar character of the environment. The absorption of acid solutions of the hydrocarbon resembles that in neutral solvents in general form but with a bathochromic displacement in the ultra-violet region. The
visible absorption in acid solution is largely extinguished due to acceptance by carbon atom (10) of a proton and consequent disappearance of the anionic centre on which the deep colour of the parent is dependent (c.f. Stafford and Reid, Chem. and Ind., 1954, 277).

Further study of the effect of the cyclopentano ring in cyclopenta[def]phenanthrene on the phenanthrene nucleus was carried out using the more selective osmium tetroxide oxidation. Osmium tetroxide is another reagent which adds across unsaturated linkages. It reacts readily with ethylenic compounds and more slowly with some aromatic compounds to form organo-osmium compounds which co-ordinate with two molecules of a tertiary base such as pyridine to give in high yield crystalline complexes of probable structure XLII.

\[
\text{XLII} \quad \xrightarrow{\text{Reductive hydrolysis}} \quad \text{XLIII}
\]

Reductive hydrolysis of such a complex gives the corresponding cis diol (XLIII). Thus, phenanthrene gives cis-9:10-dihydroxy-9:10-dihydrophenanthrene (Criegee, Marchand and Wannowius, Annalen, 1942, 550, 99). Cook and Schoental (J., 1948, 170) have shown that pyrene, 3:4-benzopyrene and 1:2-benzanthracene afford the products XLIV, XLV and XLVI respectively on similar oxidation with osmium tetroxide.
These sites of addition of the reagent are not those normally attacked by electrophilic reagents, and since they are again at the bond of highest order in each molecule osmium tetroxide and diazoacetic ester have been classed together as "double bond reagents."

With cyclopenta[def]phenanthrene no evidence of reaction at other than the 8:9 bond was found. The resulting diol (XLVII) was oxidised readily to fluorenone-4:5-dicarboxylic acid. The indication is therefore that little reliance should be placed on the use of diazoacetic ester for the determination of bond order unless a more specific reagent is used comparatively and proof of homogeneity of product and of its structure is obtained. Cyclopenta[def]phenanthrene and pyrene are both examples of compounds each containing one bond of outstandingly high double-bond character in which multiple attack occurs on reaction with diazoacetic ester but in which reaction with osmium tetroxide occurs only at the expected sites, namely the bonds of highest order.

Since fluorenone-4:5-dicarboxylic acid was a key compound in the foregoing work it was prepared according
FIGURE 4. (Spectra determined in ethanol).
to Kruber (Ber., 1934, 67, 1000), and the absorption spectra of the acid and its dimethyl ester were recorded (figure 4). The spectra of all the above bridged diphenyl derivatives, apart from that of the diol (figure 4) are in accord with those for 9:10-dihydrophenanthrene, fluorene and 8:9-dihydrocyclopenta[def]phenanthrene (Jones, J. Amer. Chem. Soc., 1945, 67, 2130). This last compound differs from the first two in one respect. The fine side maxima (ca. 310 \( \mu \)) on the principal diphenyl absorption (ca. 270 \( \mu \)) are absent when two bridges join the 2:2'-positions of the diphenyl nucleus. Only in the diol XLVII are two such bridges found and also these side maxima. The presence of the cinnamic acid type side chain in 4:8-dihydrocyclohepta[def]-fluorene-9-carboxylic acid has apparently little influence on the ultra-violet absorption. The broadening of the band in the 220-230 \( \mu \) region which disappears on lithium aluminium hydride reduction is common to the spectra of trans-4b:5a-dihydro-5H-cyclopropa[def]phenanthrene-5-carboxylic acid and its methyl ester (figures 1 and 2). The spectra of cis-4b:5a-dihydro-5H-cyclopropa[def]-phenanthrene-5-carboxylic acid and its methyl ester (figures 1 and 2) in the 220-230 \( \mu \) region are unusual in that they resemble more closely the spectra of the hydroxy-methylene compounds in this region.
EXPERIMENTAL

In the following section all yields are reported directly as weight of product obtained from given weights of starting materials.

All melting points were determined by means of a Kofler micro-melting point apparatus.

Chromatographic separations were carried out on columns prepared from Activated Alumina Type "H", supplied by Peter Spence & Sons Ltd., Widnes.

Spectral determinations were made using a Unicam SP500 spectrophotometer and with 10 mm. silica cells.

Analyses were performed by Drs. Weiler and Strauss, Oxford.
The reaction between cyclopenta[def]phenanthrene (supplied by Dr. O. Kruber) and diazoacetic ester (prepared according to Grundmann and Ottmann, Annalen, 1953, 582, 163) was carried out in a 50-ml. pear-shaped flask, heated in an oil bath and supplied with a small capillary dropping funnel, a nitrogen inlet tube and an air-condenser drawn to a wide capillary at the exit end. The hydrocarbon (10.0 g.) was fused by raising the bath temperature to 140° and this temperature was maintained while the diazoacetic ester (6.5 g.) was added dropwise during 2 hr. The mixture was stirred during this time by a stream of nitrogen, and became reddish-brown in colour. The temperature of the bath was finally raised during 5 hr. to 200°, with only occasional stirring with the nitrogen stream. The reaction mixture when cool was dissolved in 200 ml. of a mixture of benzene and light-petroleum (3:1), and azulenic material was extracted into syrupy phosphoric acid (4 x 50 ml.). The acid layer was washed with further quantities of the same solvent mixture and was poured into iced water (2 l.). Extraction with ether gave the azulenic fraction. The extract was dried over anhydrous sodium sulphate and removal of the solvent gave a residue weighing 4-5 g. in different
experiments. When chromatographed on neutral alumina this gave two main bands. Elution with benzene gave the starting hydrocarbon (1.2 g.) which thus passes to some extent through the acid separation. Elution with a mixture of benzene and ether (1:3) gave a band yielding a red azulenic oil (2.0 g.) on evaporation of the solvent. A strongly adsorbed brown oil (0.5 g.) which was eluted with acetone accounted for the total amount chromatographed.

Chromatography of the red oil with slow elution with a mixture of benzene and light-petroleum (3:1) gave two bands appearing green on the column but giving red eluates. The first yielded a red oil (1.4 g.) which tended to crystallise as needles but could not be obtained pure and free from oily material. The second gave an oil (0.6 g.) which showed no tendency to solidify. The two fractions were separately boiled for 2.5 hr. with 3% ethanolic potassium hydroxide (50 and 30 ml. respectively) and the mixtures poured into water. Each was extracted with benzene to remove neutral material, then the aqueous layers were acidified with dilute hydrochloric acid and extracted with ether. The extracts were dried over anhydrous sodium sulphate and evaporation of the solvent gave the azulenic acids as amorphous solids (1.0 and 0.5 g. respectively). Each acid was decarboxylated in quinoline (20 ml. per g.) containing copper bronze (0.5 g. per g.) for 1 hr. at the boiling point.
The mixtures were cooled, diluted with ether and the copper bronze filtered off. The quinoline was removed by repeated extraction of the ethereal solutions with dilute hydrochloric acid. The ether solutions were washed with water and then extracted with sodium hydrogen carbonate solution to removed unchanged azulene acid (of which there was only a trace). The ether solutions were finally washed with water, dried over sodium sulphate and evaporated. The residues were chromatographed on alumina and each yielded one red band which was eluted with light-petroleum. The eluates yielded 150 and 30 mg. respectively of the same crystalline hydrocarbon which formed from light-petroleum beautiful deep red plates, m.p. 143.5-144.5°, identical (mixed m.p.) with authentic cyclohepta[bc]acenaphylene synthesised from acenaphthene. The trinitrobenzene complex was prepared in the usual way and crystallised from ethanol as orange-brown needles m.p. 228-230° which did not depress the m.p. of the derivative prepared from authentic material.

The brown oil eluted from the original column was subjected to the same procedure and gave a few mg. of the trinitrobenzene complex as above.

Determination of the Hammet function of cyclohepta[bc]-acenaphthylene.

Acta, 1949, 32, 574.

The optical density of a standard solution of cyclohepta[bc]acenaphthylene in spectroscopically pure hexane was determined at two wavelengths, 575 and 525 μm. 10 ml. aliquots of this solution were shaken for 6 minutes with 10 ml. portions of aqueous "AnalaR" sulphuric acid solutions of known concentration (w/w) in a 50 ml. separating funnel at room temperature. The layers were allowed to settle for a further 4 minutes. The acid layers were separated and the organic layers decanted. The optical densities of the organic layers were re-determined for the two wave lengths. (Dilution of the acid extracts regenerated the unchanged hydrocarbon).

If D is the optical density of the standard solution and D' that of an acid extracted solution then D' is proportional to the concentration of azulene hydrocarbon remaining in the organic layer, and (D-D') is proportional to the concentration of azulene hydrocarbon extracted into the acid layer, the volumes being the same for each solution. The distribution coefficient K of the azulene between the organic phase and the acid phase is then given by

$$K = \frac{D'}{D - D'}$$

On plotting the logarithms of the distribution coefficients determined from readings at both the chosen wavelengths against the sulphuric acid concentrations (w/w)
a single straight line was obtained. Interpolation to zero on the logarithm axis gave the value 44.2 for the Hammet function of cyclohepta[bc]acenaphthylene. The figure is shown opposite.

<table>
<thead>
<tr>
<th>Conc. of H₂SO₄ (w/w)</th>
<th>K₅₇₅</th>
<th>log₁₀ K₅₇₅</th>
<th>K₅₂₅</th>
<th>log₁₀ K₅₂₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>34.73</td>
<td>63.98</td>
<td>1.806</td>
<td>17.66</td>
<td>1.247</td>
</tr>
<tr>
<td>39.91</td>
<td>5.79</td>
<td>0.763</td>
<td>6.00</td>
<td>0.778</td>
</tr>
<tr>
<td>44.70</td>
<td>0.764</td>
<td>-0.117</td>
<td>0.867</td>
<td>-0.062</td>
</tr>
<tr>
<td>49.36</td>
<td>0.116</td>
<td>-0.936</td>
<td>0.122</td>
<td>-0.914</td>
</tr>
<tr>
<td>55.33</td>
<td>0.017</td>
<td>-1.770</td>
<td>0.018</td>
<td>-1.745</td>
</tr>
</tbody>
</table>

The concentrations of the sulphuric acid solutions were determined by titrating weighed portions with standard sodium hydroxide solution using phenolphthalein as indicator.

The divergence from linearity of log K for the sulphuric acid solutions of lowest and highest concentration is due in the former to the difficulty of measuring accurately the small difference (D-D'), and in the latter to measuring the small value of D', the hydrocarbon being almost completely extracted from the organic layer by the more concentrated sulphuric acid.

4:8-Dihydrocyclohepta[def]fluorene-9-carboxylic Acid.

The material from the reaction of cyclopenta[def]-phenanthrene with diazoacetic ester which was not extracted
into phosphoric acid was examined. The original benzene-light petroleum solution of the reaction mixture was washed with water and dried over sodium sulphate. The solvent was distilled off and the residue boiled for 3 hr. in 3% ethanolic potassium hydroxide (100 ml.). Most of the ethanol was removed by distillation under reduced pressure and the residue was taken up in water. Insoluble material was extracted into benzene and was examined for starting material, which, when combined with the cyclopenta[def]phenanthrene obtained from the chromatogram described above, amounted to 6.5 g. of pure hydrocarbon. The aqueous phase was acidified with dilute hydrochloric acid and the precipitated solid was found to be contaminated with a considerable amount of red material. The solid was taken up in benzene and was again extracted with phosphoric acid. The phosphoric acid extract was diluted and the azulen material recovered, and decarboxylated giving further small amounts of cyclohepta[bc]acenaphthylene, as described above. The benzene solution containing material insoluble in phosphoric acid was washed and dried as before and the solvent distilled off. The residue was crystallised repeatedly from ethanol and the product, 4:8-dihydrocyclohepta[def]fluorene-9-carboxylic acid, was obtained as colourless needles (720 mg. of pure material), m.p. 258°.

Analysis. Found: C, 82.0%; H, 4.7%.

C_{17}H_{12}O_2 requires C, 82.2%; H, 4.9%.
The methyl ester (105 mg.) was obtained from the above acid (100 mg.) using 3% methanolic hydrochloric acid and was crystallised from a mixture of benzene and light-petroleum as colourless needles, m.p. 139-140°. Esterification of the acid with diazomethane gave the same product.

Analysis. Found: C, 82.9%; H, 5.5%.

C₁₈H₁₄O₂ requires C, 82.4%; H, 5.4%.

The ethyl ester was prepared similarly with 3% ethanolic hydrochloric acid and formed colourless needles from a mixture of benzene and light-petroleum m.p. 141.5°.

Analysis. Found: C, 82.3%; H, 5.9%.

C₁₉H₁₆O₂ requires C, 82.6%; H, 5.8%.


The foregoing acid (190 mg.) was reduced with lithium aluminium hydride (50 mg.) in dry ether (25 ml.), the mixture being boiled under reflux on a water bath for 30 minutes after the addition of the lithium aluminium hydride. The mixture was poured into ice water and the complex further decomposed with dilute sulphuric acid. The mixture was extracted with ether and the extract washed with sodium hydrogen carbonate solution to remove acid. The ether extract was dried and removal of the solvent gave a residue (180 mg.) which was recrystallised from a mixture of benzene and light-petroleum, forming colourless needles, m.p. 143°.
Analysis. Found: C, 87.0, 87.1%; H, 5.6, 5.1%.

C\textsubscript{17}H\textsubscript{14}O requires C, 87.1%; H, 6.0%.

In concentrated sulphuric acid this alcohol gave an intense blue-black colour.

**Oxidation of 4:8-dihydrocyclohepta[def]fluorene-9-carboxylic acid.**

4:8-Dihydrocyclohepta[def]fluorene-9-carboxylic acid (700 mg.) was boiled for 12 hr. in "AnalaR" acetic acid (60 ml.) containing "AnalaR" chromic oxide (4.5 g.). The mixture was poured into water and was exhaustively extracted with ether. The yellow ether extract was washed with water and acidic material was extracted from it with sodium hydrogen carbonate solution, giving a yellow salt in solution. The aqueous extract was acidified with dilute hydrochloric acid and the precipitated acid was extracted into ether. The ether extract was washed with water, dried over sodium sulphate, and the solvent was removed by distillation. The residue (containing a little acetic acid) was crystallised three times from a mixture of acetone and benzene and yielded fluorenone-4:5-dicarboxylic acid (125 mg.) as yellow prisms, m.p. 285-287° with gas evolution. (Kruber, Ber., 1934, 67, 1000, gives m.p. 285° "with frothing").

The dimethyl ester (53 mg.) was prepared from the above acid (50 mg.) using a large excess of ethereal diazomethane and was recrystallised from a mixture of
light petroleum and benzene, giving yellow needles, m.p. 191°.

Analysis. Found: C, 69.0%; H, 4.2%.

\[ \text{C}_{17}\text{H}_{12}\text{O}_5 \] requires C, 68.9%; H, 4.1%.

The melting points of the acid and ester were not depressed on admixture with authentic samples prepared via oxidation of cyclopenta[def]phenanthrene according to Kruber (ibid.).

Cis-8:9-dihydroxy-8:9-dihydrocyclopenta[def]phenanthrene. Cyclopenta[def]phenanthrene (410 mg.) was treated with osmium tetroxide (550 mg., 1 mol.) in dry thiophen-free benzene (15 ml.) containing pure pyridine (345 mg., 2 mols.). The mixture was left for 4 days, during which dark brown crystals separated. After filtration the residue was washed with a little benzene, and was then taken up in methylene chloride. The solution was filtered and evaporation of the solvent gave a crystalline residue (1.20 g., 91% yield). The complex was redissolved in methylene chloride and was shaken with an aqueous solution of mannitol (10 g. in 100 ml.) containing potassium hydroxide (1.0 g.). The methylene chloride layer was separated and dried. Removal of the solvent left a pale crystalline residue which was carbon screened in boiling ethanol for 10 minutes. Removal of the ethanol after filtration gave a bright yellow crystalline residue (300 mg., 67% based on
complex) which after several crystallisations from benzene gave colourless needles of the cis-diol, fusing to a yellow liquid at 180°.

Analysis. Found: C, 80.3%; H, 5.5%.

C\textsubscript{15}H\textsubscript{22}O\textsubscript{2} requires C, 80.4%; H, 5.4%.

The ready formation of a yellow colour on heating this diol is possibly due to oxidation giving the corresponding ortho-quinone.


Cis-8:9-dihydroxy-8:9-dihydrocyclopenta[def]-phenanthrene (90 mg.) was boiled in "AnalaR" acetic acid (25 ml.) containing "AnalaR" chromic oxide (0.5 g.) for 2 hr. The mixture was poured into water and extracted with ether. The ether extract was washed with water and extracted with sodium hydrogen carbonate solution. The yellow salt solution was acidified with dilute hydrochloric acid and the precipitated solid extracted into ether. The extract was dried and removal of the solvent gave a yellow crystalline residue which was contaminated with a little acetic acid which was allowed to evaporate under reduced pressure. The residue was crystallised three times from a mixture of benzene and acetone, giving fluorenone-4:5-dicarboxylic acid (15 mg.) as yellow needles, m.p. 286°, which did not depress the melting point of authentic fluorenone-4:5-
dicarboxylic acid and which had an identical absorption spectrum.

**THE REACTION OF PHENANTHRENE WITH DIAZOACETIC ESTER.**

Cis- and trans-4b:5a-dihydro-5H-cyclopropa[def]phenanthrene-5-carboxylic Acids.

Phenanthrene (25.0 g.) was treated with diazoacetic ester (6.0 g.) under the conditions described by Drake and Sweeney (J. Org. Chem., 1946, 11, 67). The reaction mixture was taken up in 5% ethanolic potassium hydroxide and reaction product separated from unchanged phenanthrene by hydrolysis, as described previously (p.45). The alkali-soluble material was isolated by acidification with dilute hydrochloric acid and extraction into ether, and was converted to the methyl ester by esterification with diazomethane, giving a brown syrupy product (4.5 g.). This was chromatographed on neutral alumina and eluted with a mixture of benzene and light-petroleum (1:9). The first eluates gave on evaporation a crystalline residue (200 mg.) which was recrystallised from a mixture of benzene and light-petroleum, giving colourless needles, m.p. 210°. This product is the methyl ester of cis-4b:5a-dihydro-5H-cyclopropa[def]phenanthrene-5-carboxylic acid and on admixture with the methyl ester of the authentic trans isomer (supplied by Dr. Loudon) its melting point
was depressed.

Analysis. Found: C, 81.4%; H, 5.7%.

C₁₇H₁₄O₂ requires C, 81.6%; H, 5.6%.

The above cis ester (120 mg.) was hydrolysed with 3% ethanolic potassium hydroxide and the crystalline acid obtained (110 mg.) was crystallised from methanol to give colourless needles, m.p. 247-248°. The melting point was not raised by further crystallisation from methanol or from benzene.

Analysis. Found: C, 81.0%; H, 5.0%.

C₁₆H₁₂O₂ requires C, 81.3%; H, 5.1%.

This is cis-4b:5a-dihydro-5H-cyclopropa[def]-phenanthrene-5-carboxylic acid.

Further elution of the column (above) with a mixture of benzene and light-petroleum (1:1) removed the bulk of the product which on removal of the solvent was obtained as a pale yellow resinous oil (3.0 g.). One half of this product was hydrolysed with 3% ethanolic potassium hydroxide and the acid obtained (1.3 g.) was likewise a pale yellow viscous oil. After standing for some time in benzene solution each of these products deposited crystals, the ester giving colourless needles, m.p. 145° identical (mixed m.p.) with the authentic methyl ester of trans-4b:5a-dihydro-5H-cyclopropa[def]phenanthrene-5-carboxylic acid, the acid giving colourless needles, m.p. 260-261°, identical with the authentic trans acid itself (mixed m.p. 258-260°).
Reduction of the methyl ester of cis-4b:5a-dihydro-5H-
cyclopropa[def]phenanthrene-5-carboxylic acid.

The above methyl ester, m.p. 210°, (180 mg.) was reduced with lithium aluminium hydride (40 mg.) in dry ether (25 ml.) and the hydroxymethylene compound (160 mg.) was obtained (as described on p. 46) as colourless needles from benzene solution, m.p. 148°.

Analysis. Found: C, 86.1%; H, 6.1%.
C_{16}H_{14}O requires C, 86.4%; H, 6.4%.

Reduction of trans-4b:5a-dihydro-5H-cyclopropa[def]-
phenanthrene-5-carboxylic acid.

The above acid (6.0 g.) was reduced with lithium aluminium hydride (1.0 g.) in dry ether as described above. Unchanged acid was removed from the mixture containing the reduction product by extraction with sodium hydrogen carbonate solution. The hydroxymethylene compound (3.1 g.) was obtained as colourless needles from benzene, m.p. 125-125.5°.

Analysis. Found: C, 86.6%; H, 6.2%.
C_{16}H_{14}O requires C, 86.4%; H, 6.4%.

Oxidation of cis-4b:5a-dihydro-5H-cyclopropa[def]phenanthrene-
5-carboxylic acid.

Cis-4b:5a-dihydro-5H-cyclopropa[def]phenanthrene-5-
carboxylic acid (160 mg.) was heated with "AnalaR" chromic oxide (0.5 g.) in "AnalaR" acetic acid (30 ml.) on a water
bath at 85° for 3 hr. The mixture was poured into water and extracted with ether. The yellow ether extract was washed with water, extracted with sodium hydrogen carbonate solution, washed again with water and finally dried over sodium sulphate. Removal of the solvent left a crystalline residue (120 mg.) which was recrystallised from ethanol, giving orange-yellow plates, m.p. 206-207°, identical (mixed m.p.) with authentic phenanthra-9:10-quinone, m.p. 207-208°.

The quinoxaline derivative was prepared from o-phenylenediamine in the usual way and was recrystallised from glacial acetic acid, giving yellow needles, m.p. 222-224°, identical (mixed m.p.) with the derivative prepared from authentic phenanthra-9:10-quinone.

The m.p. of this derivative recorded in the literature is 217° (Hinsberg, Annalen, 1887, 237, 340). The difference is due probably to the different method of determining it.

A new method was developed for the separation and purification of the mixture of products from the reaction of phenanthrene (180 g.) with diazoacetic ester (25 g.). The mixture of acidic products (separated from neutral material by alkaline hydrolysis as described above) was redissolved in boiling 2N sodium hydroxide, and then the solution was carbon screened and filtered. On cooling, the sodium salt of trans-4b:5a-dihydro-5H-cyclopropa[def]phenanthrene-5-carboxylic acid crystallised
and was collected. It was converted to the acid by suspension in water and acidification with dilute hydrochloric acid. The precipitated acid was recrystallised from ethanol and had m.p. 258-259°. (Yield 15·2 g.).

Concentration of the aqueous mother liquor containing the sodium salts and cooling failed to give any further amount of crystalline salt deposited. The solution was neutralised by stepwise addition of dilute hydrochloric acid and three indistinguishable amorphous fractions were obtained which were then recombined and esterified with diazomethane. The ester product was chromatographed on neutral alumina and eluted with a mixture of benzene and light-petroleum (1:9). The eluates yielded on evaporation the methyl ester of cis-4b:5a-dihydro-5H-cyclopropa[def]phenanthrene-5-carboxylic acid, m.p. 210°, as above. (Yield 850 mg.). The residue on the column was eluted with benzene and was a sticky resinous material, a product commonly associated with reactions involving diazoacetic ester, arising from decomposition of the diazo-compound itself.

The composition of the reaction mixture from phenanthrene and diazoacetic ester remained unchanged when hydrolysis was effected by sulphuric acid in aqueous ethanol. Likewise, it remained unchanged on heating for 3 hr. at 200 followed by either alkaline or acid hydrolysis.
DISCUSSION
SYNTHESIS AND PROPERTIES OF 4- AND 5-ALKOXYAZULENES

Azulene ethers and hydroxy compounds bearing an oxygen atom directly united to the seven-membered ring are of considerable interest because of the close structural relationship they bear to tropone and the ethers of tropolone. Only few accounts of such compounds have appeared in the literature however. Wagner-Jauregg, Arnold, Hütter and Schmidt (Ber., 1941, 74, 1522) described a lilac-blue compound presumed to be 2-ethyl-4-methyl-8-methoxyazulene (II) prepared by ring-expansion with diazoacetic ester of 2-ethyl-4-methyl-7-methoxyindan (I), but it could not be obtained analytically pure, being contaminated by azulenic hydrocarbon material resulting from loss of methoxyl during the dehydrogenation-decarboxylation stage.

Anderson and Nelson (J. Amer. Chem. Soc., 1951, 73, 232) have described a red oil obtained on dehydrogenation of the cyclopentenocycloheptanone III.
In view of its colour and its alkali-soluble properties it is probably 4-hydroxyazulene (IV) but it also could not be obtained analytically pure, being rather unstable. Treibs has reported the isolation of 4:5-dimethoxyazulene (Angew. Chem., 1951, 63, 487) but no details of the work have yet appeared. A description has appeared however of Treibs' synthesis of 1:2-benz-6-methoxyazulene (V) (Treibs and Ziegenbein, Annalen, 1955, 595, 211) and of 1-alkoxyazulenes (VI) (Treibs and Stein, Annalen, 1951, 572, 161) by ring expansion of 2-methoxyfluorene and 1-alkoxy-indans respectively.

Interest in azulene ethers is heightened by the observations that while the methoxyl group of 1:2-benz-6-methoxyazulene causes a hypsochromic displacement in the visible spectrum of about 15 mμ with respect to that of 1:2-benzazulene, the visible and ultra-violet spectra of the 1-alkoxyazulenes are practically identical with those of azulene itself. This is in contradistinction to the spectra of monosubstituted
azulenes generally and particularly to those of azulenes substituted in the 1-position for which relatively the largest bathochromic displacements are observed in both regions.

Ring-expansion with diazoacetic ester of aryl ethers was first developed by the Cambridge School under Johnson who employed it in the synthesis of tropone and tropolone derivatives. Johnson, Bartels-Keith and Langeman (J., 1952, 4461) found that reaction of anisole (VII) with diazoacetic ester gave 4-methoxycycloheptatriene-1-carboxylic ester. Treatment of the acid with bromine

\[
\text{VII} \quad \text{VIII} \quad \text{IX} \quad \text{X}
\]

in chloroform caused dehydrogenation and demethylation, giving tropone-4-carboxylic acid (VIII). Similarly, stipitatic acid (X) was obtained from 1:2:4-trimethoxybenzene (IX). The advantages of these syntheses are that the introduction of the oxygen functions is controlled, the intermediate cycloheptatriene carboxylic acids can be obtained pure and crystalline, and the bromine method of dehydrogenation and demethylation is generally applicable. While the overall yields in such syntheses are small, most of the unreacted starting material is recoverable and can be reprocessed.

Treatment of ethers with diazoacetic ester is of
further interest since it involves a second important type of reaction, namely, the formation of oxyacetic acid derivatives. Anisole, in addition to a cycloheptatriene derivative, gives also phenoxyacetic ester on reaction with diazoacetic ester, which is obtained as the acid (XI) on hydrolysis of the reaction product. Veratrole gives,

\[ \text{XI} \]

\[ \text{XII} \]

similarly, o-methoxyphenoxyacetic acid (XII). Johnson, Langeman and Murray (J., 1953, 2136) found this scission of the O-alkyl bond a general one for alkoxy benzenes but there was no evidence to indicate scission of the O-aryl bond. The influence of the second methoxyl group in the dimethoxybenzenes caused an increased yield of oxyacetic acid derivative compared with the yield of phenoxyacetic acid derivative from the mono-alkoxybenzenes. Since the ortho- and para-isomers were formed in considerably larger amounts than the meta- it appears that in further substituted aryl ethers attack on the alkoxy group by the reagent proceeds more readily when it occupies a position in the aromatic nucleus where the electron density is increased. De Graf, van Dijk-Rothuis and van de Kolk (Receuil, 1955, 144) found that dialkyl ethers react similarly, and that scission of both O-alkyl bonds occurred, giving mixtures of oxyacetic esters from unsymmetrical ethers. From
butoxybutane (XIII) they obtained both butoxyacetic ester (XIV) and butene-1 (XV), the latter from the expelled alkyl radical. The following mechanism was proposed in which it is postulated that addition to the oxygen atom of the dipolar ethoxycarbonylmethylene radical is followed by expulsion of the alkyl group as an olefine, and rearrangement.

\[
\begin{align*}
\text{C}_4\text{H}_9\text{-O-CH}_2\text{C}_3\text{H}_7 + \text{CH}=\text{C}^\text{O}\text{C}_2\text{H}_5 & \rightarrow \text{C}_3\text{H}_7\text{CH}_2\text{-O-CH=O}\text{C}_2\text{H}_5 \\
\text{C}_4\text{H}_9\text{-O.C.H}_2\text{COOC}_2\text{H}_5 & \leftarrow \text{C}_4\text{H}_9\text{-O-}\text{C}=\text{C}^\text{OH}\text{O}\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{CH=CH}_2
\end{align*}
\]

Similar attack by a dipolar radical is presumed to occur on reaction of aryl-alkyl ethers, leading to expulsion of only the alkyl group, however. Although the isolation of oxyacetic acid derivatives is not reported in the forementioned syntheses of azulene ethers by diazoacetic ester ring-expansion experiments, it seems probable that they were formed.

4- And 5-methoxyindan were used for the synthesis of the 4- and 5-alkoxyazulenes. The higher boiling residues from the reaction of 4-methoxyindan with diazoacetic ester were fractionally distilled and an ester mixture obtained. The acid product from its hydrolysis consisted mostly of 4-indanyloxyacetic acid which was readily obtained pure and crystalline. The high yield of this product - about 80% of the acid mixture - must be due to activation of the ether oxygen atom by the adjacent methylene group similar to that in the examples described above. The
residual acid fraction, 20% by weight, represents the cycloheptatriene derivatives later obtained as azulenes. Attempted dehydrogenation and decarboxylation of the mixture of acids with palladium charcoal and with selenium caused almost instantaneous charring. No soluble coloured products were isolable. The mixture of esters was dehydrogenated with sulphur at a lower temperature and a mixture of azulenic products was obtained.

Considering the small amount of cycloheptatriene compounds present in the original ester mixture the total yield of azulene esters represents a conversion of about 40%. This is surprisingly high. The best yields reported for dehydrogenation of bicyclodecane derivatives are those of Kovats, Plattner and Günthard (Helv. Chim. Acta, 1954, 37, 983) who obtained azulene in 60% yield from bicyclo-[5:3:0]dec-1(7)ene (XVI).

\[
\text{XVI} \xrightarrow{\text{Pd-C, 450°}} \text{azole}
\]

The process, however, was a catalytic one, requiring specialised apparatus and carefully controlled conditions. They obtained similar yields using carbon disulphide as dehydrogenating reagent, but again the process was catalytic (Helv. Chim. Acta, 1954, 37, 2123). In contrast to these yields Anderson and Tazuma (J. Amer. Chem. Soc., 1953, 75, 4979) dehydrogenated the ester XVII with sulphur for thirty
minutes at two hundred degrees and obtained 1-methoxy-carbonylazulene (XVIII) in a final yield of about 3% pure material.

\[ \text{XVII} \quad \text{XVIII} \]

The dehydrogenation in high yield of the cyclohepta-triienes present in the reaction mixture from 4-methoxyindan and diazoacetic ester bears a resemblance to the experiments of Baker, Warburton and Breddy (J., 1953, 4149). These authors found that when decahydroazulene was present in decalin as a diluent it could be catalytically dehydrogenated with palladium charcoal to give azulene in 24% yield without the use of special apparatus. It is possible perhaps that in the mixture of indanyloxyacetic ester and cycloheptatriene esters the former acts as a diluent similar to decalin, resulting in increased yield, or survival, of dehydrogenation product. The greater increase in the yield could be attributed to the fact that only two more "double bonds" require to be introduced, whereas in decahydroazulene five are required.

The azulene mixture obtained on dehydrogenation of the reaction mixture from 4-methoxyindan and diazoacetic ester was purified by acid extraction and separated by chromatography into three components coloured blue, violet and blue respectively. The first two were in major amounts
and were finally obtained pure and crystalline. Analysis proved them to be ethoxycarbonyl-4-methoxyazulenes. The third compound was present in only very small amount.

All three azulenes gave crystalline isomeric trinitrobenzene complexes. There was no evidence that dehydrogenation of the methoxycycloheptatriene derivatives caused any loss of methoxyl to give ethoxycarbonylazulenes for no other azulenic product was found. This dehydrogenation under milder conditions is perhaps hardly comparable to that of Wagner-Jauregg et al. (ibid.), however, who dehydrogenated and decarboxylated an acid mixture at higher temperatures with simultaneous loss of methoxyl group.

The blue ester in major amount was hydrolysed in ethanolic potassium hydroxide and the resulting acid analysed not for the expected methoxyazulene carboxylic acid but for an ethoxy carboxylic acid. Hydrolysis must therefore have been accompanied by ether interchange with the ethanol. Both the ethoxycarbonyl-4-methoxyazulenes present as major constituents of the azulene ester mixture undergo this interchange, for on hydrolysis in ethanol and decarboxylation of the resultant acid mixture a homogeneous violet product was obtained whose crystalline trinitrobenzene complex analysed for that of an ethoxyazulene. Some azulene was also formed during the decarboxylation by loss of the alkoxy group. Hydrolysis of the azulene ester mixture in methanol followed by decarboxylation gave a homogeneous violet product whose trinitrobenzene complex
was different from that above and which analysed for that of the expected methoxyazulene. Again, some azulene was formed, but reduction of the time of decarboxylation caused no azulene to be formed and at the same time an increased yield of 4-methoxyazulene was obtained. This suggests that loss of methoxyl occurs after decarboxylation and not simultaneously with it. The following mechanism seems likely to explain the ether interchange.

The ester (+E) group in the seven-membered ring promotes the susceptibility to nucleophilic replacement (c.f. p.2) for 4-methoxyazulene itself could not be made to undergo replacement in ethanolic potassium hydroxide or potassium ethoxide solution. Replacement must occur before hydrolysis of the ester group because the presence of an ionised carboxyl group in the same ring as the alkoxy group would cause deactivation to nucleophilic replacement in that ring. The lability of the alkoxy group suggested that hydrolysis of the methoxyazulene esters in aqueous solution should cause also replacement of methoxyl by hydroxyl. In fact the same blue ester as above yielded another acid which analysed for a hydroxyazulene carboxylic acid.

The preparation of 5-methoxyazulene paralleled that
of 4-methoxyazulene. Reaction of 5-methoxyindan with diazoacetic ester led to the formation of 5-indanyl oxyacetic ester which comprised about 75\% of the acid obtained on hydrolysis of the reaction mixture. Again the hydrolysate charred on attempted dehydrogenation and decarboxylation with palladium charcoal and with selenium. Dehydrogenation of the ester mixture with sulphur gave a single blue methoxyazulene ester in about 35\% yield based on the amount of cycloheptatriene derivative in the mixture. There was no evidence of loss of methoxyl at this stage. The methoxyazulene ester was purified by acid extraction and by chromatography but failed to crystallise. Its crystalline trinitrobenzene complex analysed for that of an ethoxycarbonylmethoxyazulene. The corresponding methyl ester likewise failed to crystallise but gave a crystalline trinitrobenzene complex. The ethyl ester was hydrolysed in ethanolic potassium hydroxide and the resulting acid was decarboxylated to give a single pure blue product whose crystalline trinitrobenzene complex analysed for that of a methoxyazulene. In this case, therefore, no ether interchange with the solvent had occurred so that the 5-position is apparently less susceptible to nucleophilic replacement than is the 4-position (see p.12). In contrast to the decarboxylation of the mixture of 4-methoxyazulene carboxylic acids no loss of methoxyl from the 5-position occurred when similar experimental conditions were used for decarboxylation of
FIGURE 1.
the 5-methoxyazulene carboxylic acid. This may be a further manifestation of the relatively high positive charge at the 4-position.

The visible spectra of most of the azulenic compounds described above were found to be devoid of pronounced fine structure (see figures 1 and 2) and displacements relative to the visible absorption band of azulene were determined by comparing the wave length of maximum absorption for each, which is situated about the middle of the visible absorption band. The visible spectra of 4-methoxy- and 4-ethoxyazulene were almost identical (figures 1 and 6). For each the wave length of maximum absorption is at 545 m\textmu. The corresponding wave length in the spectrum of azulene is 580 m\textmu, so that substitution of an alkoxyl group in the 4-position of azulene causes a hypsochromic displacement of 35 m\textmu in the visible absorption band. The colour of the 4-alkoxyazulenes is consequently violet. The visible spectrum of the isomeric methoxyazulene derived from 5-methoxyindan is similar to that of the 4-alkoxyazulenes in that it lacks marked fine structure (see figure 1). The visible absorption band has its wave-length of maximum absorption at 615 m\textmu, that is, moved bathochromically 35 m\textmu with respect to that of azulene. Since substitution of a methyl group in the 4-position and in the 5-position of azulene to give 4-methyl- and 5-methylazulene likewise causes equal and opposite displacements in their visible spectra it is
FIGURE 2.
evident that ring enlargement of 5-methoxyindan leads to the expected 5-methoxyazulene.

While substitution of an alkoxy group in the 5- and 4-positions of azulene causes displacements in the visible absorption band similar to those caused by the methyl group in the same positions, the magnitudes for the former are much greater, namely, $\pm 35 \text{ m\mu}$ for the alkoxy group compared with $\pm 12 \text{ m\mu}$ for the methyl group. This may be attributed to the greater electron donating (electromeric or $-E$) effect of the alkoxy group (c.f. p.13). If indeed the electromeric effect is operative, the behaviour of the alkoxy group in the seven-membered ring of the azulene nucleus is typical of that found when alkoxy, which carries unshared $p$-electrons, conjugates with an aromatic nucleus carrying $\pi$-electrons. The molar extinction coefficients at the wave-lengths of maximum absorption are higher for the methylazulenes than for azulene itself, and they are higher still for the alkoxyazulenes (see Table 1). This also may be due to the more powerful electromeric effect of the alkoxy group. Since the negative inductive ($-I$) effect of an ethyl group is greater than that of a methyl group, the electromeric ($-E$) effect of the ethoxy group should be greater than that of the methoxy group but this is not reflected in the visible spectra of 4-methoxy- and 4-ethoxyazulene which are practically identical. This is in agreement with the observation that spectral displacements are not affected
by second order effects (c.f. p.13).

Table 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda_{\text{max}} )</th>
<th>( \log_{10} \varepsilon )</th>
<th>( \Delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azulene</td>
<td>580 ( \mu )</td>
<td>2.48</td>
<td>-</td>
</tr>
<tr>
<td>4-Methoxyazulene</td>
<td>545 &quot;</td>
<td>2.81</td>
<td>-35 &quot; ( \mu )</td>
</tr>
<tr>
<td>4-Ethoxyazulene</td>
<td>545 &quot;</td>
<td>2.81</td>
<td>-35 &quot;</td>
</tr>
<tr>
<td>5-Methoxyazulene</td>
<td>615 &quot;</td>
<td>2.68</td>
<td>+35 &quot;</td>
</tr>
<tr>
<td>4-Methylazulene</td>
<td>568 &quot;</td>
<td>2.63</td>
<td>-12 &quot;</td>
</tr>
<tr>
<td>5-Methylazulene</td>
<td>592 &quot;</td>
<td>2.56</td>
<td>+12 &quot;</td>
</tr>
<tr>
<td>6-Methylazulene</td>
<td>565 &quot;</td>
<td>2.53</td>
<td>-15 &quot;</td>
</tr>
<tr>
<td>5-Methoxycarbonylazulene</td>
<td>565 &quot;</td>
<td>2.58</td>
<td>-15 &quot;</td>
</tr>
<tr>
<td>6-Methoxycarbonylazulene</td>
<td>635 &quot;</td>
<td>2.50</td>
<td>+55 &quot;</td>
</tr>
<tr>
<td>4-Methoxy-6-ethoxycarbonylazulene</td>
<td>605 &quot;</td>
<td>2.74</td>
<td>+25 &quot;</td>
</tr>
<tr>
<td>4-Methoxy-7-ethoxycarbonylazulene</td>
<td>535 &quot;</td>
<td>2.58</td>
<td>-45 &quot;</td>
</tr>
<tr>
<td>4-Methoxy-8-ethoxycarbonylazulene</td>
<td>590 &quot;</td>
<td>2.81</td>
<td>+10 &quot;</td>
</tr>
<tr>
<td>5-Methoxy-7-ethoxycarbonylazulene</td>
<td>612 &quot;</td>
<td>2.77</td>
<td>+32 &quot;</td>
</tr>
<tr>
<td>4-Hydroxyazulene-6-carboxylic acid (in ethanol)</td>
<td>590 &quot;</td>
<td>2.47</td>
<td>+10 &quot;</td>
</tr>
<tr>
<td>4-Hydroxyazulene-6-carboxylic acid (in alkali)</td>
<td>570 &quot;</td>
<td>2.62</td>
<td>-10 &quot;</td>
</tr>
</tbody>
</table>

Structures were assigned to the four isomeric methoxyazulene carboxylic esters described above by
examination of their visible spectra and comparison with those of azulene-5- and 6-carboxylic esters (XX and XXI). When the mixture of products from the reaction of indan (XIX) with diazoacetic ester was dehydrogenated two azulene esters were obtained, one blue, the other violet (Plattner, Fürst, Müller and Somerville, Helv. Chim. Acta, 1951, 34, 971). These were studied as the methyl esters. The structures originally assigned to them as esters of azulene-6- and 5-carboxylic acids respectively on the basis of the relatively higher melting points of the symmetrical 6-substituted derivatives were confirmed by conversion of the 5-ethoxycarbonyl group to an isopropyl group, giving the known 5-isopropylazulene (Plattner, Fürst, Müller and Keller, Helv. Chim. Acta, 1954, 37, 271).

Azulene-5- and 6-carboxylic esters must arise by ring expansion occurring at the 4:5 (6:7) and 5:6 bonds respectively of the original indan molecule, as indicated in XIX.

In the absence of any other azulene ester it was considered that ring expansion did not occur to any appreciable extent at the angular 4:9 (7:8) bonds of indan when the other unsubstituted and sterically less hindered bonds were available. Such reaction would have given the ester of azulene-4-carboxylic acid after dehydrogenation.
Nevertheless, that reaction can occur at such angular bonds is shown by the synthesis of 6:7-benzazulene (XXIII) from the cyclopentatetralin XXII, which like mesitylene

![XXII](image)
![XXIII](image)


Plattner, Fürst, Müller and Somerville (ibid.) found that an ester group in the 5-position of azulene caused a hypsochromic displacement of 15 mμ in the visible spectrum, and in the 6-position a bathochromic displacement of 55 mμ. These observations were supported by examination of the two esters obtained similarly from 2-methylindan and comparison of their visible spectra with that of 2-methylazulene, the relative displacements being -7 mμ for the ester group in the 5-position and +55 mμ for the ester group in the 6-position. Furthermore, the spectra of the carboxylic acids in alcohol and of their methyl esters in petrol-ether were found to be not significantly different.

4-Methoxyindan (XXIV) has only two unsubstituted C=C bonds available for reaction with diazoacetic ester, the 5:6 and 6:7 bonds.
Reaction at these positions followed by dehydrogenation should give 4-methoxy-6-ethoxycarbonylazulene and 4-methoxy-7-ethoxycarbonylazulene, respectively. The observed displacement in the visible spectrum of the first blue ester obtained from 4-methoxyindan is +25 m\mu (i.e. bathochromic) relative to the visible band for azulene. The calculated value for 4-methoxy-6-ethoxycarbonylazulene is +20 m\mu (i.e. -35+55). There is, therefore, sufficiently good agreement between the observed and calculated values to indicate that the crystalline blue ester is 4-methoxy-6-ethoxycarbonylazulene (XXV). Similarly, the observed displacement in the visible spectrum of the crystalline violet ester is -45 m\mu, and, since the 5- and 7-positions of the azulene nucleus are equivalent, the calculated value for 4-methoxy-7-ethoxycarbonylazulene is -50 m\mu (i.e. -35-15). The crystalline esters are, therefore, the two expected products of ring expansion at the unsubstituted C:C bonds of 4-methoxyindan.

The identity of the third ester is problematical. One possible structure is that which would arise by ring expansion at the 4:5 bond of 4-methoxyindan, that is, the bond substituted with the methoxyl group. Johnson, Johns
and Tisler (J., 1954, 4605) showed that a further product of the reaction of veratrole with diazoacetic ester was a dimethoxycycloheptatriene ester which on hydrogenation gave 2:7-dimethoxy-1-ethoxycarbonylcycloheptane (XXVII) and which must therefore have been formed by ring expansion at the disubstituted C:C bond of veratrole.

Similarly, the third methoxyazulene ester might be 4-methoxy-5-ethoxycarbonylazulene (XXVIII), and its visible absorption spectrum should be similar to that of 4-methoxy-7-ethoxycarbonylazulene (XXVI). But the observed displacement for the third ester is +10 μm and not -45 or -50 μm which the structure XXVIII requires.

Alternatively, if reaction occurred at the angular 4:9 or 7:8 bonds (as in the example on p.69) then the final products would be 5-methoxy-4-ethoxycarbonylazulene (XXIX) and 4-methoxy-8-ethoxycarbonylazulene (XXX) respectively.

The effect on the visible spectrum of an ester group in the 4-(8-)position of azulene is not known but it might reasonably be expected to cause a displacement similar in
direction and magnitude to that caused by an ester group in the 6-position, that is, possibly a large bathochromic displacement (see p.14). The visible spectrum of 5-methoxy-4-ethoxycarbonylazulene should, therefore, undergo a very large bathochromic displacement because of the large bathochromic effect (+35 m\( \mu \)) already caused by the methoxyl group in the 5-position, whereas the visible spectrum of 4-methoxy-8-ethoxycarbonylazulene would resemble that of 4-methoxy-6-ethoxycarbonylazulene. The visible spectrum of the third methoxyazulene ester does closely resemble that of 4-methoxy-6-ethoxycarbonylazulene and has its wave-length of maximum absorption at 590 m\( \mu \). This compound is then most probably 4-methoxy-8-ethoxycarbonylazulene (XXX). Allowing a displacement of -35 m\( \mu \) for the effect of the methoxyl group in the 4-position, it is assumed that an ester group in the 8-position of the azulene nucleus causes a bathochromic displacement of 45 m\( \mu \) in the visible absorption band.

In the reaction of 4-methoxyindan with diazoacetic ester the sites of attack of the reagent are found to include the 7-position both in the unsubstituted 6:7 bond and in the substituted 7:8 bond. The 7-position is activated to electron-seeking reagents by the \(-I\) effect of the adjacent methylene group of the cyclopentano ring and by the much more powerful \(-E\) effect of the methoxyl group in the 4-position. That is, there is at the 7-position of 4-methoxyindan a relatively high electron density.
The 5-position is activated similarly and the 5:6 bond also undergoes reaction. This is consistent with the hypothesis that the reacting form from diazoacetic ester is a dipolar radical formed by loss of nitrogen on heating.

The only unsubstituted C:C bond in the aromatic ring of 5-methoxyindan (XXXI) is the 6:7 bond at which ring-expansion would be expected to occur to give after dehydrogenation 5-methoxy-7-ethoxycarbonylazulene (XXXII).

![XXXI](image1)

![XXXII](image2)

The visible spectrum of this compound should be moved about +20 μμ (+35-15) relative to that of azulene. The visible spectrum of the single azulene ester isolated is one of the few possessing fine structure in which it is possible to identify and compare features with the corresponding features in the spectrum of azulene. The data for the comparable wave-lengths are given in Table 2 and are taken from figures 1 and 2 where the spectra of azulene and the methyl ester appear.
Table 2

<table>
<thead>
<tr>
<th>Azulene</th>
<th>5-Methoxy-7-methoxycarbonylazulene</th>
<th>△</th>
</tr>
</thead>
<tbody>
<tr>
<td>695 mμ</td>
<td>705 mμ</td>
<td>+10 mμ</td>
</tr>
<tr>
<td>657 &quot;</td>
<td>677 &quot;</td>
<td>+20 &quot;</td>
</tr>
<tr>
<td>627 &quot;</td>
<td>645 &quot;</td>
<td>+18 &quot;</td>
</tr>
<tr>
<td>580 &quot;</td>
<td>612 &quot;</td>
<td>+32 &quot;</td>
</tr>
<tr>
<td>555 &quot;</td>
<td>588 &quot;</td>
<td>+33 &quot;</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>+25 &quot;</td>
</tr>
</tbody>
</table>

Since the average displacement of the visible absorption band is in sufficiently good agreement with that expected, the azulene product from the ring-expansion of 5-methoxyindan with diazoacetic ester is most probably 5-methoxy-7-ethoxycarbonylazulene. In 5-methoxyindan the 6-position is activated by the -E effect of the methoxyl group, and the 7-position is activated by the -I effect of the adjacent methylene group. Since the 6:7 bond is also the only unsubstituted C:C bond in the molecule it appears that reaction and ring-expansion occur at this bond to the total exclusion of others in the molecule.

The acids obtained from hydrolysis of the crystalline blue ester 4-methoxy-6-ethoxycarbonylazulene (XXV) in ethanolic and aqueous potassium hydroxide solution must be respectively 4-ethoxy- and 4-hydroxyazulene-6-carboxylic
acids, XXXIII and XXXIV.

XXXIII

XXXIV

The visible spectra in alkaline solution of these acids in common with the findings of Plattner, Fürst, Müller and Somerville (ibid.) are not significantly displaced with respect to their spectra in neutral solution. The alkaline solutions owe their somewhat violet colour not to a significant hypsochromic displacement of the wave-length of maximum absorption but to increased absorption in the 400-500 \( \mu \) region. This is particularly noticeable on comparing the spectra in neutral and in alkaline solution of 4-hydroxyazulene-6-carboxylic acid (figure 3). The overall increase in the molar extinction coefficients in alkaline solution may also indicate ionisation of both the hydroxyl and the carboxyl group (c.f. the solubility in alkali of 4-hydroxyazulene, p.56).

It is more difficult to systematise the ultra-violet spectra of the above azulenes. The ultra-violet spectra of azulenes in neutral solution fall broadly into three main bands. In the spectrum of azulene itself these are at 200-250, 250-310 and 310-360 \( \mu \), respectively (figure 1). While in the ultra-violet spectra of substituted azulenes there is a general bathochromatic displacement, the greatest
differences in the absorption are observed in the third region, that is, in the near ultra-violet. It is found moreover that a methyl group in the 4-position causes a slightly greater bathochromic displacement in this region than a methyl group in the 5-position (Plattner and Heilbronner, Helv. Chim. Acta, 1947, 30, 910). In the ultra-violet spectra of the 4-alkoxyazulenes this band is also displaced somewhat more than the corresponding band for 5-methoxyazulene. The data are summarised in Table 3 for the principal features in the near ultra-violet band.

<table>
<thead>
<tr>
<th>Azulene</th>
<th>4-Methoxyazulene</th>
<th>4-Ethoxyazulene</th>
<th>5-Methoxyazulene</th>
</tr>
</thead>
<tbody>
<tr>
<td>353 (\mu) (inf.)</td>
<td>365 (\mu)</td>
<td>368 (\mu)</td>
<td>355 (\mu)</td>
</tr>
<tr>
<td>340 &quot;</td>
<td>343 &quot; (inf.)</td>
<td>345 &quot; (inf.)</td>
<td>340 &quot;</td>
</tr>
<tr>
<td>326 &quot;</td>
<td>335 &quot;</td>
<td>333 &quot;</td>
<td>332 &quot;</td>
</tr>
<tr>
<td>291 &quot; (inf.)</td>
<td>307 &quot;</td>
<td>307 &quot;</td>
<td>-</td>
</tr>
<tr>
<td>275 &quot;</td>
<td>282 &quot;</td>
<td>282 &quot;</td>
<td>272 &quot;</td>
</tr>
<tr>
<td>224 &quot;</td>
<td>250 &quot;</td>
<td>250 &quot;</td>
<td>-</td>
</tr>
</tbody>
</table>

Plattner, Fürst, Müller and Somerville (ibid.) found that in the 300-400 \(\mu\) region the bathochromic displacement of the bands is greater for 5-methoxycarbonylazulene.
**FIGURE 4.**

Graph showing the spectral analysis of different compounds. The graph includes two lines:
- Red line: *α*-Ethoxyazulene in conc H2
- Blue line: *β*-Ethoxyazulene
than for 6-ethoxycarbonylazulene. Displacements in this region cannot be additive for the displacement for 4-methoxy-7-ethoxycarbonylazulene would require to be greater than that for 4-methoxy-6-ethoxycarbonylazulene and this is not so (figure 2). The displacements in this region of the spectra of these 4-methoxyazulene esters is, however, relatively much greater than for 4-methoxyazulene. The ultra-violet spectrum of 4-methoxy-8-ethoxycarbonylazulene is noticeably different from the other two in that the band in the 340-400 m\(\mu\) region is much depressed and moved only a little towards longer wavelengths. In the ultra-violet spectrum of 5-methoxy-7-methoxycarbonylazulene there is a distinct maximum at 320 m\(\mu\) which corresponds to only points of inflection in the same region of the spectra of the 4-methoxyazulene esters.

The alkoxyazulenes are soluble in concentrated mineral acids from which they can be recovered unchanged on dilution. The ultra-violet spectra in acid solution of the alkoxyazulenes resemble those determined in neutral solvents (figures 4 and 5). There is however a considerable broadening and bathochromic displacement in the near ultra-violet compared with the spectra in neutral solution. The spectra in acid solution of the 4- and 5-alkoxyazulenes are in general agreement with those for other azulenes determined by Plattner, Heilbronner and Weber (Helv. Chim. Acta, 1952, 35, 1036) and Chopard-dit-Jean and Heilbronner (ibid., p.2170). In the spectra of the alkoxyazulene
A: 4'-METHOXY - 6'-ETHOXYCABONYL (in con. HBr)
B: 2'-METHOXY - 7'-ETHOXYCABONYL (... )
C: 4'-METHOXY - 8'-ETHOXYCABONYL (in 65% H2SO4)
D: 6'-METHOXY - 7'-METHOXYCABONYL (... )

FIGURE 5.
esters in acid solution this broadening appears as a fourth distinct band in the region 360-420 m\(\mu\) (figure 5). While in neutral solution there is no significant difference in the extinction coefficients in the ultra-violet region of the spectra of the 4-alkoxy- and 5-methoxyazulenes and their derivatives, in acid solution the curves for the 5-methoxy-compounds are consistently lower than those for the 4-methoxy- derivatives, but otherwise the shapes of the curves are very similar. In acid solution the visible absorption of the above alkoxyazulenes and ester derivatives is extinguished due to proton acceptance at the carbanionic centres. Two sites are available in each molecule for protonation and since the molecules are unsymmetrical this could give rise to two different cations from each. The sites of protonation are unknown but are represented as in XXXV for convenience.

\[
\begin{array}{c}
\text{XXXVa} \\
\text{XXXVb}
\end{array}
\]

The stability of the alkoxyazulenes to acid hydrolysis is in very marked contrast to the ease of scission of the O-alkyl bond of tropolone ethers in acid solution. The methyl ether of tropolone bears a formal resemblance to 4-methoxy- and 5-methoxyazulene for in each the ether oxygen atom is directly united to a seven-membered
carbocyclic system in which cycloheptatrienylium structures contribute.

The ease of hydrolysis of tropolone methyl ether in acid solution can be explained by postulating the protonated ion XXXVIa in which the positive charge is shared by all the ring atoms (c.f. Pauson, Chem. Rev., 1955, 55, 43 and 63-64). Loss of the proton (solvated in aqueous solution) leads to the re-formation of tropolone methyl ether but if, as is equally probable, a methyl carbonium ion is lost from the cation XXXVIc then tropolone is the product. In an aqueous acid medium methyl carbonium ion would be removed from the system as quickly as it was formed and so scission of the O-methyl bond proceeds rapidly to completion. In acid solution the 4- and 5-alkoxyazulenes must exist substantially as the cycloheptatrienylium salts of the type XXXVa for if structures of the type XXXVb contributed significantly then this would be expected to lead to ease of hydrolysis similar to that found for tropolone methyl ether. The tetramethoxybenzotropylium cation XXXVII of Schaeppi, Schmid, Heilbronner and Eschenmoser (Helv. Chim. Acta, 1955, 38, 1874) is similar to the cations formed by solution in acid of the above alkoxyazulenes, and like them
is stable against hydrolysis of the methoxyl groups in acid solution. The fact that a stable 4-hydroxyazulene could be isolated indicates that there is little tendency for conversion from the azulene to the tropone series, for all that is required to bring this about is a tautomeric shift.

![Structural diagram](image)

Of the five isomeric mono-methoxyazulenes possible only the 2- and 6-isomers remain to be synthesised. Attempts to prepare 2-methoxyazulene, or ester derivatives of it, by ring expansion with diazoacetic ester of 2-methoxyindan failed because of the lability of the methoxyl group. 2-Methoxyindan was treated with diazoacetic ester and on distillation of the higher boiling reaction products a blue oil was obtained. This was separated by chromatography into a deep blue fraction which contained a little violet material, and a pale green oil which on heating with sulphur afforded more blue material. The oxyacetic acid derivative presumed present was not isolated. Analysis of the blue oil which was purified by acid extraction, chromatography and distillation showed it to be an ethoxycarbonylazulene which must be the 6-derivative. Unlike the methyl esters described by Plattner, Fürst, Müller and Somerville this ester failed to give a
trinitrobenzene complex, but although these workers obtained 5-ethoxycarbonylazulene pure and crystalline they do not report that it gave a trinitrobenzene complex. Hydrolysis of the blue ester and decarboxylation afforded only azulene. Reduction with lithium aluminium hydride of the blue ester gave a crystalline violet-blue hydroxymethyleneazulene which must also be the 6-derivative.

The ease with which the methoxyl group is lost from the 2-position of the products of reaction of 2-methoxy-indan with diazoacetic ester is in contrast to the stability of the same group in the 1-position which apparently survives heating at 280 degrees with selenium for twenty minutes.

The absorption spectrum of 6-hydroxymethyleneazulene is shown in figure 6. The ultra-violet absorption shows the expected slight bathochromic displacement similar to that caused by a methyl group. In the visible region, while the maximum is at 580 m\(\mu\), the expected small hypsochromic displacement is evident in the 630 and 690 m\(\mu\) regions.
In the following section all yields are reported directly as weight of product obtained from given weights of starting materials.

All melting points were determined by means of a Kofler micro-melting point apparatus.

Chromatographic separations were carried out on columns prepared from Activated Alumina Type "H", supplied by Peter Spence & Sons Ltd., Widnes.

Spectral determinations were made using a Unicam SP500 spectrophotometer and with 10 mm. silica cells.

Analyses were performed by Drs. Weiler and Strauss, Oxford.
THE SYNTHESIS OF 4- AND 5-ALKOXYAZULENES.

The reaction of 4-methoxyindan with diazoacetic ester.

4-Methoxyindan was prepared from 4-hydroxyindan with dimethyl sulphate and potassium hydroxide in the usual way and was obtained as a colourless liquid, b.p. 127-128°/31 mm.

4-Methoxyindan (30.0 g.) was placed in a 100 ml. round bottomed flask fitted with a dropping funnel, a stirrer and an air condenser drawn out to a wide capillary at the exit end, and was heated in an oil bath to 140°. This temperature was maintained while diazoacetic ester (13.0 g.) was added dropwise during 3 hr. The temperature of the bath was then raised to 200° during 2 hr., with continued stirring of the mixture. Unreacted 4-methoxyindan (17.0 g., b.p. 133°/50 mm.) was distilled off and was preceded by a colourless liquid (3.0 g., b.p. 72-75°/47 mm.) arising possibly from the decomposition of diazoacetic ester.

Analysis. Found: C, 45.1%; H, 7.0%.

The high boiling residue was fractionally distilled under reduced pressure to give the following fractions:

(i) unreacted 4-methoxyindan (2.0 g.) boiling about 85°/1.5 mm.

(ii) a mobile oil (4.5 g.), green in reflected light, red in transmitted, boiling up to 150°/0.3 mm.
(iii) a viscous red oil (2.4 g.) boiling 150-180°/0.3 mm.
(iv) a residual brown tar (8.0 g.).

4-Indanyloxyacetic acid.

Fraction (ii) (720 mg.) was boiled in 3% ethanolic potassium hydroxide for 2 hr. The mixture was poured into water and extracted with ether to remove neutral material. The aqueous layer was acidified with dilute hydrochloric acid and the precipitated material extracted with ether. The ether extract was washed with water, dried over sodium sulphate, and on evaporation gave an oily residue (600 mg.) which gave colourless needles or prisms from benzene (480 mg.), m.p. 184°, identical (mixed melting point) with authentic 4-indanyloxyacetic acid prepared in the usual way from the phenol and chloroacetic acid.

Analysis. Found: C, 68.6%; H, 6.4%.
C_{11}H_{12}O_{3} requires C, 68.7%; H, 6.3%.

The benzene mother liquors on evaporation gave a green oil.

Fraction (iii) on hydrolysis gave similarly a small amount of this same acid (melting point and mixed melting point), the bulk of the hydrolysis product being a green oil.

Heating with selenium at 270° and with 20% palladium charcoal at 320° failed to convert any of these mixed acid products to azulenin material. Only charring occurred.
The isomeric ethoxycarbonyl-4-methoxyazulenes.

The above fraction (ii) (7.0 g.) from the distillation of the reaction products of 4-methoxyindan and diazo-acetic ester was heated with sulphur (2.0 g.) for 5 minutes in an oil bath at 200°. The colour of the mixture changed to a dark blue-green and hydrogen sulphide was evolved. Longer heating causes the mixture to become brown and does not improve the yield. The mixture was cooled, taken up in the minimum amount of benzene and was chromatographed on neutral alumina. A broad blue band developed which was eluted with a mixture of benzene and light-petroleum (1:1). This was followed by a broad green band which was eluted with benzene. Finally, ethanol was passed down the column and gave a brown tarry eluate which was not examined further.

The blue eluate was diluted with light-petroleum and was extracted with syrupy phosphoric acid to give an orange coloured acid layer. Excess sulphur and some green material was retained by the organic layer. The acid layer was washed with a mixture of benzene and light-petroleum (1:1), and was then poured into ice-water. The precipitated blue material was extracted into ether, the extract dried over anhydrous sodium sulphate, and the solvent evaporated. The residue was a mobile blue oil (510 mg.).

The above green eluates gave a green oil (2.1 g.) which contained some sulphur. Attempted further
dehydrogenation of this oil with sulphur gave no more blue products. Hydrolysis of this green oil gave a small amount of 4-indanyloxyacetic acid, as above.

Similarly, dehydrogenation of fraction (ii) (1.2 g.) with 20% palladium charcoal for 8 minutes at 240° gave a blue oil (130 mg.) recovered from phosphoric acid, and a green oil (0.7 g.) which could not be further dehydrogenated.

Dehydrogenation with sulphur (0.8 g.) of fraction (iii) (2.0 g.) gave similarly a small amount of a blue oil (30 mg.).

The above blue oils (650 mg.) were combined and chromatographed on neutral alumina, giving the following products:

(i) on elution with a mixture of benzene and light-petroleum (1:9), a blue eluate which on evaporation gave a blue oil (380 mg.). This oil gave a crystalline trinitrobenzene complex which was decomposed on a column of neutral alumina in the usual way. The blue oil which was eluted with the same mixture of benzene and light-petroleum was further chromatographed, until finally it deposited from a mixture of light-petroleum and benzene dark blue blades with a green reflection, m.p. 63.5-64.5°. This is 4-methoxy-6-ethoxycarbonylazulene.

Analysis. Found: C, 73.1%; H, 6.2%.

C_{14}H_{14}O_3 requires C, 73.0%; H, 6.1%.

The trinitrobenzene complex was prepared in the
usual way and crystallised from ethanol as brown needles, m.p. 90-92°.

Analysis. Found: C, 53.7%; H, 3.7%; N, 10.0%.
C₂₀H₁₇O₉N₃ requires C, 54.2%; H, 3.9%; N, 9.5%.

(ii) on elution with a mixture of benzene and light-petroleum (1:1), a violet eluate which gave a violet oil (200 mg.) on removal of the solvent. This oil was further purified by chromatography until an ethanolic solution of it, on cooling, deposited violet needles, m.p. 76.5-77.5°. This compound is 4-methoxy-7-ethoxycarbonylazulene.

Analysis. Found: C, 73.2%; H, 6.1%.
C₁₄H₁₄O₃ requires C, 73.0%; H, 6.1%.
The trinitrobenzene complex was prepared in the usual way and crystallised from ethanol as orange needles, m.p. 102-103°.

Analysis. Found: C, 53.7%; H, 3.6%; N, 9.4%.
C₂₀H₁₇O₉N₃ requires C, 54.2%; H, 3.9%; N, 9.5%.

(iii) on elution with benzene, a blue eluate which on evaporation gave a blue oil (8 mg.). This was converted to the trinitrobenzene complex which was recrystallised twice from ethanol, giving brown plates, m.p. 123°. The blue oil is 4-methoxy-8-ethoxycarbonylazulene.

Analysis. Found: C, 54.1%; H, 4.0%; N, 9.2%.
C₂₀H₁₇O₉N₃ requires C, 54.2%; H, 3.9%; N, 9.5%. 
4-Ethoxyazulene-6-carboxylic Acid.

4-Methoxy-6-ethoxycarbonylazulene (125 mg.) was hydrolysed with 4% ethanolic potassium hydroxide (25 ml.) for 2 hr. under reflux. The mixture was poured into water giving a violet-blue aqueous solution which was extracted with ether to remove neutral material. The aqueous solution was acidified with dilute hydrochloric acid and the precipitated solid was extracted into ether, giving a deep blue ethereal layer. The ether extract was washed with water and dried over sodium sulphate. On evaporation it gave a green crystalline residue (100 mg.) which was recrystallised from a mixture of benzene and ethanol, giving green needles, m.p. 234-236° (with decomposition).

Analysis. Found: C, 72.1%; H, 5.4%.

C_{13}H_{12}O_3 requires C, 72.2%; H, 5.6% (i.e. for ethoxy-)

While C_{12}H_{10}O_3 requires C, 71.3%; H, 5.0% (i.e. for methoxy-).

4-Hydroxyazulene-6-carboxylic Acid.

4-Methoxy-6-ethoxycarbonylazulene (30 mg.) was boiled under reflux with 4% aqueous potassium hydroxide (25 ml.) for 2 hr. The intense violet coloured solution was filtered and extracted with ether to remove neutral material. The solution was acidified with dilute hydrochloric acid and the precipitated solid was extracted into ether giving a deep blue solution. The ether extract was washed and dried and on evaporation of the solvent gave a
green crystalline residue (20 mg.) which was recrystallised from a mixture of benzene and ethanol, giving green needles decomposing at 235°.

Analysis. Found: C, 69.6%; H, 4.8%.

C₁₁H₈O₃ requires C, 70.2%; H, 4.3% (i.e. for hydroxy-)
while C₁₂H₁₀O₃ requires C, 71.3%; H, 5.0% (i.e. for methoxy-).

The foregoing acid in admixture with this one begins to melt about 195° and melting, with decomposition, is complete at 230°.

4-Ethoxyazulene.

The crude mixture of blue oils (190 mg.), recovered from the phosphoric acid extraction as described on p.85 was hydrolysed with 4% ethanolic potassium hydroxide and after treatment as above gave a green crystalline acid mixture (140 mg.). This mixture was heated with copper bronze (1.0 g.) in quinoline (20 ml.) at 240° for 45 minutes. The decarboxylation product was freed from unchanged azulene acids by extraction with sodium hydrogen carbonate solution as described for similar experiments on p.42. Quinoline was removed by repeated extraction with dilute hydrochloric acid. The neutral residual solid material was chromatographed on alumina, giving the following fractions:

(i) on elution with light-petroleum, a blue oil (4 mg.) which showed some tendency to crystallise. This oil gave a crystalline trinitrobenzene complex, melting about 150°,
which was decomposed on alumina in the usual way. The blue solid which was obtained by elution with petrol and evaporation of the solvent was again converted to the trinitrobenzene complex which was recrystallised from ethanol, giving brown needles, m.p. 166-167°, identical (mixed melting point) with the trinitrobenzene complex of azulene.

(ii) on elution with a mixture of benzene and light-petroleum (1:3), a violet oil (12 mg.) which could not be obtained crystalline. This violet oil is 4-ethoxyazulene and it gave a crystalline trinitrobenzene complex which was recrystallised from ethanol, giving red-brown needles, m.p. 143°.

Analysis. Found: C, 56.2%; H, 4.0%; N, 10.4%.
C₁₈H₁₅O₇N₃ requires C, 56.1%; H, 3.9%; N, 10.9%.

The bulk of the material chromatographed remained as a brown band at the top of the column.

On distillation of the eluate containing 4-ethoxyazulene a violet colour appeared in the distillate, i.e. the compound is volatile in organic solvents.

4-Methoxyazulene.

The same crude mixture of blue oils (110 mg.) was hydrolysed for 2 hr. in 4% methanolic potassium hydroxide (25 ml.) and gave a green crystalline acid mixture (80 mg.) as above. This was decarboxylated in quinoline (20 ml.) containing copper bronze (0.5 g.) by heating at 240° for
45 minutes. The neutral product was chromatographed on alumina and gave a faint blue band eluted with light-petroleum, which, as above, gave a trace of the trinitrobenzene complex of azulene. Elution with a mixture of benzene and light-petroleum (1:3) gave a violet eluate which on evaporation of the solvent gave a violet oil (7 mg.). This is 4-methoxyazulene and it gave a crystalline trinitrobenzene complex which was recrystallised from ethanol as red-brown needles, m.p. 163°.

Analysis. Found: C, 55.2%; H, 3.6%; N, 10.8%. C_{17}H_{13}O_7N_3 requires C, 55.0%; H, 3.5%; N, 11.3%.

4-Methoxyazulene was found to be volatile in organic solvents.

The bulk of the material chromatographed remained as a strongly adsorbed brown band at the top of the column.

On reducing the time of decarboxylation a better yield of product was obtained. Thus, 90 mg. of the same acid mixture was heated with copper bronze in quinoline for 20 minutes at 240° and gave 14 mg. of 4-methoxyazulene which was converted to the crystalline trinitrobenzene complex. In this experiment no azulene was found. Further significant reduction of the decarboxylation time resulted only in the major part of the azulene acid mixture being recovered unchanged.

The reaction of 5-methoxyindan with diazoacetic ester.

5-Methoxyindan was prepared from 5-hydroxyindan with
dimethyl sulphate and potassium hydroxide in the usual manner and was obtained as a colourless liquid, b.p. 143-145°/60 mm.

The reaction of 5-methoxyindan (40·0 g.) with diazoacetic ester (16·0 g.) was carried out as on p.83 the ester being added during 4 hr. at 140° and the temperature being raised to 200° during 3 hr. Unreacted 5-methoxyindan (25·5 g., b.p. 132°/39 mm.) was distilled off under reduced pressure. The residue was distilled to give:

(i) unreacted 5-methoxyindan (1·9 g.) boiling about 95°/0·6 mm.
(ii) a mobile green oil (6·8 g.) boiling up to 145°/0·6 mm.
(iii) a viscous green oil (2·3 g.) boiling up to 190°/0·6 mm.
(iv) a residual tar (12·5 g.).

5-Indanyloxyacetic Acid.

Fraction (ii) (1·0 g.) was hydrolysed with 3% ethanolic potassium hydroxide (30 ml.) under reflux for 2 hr. and the acidic product obtained as above was a green oil (0·8 g.) which gave colourless plates from benzene (580 mg.), m.p. 157°. (Kruber et al., Ber., 73b, 1176, give the melting point of 5-indanyloxyacetic acid as 157°).

Analysis. Found: C, 68·7%; H, 6·6%.

C11H12O3 requires C, 68·7%; H, 6·3%.
5-Methoxy-7-ethoxycarbonylazulene.

Fraction (ii) (8.0 g.) was heated with sulphur (2.0 g.) for 5 minutes in an oil bath at 200°. The mixture was cooled, taken up in a small amount of benzene and chromatographed on a column of neutral alumina. Elution with a mixture of benzene and light-petroleum (1:3) gave a deep blue eluate. Elution with benzene gave a green eluate. A strongly adsorbed brown tarry oil which was eluted with ethanol was not investigated further.

The blue eluate was diluted with light-petroleum and was extracted with syrupy phosphoric acid to give an orange-coloured acid layer. The acid extract was diluted, extracted with ether and the ether extract washed, dried over sodium sulphate and evaporated to give a blue oil (710 mg.). Chromatography of this oil on neutral alumina gave only one blue band which was eluted with a mixture of benzene and light-petroleum (1:3). Evaporation of the solvent left 5-methoxy-7-ethoxycarbonylazulene as a blue oil/which even after repeated chromatography could not be obtained crystalline. The trinitrobenzene complex was prepared in the usual way and was recrystallised from ethanol, giving brown needles, m.p. 70°.

Analysis. Found: C, 53.9%; H, 3.8%; N, 9.7%.

C_{20}H_{17}O_{9}N_{3} requires C, 54.2%; H, 3.9%; N, 9.5%.

5-Methoxy-7-methoxycarbonylazulene was obtained from the foregoing ester by hydrolysis and re-esterification with diazomethane and was likewise a blue oil which gave
a crystalline trinitrobenzene complex as brown needles from ethanol, m.p. 118°.

Analysis. Found: C, 53.3%; H, 3.7%; N, 9.8%. 
C_{19}H_{15}O_{9}N_{3} requires C, 53.2%; H, 3.5%; N, 9.8%.

5-Methoxyazulene.

5-Methoxy-7-ethoxycarbonylazulene (180 mg.) was hydrolysed with 4% ethanolic potassium hydroxide (25 ml.) and gave a green crystalline acid product (140 mg.). This was decarboxylated with copper bronze (0.5 g.) in quinoline (20 ml.) at 240° for 45 minutes. Chromatography of the neutral product on alumina gave a single blue band which on elution with a mixture of benzene and light-petroleum (1:3) and removal of the solvent gave a blue oil (18 mg.). This was 5-methoxyazulene which could not be obtained crystalline and which gave a crystalline trinitrobenzene complex in the usual way as shining black needles from ethanol, m.p. 125°.

Analysis. Found: C, 54.8%; H, 3.4%; N, 11.3%. 
C_{17}H_{13}O_{7}N_{3} requires C, 55.0%; H, 3.5%; N, 11.3%.

5-Methoxyazulene was found to be volatile in organic solvents.
The reaction of 2-methoxyindan with diazoacetic ester.

2-Hydroxyindan was prepared according to Whitmore and Gebhart (J. Amer. Chem. Soc., 1942, 64, 912) and was obtained as colourless needles m.p. 70°. 2-Hydroxyindan (42 g.) was methylated with methyl iodide and silver oxide in the usual way and 2-methoxyindan (32 g.) was obtained as a colourless liquid, b.p. 100-103°/14-15 mm.

Analysis. Found: C, 81·0%; H, 8·1%.
C_{10}H_{12}O requires C, 81·0%; H, 8·2%.

The reaction of 2-methoxyindan (32·0 g.) with diazoacetic ester (12·0 g.) was carried out as above, the ester being added during 4 hr. at 140° and the temperature being raised to 200° during 3 hr. Unreacted 2-methoxyindan (27·2 g., b.p. 98-100°/12 mm.) was distilled off. The distillate was colourless at first but was a distinct blue colour towards the end. The residue was distilled under reduced pressure to give:

(i) unreacted 2-methoxyindan (1·8 g.) boiling about 70°/0·3 mm.
(ii) a deep and intensely coloured blue oil (6·2 g.) boiling up to 180°/0·3 mm.
(iii) a viscous green oil (1·5 g.) boiling 180-200/0·3 mm.
(iv) a residual brown tar.
6-Ethoxycarbonylazulene.

Fraction (ii) (3.3 g.) was chromatographed on an alumina column to give:

(i) on elution with a mixture of benzene and light petroleum (1:3) a blue eluate which on evaporation of the solvent gave a blue oil (1.8 g.),

(ii) on elution with ethanol a broad buff coloured band near the top of the column was eluted giving a green coloured eluate. Removal of the solvent left a green oil (1.5 g.) which was heated with sulphur (0.5 g.) at 200° for 5 minutes. The colour became deep blue and then green. The product was chromatographed on alumina, and elution with a mixture of benzene and light-petroleum (1:4) gave a blue eluate which on evaporation gave a blue oil (160 mg.). This was added to that described above.

The blue oil was taken up in light petroleum and extracted with syrupy phosphoric acid to give a pale yellow acid layer. A faint violet colour remained in the petrol layer which was discarded. Dilution of the acid layer and extraction with ether led to recovery of the blue oil which was further purified by chromatography and which appeared to be a single substance. It was prepared for analysis by distillation in a micro-distillation apparatus heated at 120° (bath temperature), pressure 10⁻⁴ mm.

Analysis. Found: C, 77.8%; H, 6.7%.

C₁₃H₁₂O₂ requires C, 78.0%; H, 6.1%.
The blue oil is 6-ethoxycarbonylazulene. It failed to give a trinitrobenzene complex. The blue oil (1.0 g.) was hydrolysed with 3% ethanolic potassium hydroxide and the acid product was decarboxylated with copper bronze in quinoline at 240°. Chromatography of the neutral product gave a single blue-violet eluate which gave on evaporation a crystalline residue (85 mg.). This was converted to the trinitrobenzene complex, shining brown-black needles m.p. 166-167°, identical with the trinitrobenzene complex of azulene (mixed m.p.).

The blue oil (300 mg.) was reduced with lithium aluminium hydride (60 mg.) in dry ether. The deep blue colour of the ester was replaced within a few minutes by the less intense colour of the reduction complex. On adding the mixture to water the intense blue colour reappeared. The product was chromatographed on alumina to give:

(i) on elution with a mixture of benzene and light-petroleum (1:1) a very faint pink eluate followed by a faint blue eluate. Both were discarded.

(ii) on elution with a mixture of ether and light-petroleum (1:1) a pale green eluate which was discarded.

(iii) on elution with a mixture of ethanol and light-petroleum (1:9) a concentrated blue eluate. Evaporation of the solvent left a crystalline residue (190 mg.) which was recrystallised from benzene solution, giving violet-blue plates, m.p. 116-118°.
Analysis. Found: C, 83.3%; H, 6.8%.

C₁₁H₁₀O requires C, 83.5%; H, 6.4%.

The compound is 6-hydroxymethyleneazulene. It failed to give a trinitrobenzene complex.
DISCUSSION

THEREACTION OF AZULENE WITH SODAMIDE IN LIQUID AMMONIA.

The experimental evidence that the 4-position of azulene is the most susceptible to nucleophilic substitution, although strong, is less plentiful than that concerning the sites of electrophilic substitution. The only experiments on the direct nucleophilic substitution of azulene which have yet been published are those of Hafner and Weldes (Angew. Chem., 1955, 67, 302) who showed that azulene reacts with alkyl and aryl lithium compounds to give 4-alkyl- and arylidihydroazulenes which on dehydrogenation give the 4-substituted azulenes. Further treatment affords similarly 4:8-disubstituted azulenes.

The experimental conditions for nucleophilic substitution of an aromatic molecule are usually severe but in view of the fact that particularly mild reagents were used to effect electrophilic substitution of azulene it appeared that similar ease of nucleophilic substitution might obtain. Treatment of azulene with potassium alkoxides in alcoholic solution at 120 degrees caused rapid destruction. On attempted dehydrogenation of the product no blue product was isolated. Treatment with sodamide in liquid ammonia appeared more promising and in fact a basic red compound was readily isolated. This compound was solid and
crystalline but while it appeared reasonably stable in solution it very quickly decomposed in the solid state on exposure to air. It formed a crystalline trinitrobenzene complex which was more stable but which did not analyse completely satisfactorily.

The strongly basic properties of this compound indicate that it is an aminoazulene formed by direct substitution by the amide ion in the azulene nucleus. The absorption spectrum in neutral solution is typically azulenic and very similar to that of the 4-alkoxyazulenes (figure 7). The visible absorption however has its maximum at 505 m\(\mu\), i.e. the hypsochromic displacement relative to the visible absorption of azulene is 75 m\(\mu\). This is the greatest displacement which has yet been observed for a mono-substituted azulene and the magnitude is in agreement with the fact that the amino group is a stronger electromeric group than the alkoxy group which causes displacements of -35 and -15 m\(\mu\) in the 4- and 6-positions respectively. The direction of spectral displacement of the basic compound indicates substitution at either the 4- or the 6-position. It is probable that substitution in the 4-position would result in a greater displacement than that caused by substitution in the 6-position. In view of the very large displacement observed it appears unlikely that substitution has occurred in the 6-position.

Acid solutions of the basic compound formed on reaction of azulene with sodamide were colourless indicating that
protonation had occurred at the carbon atoms (1) or (3). This must mean that the canonical structure I contributes significantly to the resonance hybrid.

\[ \text{I} \]

The ultra-violet absorption spectra of neutral and acid solutions of the compound resemble those of 4-ethoxyazulene except that they are moved bathochromically. This is most marked in the near ultra-violet band for the amine in neutral solution.

Similar treatment of azulene with potassium diphenyllimide after Bergstrom, Granara and Erickson (J. Org. Chem., 1942, 7, 98) yielded no reaction product. Only unchanged azulene was recovered.

Further work is proceeding on this subject.
Sodium (2.0 g.) was dissolved in liquid ammonia (200 ml.) and ferric nitrate (0.1 g.) was added. When the blue colour was completely discharged azulene (240 mg.) in dry ether (10 ml.) was added to the mixture which was swirled vigorously. The mixture was agitated at frequent intervals during 5 hr. At the end of this time excess liquid ammonia was expelled by dipping the flask in lukewarm water.

Moist ether was added to the solid residue in the flask. To this was added ethanol and finally water to cause complete decomposition of excess sodamide. The mixture was filtered to remove the residue of iron and the layers separated. The ether layer was coloured a violet-red. It was washed with water and extracted with 4N hydrochloric acid. The very pale green acid layer was washed with ether and then neutralised with dilute sodium hydroxide solution. The mixture became bright red and was extracted with ether, giving a red ethereal solution. This was dried over sodium sulphate and evaporated leaving a bright red crystalline residue (120 mg.). Within a few minutes a brown crust had formed which was insoluble in warm ethanol. Solutions of the red compound appear relatively stable. Unchanged azulene (40 mg.) was recovered from the original acid-extracted ethereal solution. The red compound formed a crystalline trinitrobenzene complex, brown needles from ethanol, decomposing at 216°.
Analysis: Found: C, 54.4%; H, 3.6%; N, 13.9%.

53.9%; H, 3.5%; N, 12.9%.

C_{16}H_{12}N_{4}O_{6} requires C, 53.9%; H, 3.4%; N, 15.7%.

For the spectral determinations aliquots of an ethereal solution of the red compound were evaporated to dryness under reduced pressure and immediately redissolved in equal volumes of pure ethanol and 2N hydrochloric acid respectively. The acid solution was colourless.
Reviews

   See pp. 448, 449, 461.

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