218. *The Azulene Series. Part II.* The Synthesis and Properties of Alkoxyazulenes.*

By D. H. Reid, W. H. Stafford, and J. P. Ward.

4- and 5-Methoxyazulene have been synthesised by ring-expansion of the corresponding methoxyindane employing the sequence: reaction with diazoacetic ester, dehydrogenation, hydrolysis, and decarboxylation. The susceptibility of the 4-position to nucleophilic attack is proved by an ether exchange reaction leading to 4-ethoxyazulene. The relation of these substances and their derivatives to alkoxytropylium salts is examined and unsuccessful attempts to prepare 1- and 2-methoxyazulene are recorded. The reactions of azulene with sodamide and other nucleophilic reagents are briefly outlined.

Four claims have been recorded for the preparation of azulene derivatives in which an oxygen atom is directly linked to the seven-membered ring. Analytical purity was not obtained in two instances, 2-ethyl-7-methoxy-4-methylazulene [1] because of a contaminating hydrocarbon, and 4-hydroxyazulene [2] because of inherent instability. Details of the preparation of 4 : 5-dimethoxyazulene [3] are awaited but in the fourth instance, 6-methoxy-1 : 2-benzazulene,[4] the preparation and absorption spectrum have been given. In view of the structural relation [5] of this group of azulene derivatives to the alkoxytropylium salts, routes to the simple alkoxyazulenes were sought.

Treatment of 4-methoxyindane with ethyl diazoacetate, distillation, and hydrolysis of the principal fraction yielded 4-indanyloxyacetic acid [6,7] (I), in 80% yield, together with a crude acid fraction from which no azulenic material could be isolated after dehydrogenation. The balance of the ester fraction, 20%, must contain substantial quantities of ring-expanded material, for direct dehydrogenation of the ester mixture with sulphur gave an overall 8% yield of azulenic products.

Chromatography on alumina resolved the azulenic material into three ethyl methoxyazulenecarboxylates, *A* (blue), *B* (violet), and *C* (blue). *A* and *B* were obtained in a pure crystalline condition and were characterised as their *sym.*-trinitrobenzene complexes. The fraction *C* was present in minute quantities and was isolated conveniently only as its complex. There was no evidence for loss of the methoxyl group at this stage.

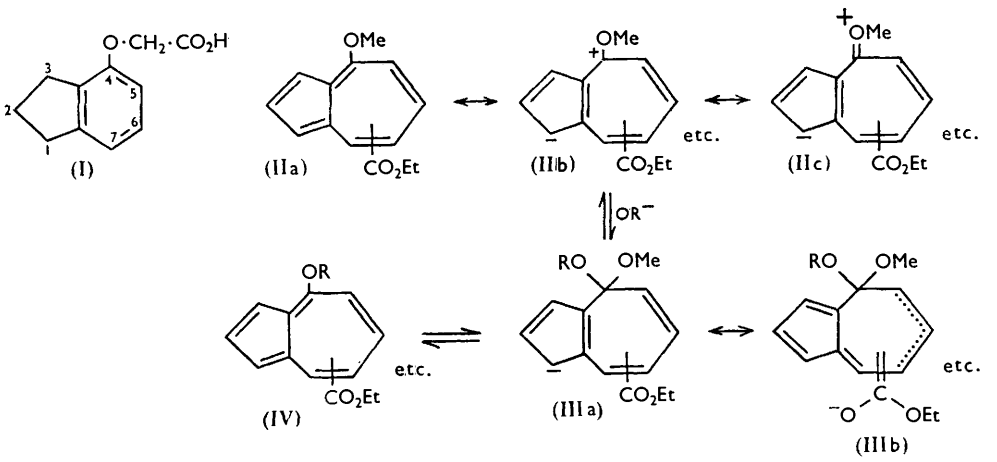
Hydrolysis of the ester with ethanolic potassium hydroxide gave an acid which, even after several recrystallisations, did not give satisfactory analyses. The mixed esters *A*, *B*, and *C* were then similarly hydrolysed and the mixed acids immediately treated with quinoline and copper bronze. The decarboxylation product was not homogeneous and chromatography separated a violet compound from azulene. The violet compound, which did not crystallise, was converted into its trinitrobenzene complex which corresponded in analysis to an ethoxyazulene rather than a methoxyazulene. Re-examination of the analytical data for the acid from *A* showed that it too was derived from an ethoxyazulene. It appeared that *A* and probably *B* had suffered displacement of the methoxyl group by an ethoxide ion during the hydrolysis.

Hydrolysis of the ester mixture with methanolic potassium hydroxide and subsequent decarboxylation gave a new violet compound whose trinitrobenzene complex gave

* Part I, *J.*, 1955, 1193, whose series title, " The Fine Structure of Azulene," has been changed to that given above.

[1] Wagner-Jauregg, Arnold, Hüter, and Schmidt, *Ber.*, 1941, **74**, 1522.
[2] Anderson and Nelson, *J. Amer. Chem. Soc.*, 1951, **73**, 232.
[3] Treibs, *Angew. Chem.*, 1951, **63**, 487.
[4] Treibs and Ziegenbein, *Annalen*, 1955, **595**, 211.
[5] Stafford, Ward, and Reid, *Chem. and Ind.*, 1955, 1258.
[6] Johnson, Bartels-Keith, and Langeman, *J.*, 1952, 4461; Johnson, Langeman, and Murray, *J.*, 1953, 2136.
[7] De Graf, van Dijk-Rothuis, and van de Kolk, *Rec. Trav. chim.*, 1955, **74**, 144.

satisfactory analyses for a methoxyazulene derivative. The production of azulene was related to the conditions of the decarboxylation; prolonged boiling in quinoline appears to reduce the alkoxyazulene to azulene. A nucleophilic replacement must occur during the alkaline hydrolysis and the resulting expectation that aqueous alkali would produce a hydroxyazulene was realised in practice. It appears likely that esters *A* and *B* are both derived from 4-methoxyazulene and that the ethoxycarbonyl group is necessary to promote the replacement as no corresponding conversion of 4-methoxyazulene into 4-ethoxyazulene could be detected. The annexed general mechanism has been proposed.

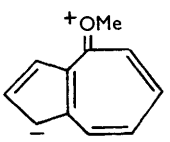


Reaction of 5-methoxyindane with ethyl diazoacetate again gave an ester fraction which on hydrolysis gave a 75% yield of 5-indanyloxyacetic acid. Dehydrogenation of the acidic residues from this gave no azulenic material but the ester fraction suffered smooth dehydrogenation, giving azulenic material in excellent yield. There was no loss of methoxyl during these stages.

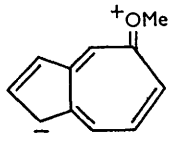
The azulenic fraction was chromatographed and appeared homogeneous although it did not crystallise. It formed a trinitrobenzene complex whose analyses were correct for an ethyl methoxyazulenecarboxylate. The ester was hydrolysed to an acid which was re-esterified with diazomethane. The methyl ester also failed to crystallise and was characterised as its trinitrobenzene complex. Decarboxylation of the acid gave a methoxyazulene which did not solidify but readily formed a trinitrobenzene complex. There was no evidence of ether interchange and during the decarboxylation there was no formation of azulene, indicating higher stability of the 5-C–OMe linkage. It appeared likely that the product was 5-methoxyazulene but the 6-methoxy-structure cannot be eliminated without further evidence. Spectroscopic work points to the former and permits the orientation of the four azulene esters described above.

The visible absorption spectra were in most instances devoid of fine structure and so displacements relative to azulene were measured at the wavelengths of maximum absorption which lie centrally in the visible band. 4-Methoxy- and 4-ethoxy-azulene gave identical curves with a visible maximum at 545 mμ. The corresponding value for azulene is 580 mμ, so that a 4-alkoxy-group causes a hypsochromic displacement of 35 mμ. The colour is consequently violet. The ether derived from 5-methoxyindane showed a bathochromic displacement of 35 mμ to 615 mμ. The possibility of the 6-methoxy-structure can confidently by discounted, for empirically it is known that 4- and 6-substituents of similar character displace the absorption in the same direction, if not always to the same extent. 6-Methoxy-1 : 2-benzazulene is recorded as showing a hypsochromic displacement of 15 mμ relative to the parent hydrocarbon. The Plattner rules indicate that

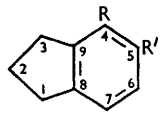
alkyl groups in positions 4 and 5 cause opposite displacements equal in degree—*ca.* 12 mμ. As would be expected, an alkoxy-group shifts absorption in the same direction as an alkyl group but to a greater distance. An electron pair apparently is accepted from the oxygen atom into the molecular orbital, and equivalent polarisations by light absorption require in the 5-case less energy than in the 4-case. If the polarisation is best explained by excited states indicated by such structures as (Va and b), then the energy differences may be associated with the preference of the molecule for a low electron density at the bond of ring fusion (Vb).



(Va)



(Vb)



(VI) : R = OMe, R′ = H

(VII) : R = H, R′ = OMe

If the mode of attack of ethyl diazoacetate on 4- and 5-methoxyindane is considered, then the various possibilities summarised in Table 1 may be recognised. The calculated shifts in $\lambda_{max.}$ are based on the assumption of the additive character of the individual

TABLE 1. *The possible products of ring-expansion of 4- and 5-methoxyindane.*

Bond attacked 4-Methoxy	Substn. in product OMe	CO_2Et	Calc. shift (mμ)	Bond attacked 4-Methoxy	Substn. in product OMe	CO_2Et	Calc. shift (mμ)
(1) 4 : 9	5	4	*	(6) 4 : 9	6	4	*
(2) 4 : 5	4	5	−50	(7) 4 : 5	6	5	−30
(3) 5 : 6 [A]	4	6	+20	(8) 5 : 6	5	6	+90
(4) 6 : 7 [B]	4	7	−50	(9) 6 : 7	5	7	+20
(5) 7 : 8 [C]	4	8	*	(10) 7 : 8	5	8	*

contributions of the substituent groups. A 5- or 7-ethoxycarbonyl group is assumed [8] to displace it by −15 mμ and a 6-ethoxycarbonyl group by +55 mμ. The values for 4- and 5-methoxy-substituents are those given. That for the 6-methoxy-compound is assumed to be *ca.* −15 mμ.

The shifts found empirically for the esters *A*, *B*, and *C* are +25, −45, and +10 mμ respectively. If possibilities (1) and (5) are ignored then *A* would correspond closely to (3) and *B* to (2) or (4) which cannot be spectroscopically differentiated. This leaves (1) and (5) as possibilities for *C*. Ethyl azulene-4-carboxylate is as yet unknown but it is likely that the shift will be bathochromic, as it is with the 6-ester. As a 5-methoxy-group also gives a large bathochromic shift the small displacement found for *C* appears inconsistent with possibility (1), leaving (5) as the more likely structure. An 8-substituent will be approximately equivalent to a 4-substituent by symmetry, so that a value of +10 mμ can be regarded as the resultant of −35 mμ (4-OMe) and +45 mμ (8-CO_2Et). The latter appears a reasonable value. The problem of *B* remains and is discussed in terms of mechanism below.

TABLE 2. *The visible absorption spectra (mμ) of azulene and the ester from 5-methoxyindane.*

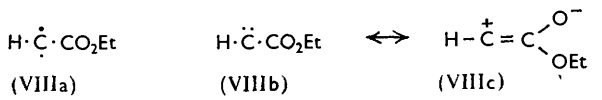
Peak	1	2	3	4	5
Azulene	695	657	627	580	555
New ester	705	677	645	612	588
Δ	+10	+20	+18	+32	+33

The unique ester from 5-methoxyindane showed fine structure with the characteristic five peaks. In Table 2 they are contrasted with those of azulene. The average displacement is +25 mμ. As the methoxy-group is known to be in the 5-position the ester

[8] Plattner, Fürst, Müller, and Somerville, *Helv. Chim. Acta*, 1951, **34**, 971.

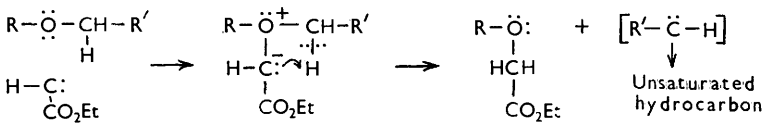
contribution must be −10 mμ. This is consistent with the 5-ester group, leaving only one permissible structure, namely, ethyl 5-methoxyazulene-7-carboxylate.

Thermal decomposition of ethyl diazoacetate is thought to produce a reactive species—ethoxycarbonylmethylene—which is responsible for the various products. There are two possible structures for this intermediate, (VIIIa) and the hybrid (VIIIb and c). The diradical (VIIIa) would attack the substrate in a bidentate manner, separating from a multiple bond or a molecular orbital two electrons to fill the two vacant positions in the partly filled orbitals. With the hybrid structure, attack would involve an electron pair in the substrate and would be essentially electrophilic. A subsequent or concerted nucleophilic process would complete the sequence of reactions.

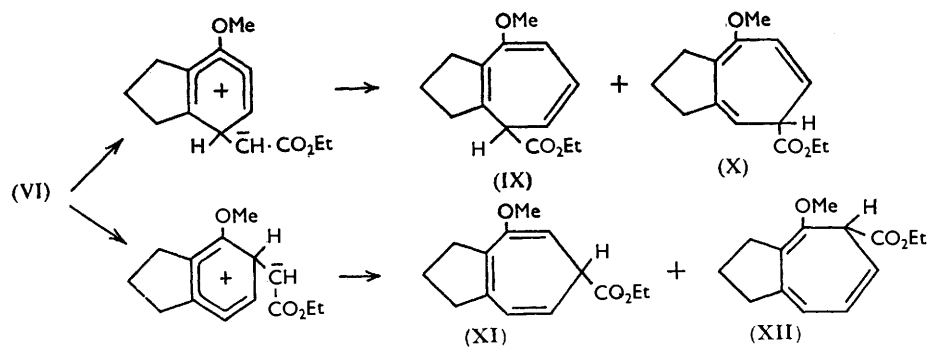


(VIIIa) (VIIIb) (VIIIc)

The latter explanation alone seems to satisfy in a consistent way the following observations. (1) The production of aryloxyacetic esters in the case of aromatic ethers. De Graf, van Dijk-Rothuis, and van de Kolk [7] convincingly interpret this reaction essentially by the following mechanism:



(2) The multiple attack on *cyclo*penta[*def*]phenanthrene. This has been described as more akin to the electrophilic substitution of this system.[9] (3) The production of norcaradiene and *cyclo*heptatriene derivatives singly in related systems. It has been suggested that the latter arise by rearrangement of the initially formed norcaradiene but it appears more likely that rearrangement of some reactive intermediate gives rise to either system. Attack at the 9 : 10-bond in phenanthrene gives a norcaradiene of high stability. *cyclo*-Penta[*def*]phenanthrene suffers analogous attack, but gives the *cyclo*heptatriene derivative.[9] The steric constraint by the five-membered ring must be responsible but it is difficult to attribute such a complete reversal of the stability of a norcaradiene to this alone. (4) Analogous reactive species—the dihalogeno" carbenes "—are, on kinetic evidence, considered to add to olefins by a concerted electrophilic–nucleophilic process.[10]



If this mechanism for the attack on benzenoid compounds is assumed, attack on ethers would occur at the *ortho*- and *para*-positions and the intermediate would pass into the

[9] Reid, Stafford, and Ward, *J.*, 1955, 1193.
[10] Skell and Garner, *J. Amer. Chem. Soc.*, 1956, **78**, 5430; Skell and Woodworth, *ibid.*, p. 4496; Woodworth and Skell, *ibid.*, 1957, **79**, 2542.

product in either or both of two possible ways. With 4-methoxyindane the substances (IX) and (XI) would lead to esters *C* and *A* respectively. Ester *B* could arise from (X) or (XII). If it arose from (XII), the two major products would have arisen from *ortho*-attack. It seems unlikely that there should be only a minor attack in the *para*-position to be represented by *C* alone (in any case the sterically less favoured of products from

FIG. 1. *The product from azulene and sodamide, (A) in* EtOH *and (B) in* 2N-HCl.

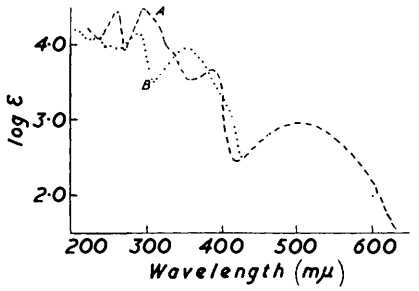


FIG. 2. *(A) Azulene. (B) 4-Methoxyazulene* (log ε + 0·5). *(C) 5-Methoxyazulene* (log ε + 1·0). *All in* EtOH.

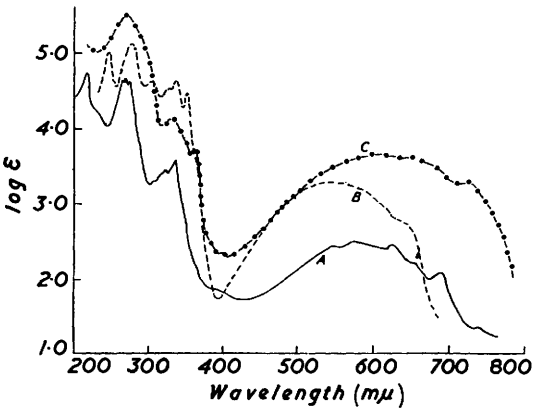


FIG. 3. *Ethyl 4-methoxyazulene-6-carboxylate (A), -7-carboxylate (B), and -8-carboxylate (C); methyl 5-methoxyazulene-5-carboxylate (D). All in* EtOH. (*B and C*, log ε + 0·5.)

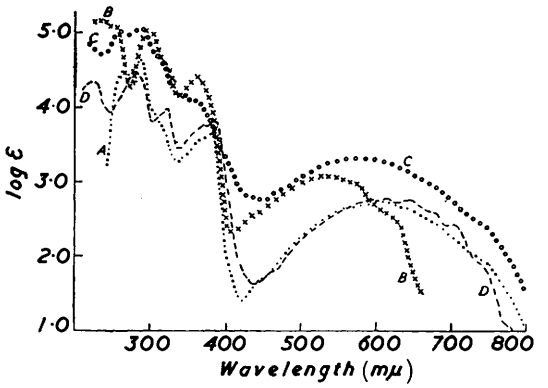
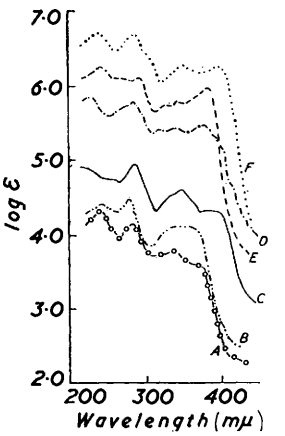


FIG. 4. *4-Ethoxy- (A) and 5-methoxy-azulene* (*B*; log ε + 0·5). *Methyl 5-methoxyazulene-7-carboxylate* (*C*, log ε + 1·0). *Ethyl 4-methoxyazulene-8-carboxylate* (*D*, log ε + 1·5), *-7-carboxylate* (*E*, log ε + 2·0), *and -6-carboxylate* (*F*, log ε + 2·5). *C and D in* 65% H_2SO_4, *the others in conc.* HCl.



para-attack). It seems more probable therefore that *B* is ethyl 4-methoxyazulene-7-carboxylate.

5-Methoxyindane could suffer *ortho*-attack at position 4 or 6. Only the latter appears to be involved and sterically this is not surprising. An additional factor may be that the 4-position is activated by an *ortho*-methylene group. whereas the 6-position is activated by a *para*-group. Examples of such preferred electrophilic attack may be found in the

fluorene series, *e.g.*, the 3-position is favoured over the 1-position in substitution of 2-acetamidofluorene.[11]

Synthesis of 1-methoxyazulene [12] by the reaction of ethyl diazoacetate and 1-methoxyindane has been claimed and it is stated that it has a spectrum identical with that of azulene. This appeared surprising. No claim for the preparation of 2-methoxyazulene exists, so samples of 1- and 2-methoxyindane were treated with ethyl diazoacetate. Distillation of both reaction mixtures gave blue oils from which the same single blue substance was isolated by chromatography. The yield of this was increased by taking

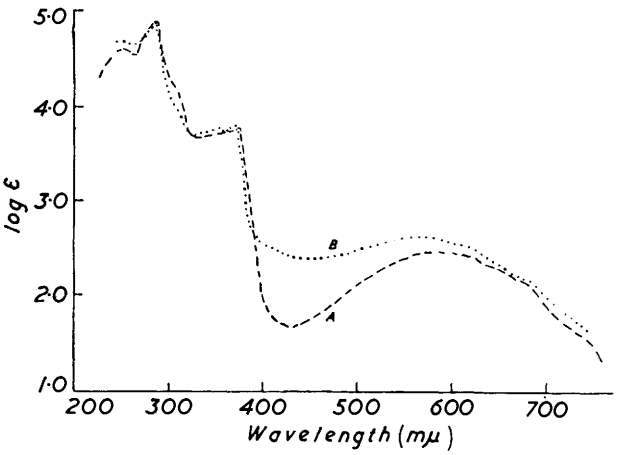


FIG. 5. *4-Hydroxyazulene-6-carboxylic acid* (*A*) *in* EtOH *and* (*B*) *in* 2N-NaOH.

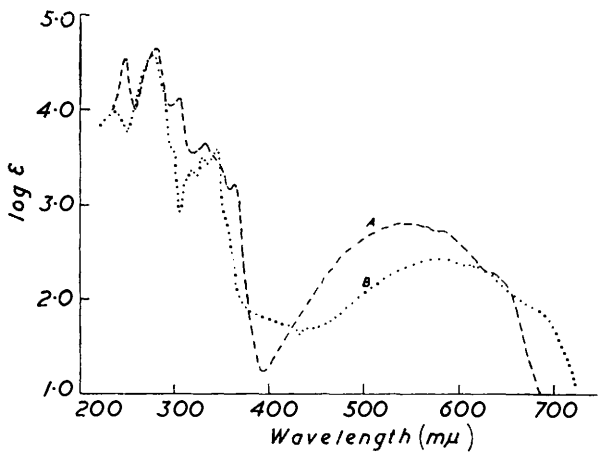


FIG. 6. (*A*) *4-Ethoxyazulene in* EtOH. (*B*) *6-Hydroxymethyleneazulene in* EtOH.

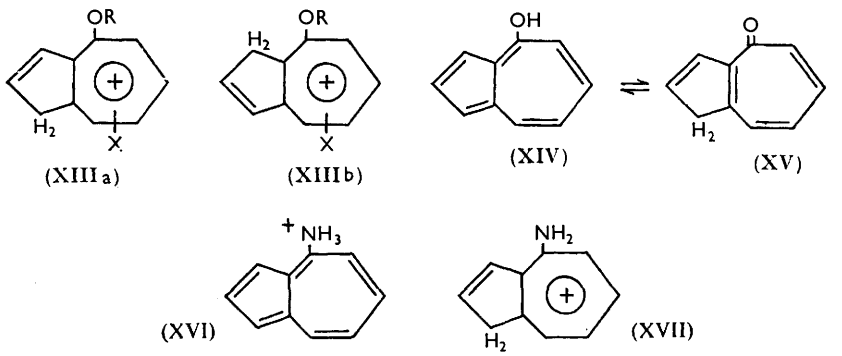
the colourless fractions from the column and treating them with sulphur. This blue compound appeared homogeneous on chromatography. It did not crystallise and did not form a trinitrobenzene derivative. It was purified by distillation and its analyses were correct for an ethyl azulenecarboxylate. Its absorption spectrum was that of ethyl azulene-6-carboxylate. Hydrolysis and decarboxylation yielded azulene and reduction with lithium aluminium hydride gave a hydroxymethyleneazulene with an absorption spectrum consistent with 6-alkyl-substitution. The analysis of the oil is therefore relevant and loss of methanol has occurred during the reaction, presumably after the ring expansion. The resulting dihydroazulene had disproportionated in some way to give the azulene ester.

[11] Eckert and Langecker, *J. prakt. Chem.*, 1928, **118**, 263.
[12] Treibs and Stein, *Annalen*, 1951, **572**, 161.

There is accordingly no evidence from our experiments to substantiate the previous surprising claims for the synthesis and properties of 1-methoxyazulene.

One purpose of this work was to provide reference compounds for the orientation of nucleophilic substitution products of azulene. Such compounds have only been available for alkyl-nucleophilic attack and the 4-position has been shown to be involved.[13] Methoxide ion caused degradation of the azulene nucleus, for heating azulene in methanolic potassium methoxide rapidly destroyed the colour. No azulenic compounds were produced by heating the material recovered from these experiments with sulphur. Reaction of azulene with sodamide gave a red unstable basic material: in solution it remained red for some time but in the solid state deterioration was very rapid; a trinitrobenzene complex was readily formed and appeared pure, but analyses of samples from different experiments were inconsistent. The absorption spectrum of the freshly prepared material was measured and is recorded in Fig. 1 (a solution of unknown concentration was used so that the absolute extinction values are unknown; the relative values are, however, accurately represented). The hypsochromic displacement is 75 mμ. This is consistent with 4- or 6-substitution, and the former is likely although not certain. The absorption spectrum of its salt is also shown in Fig. 1.

The absorption spectra of the ethers described in this paper are recorded in Figs. 2 and 3, with azulene for comparison. Fig. 4 gives their absorptions in acid solution. The ions so produced (XIIIa or/and b) have very similar absorptions, consistent with the alkoxy-*cyclo*pentadienotropylium formulation. 4-Hydroxyazulene (XIV) is a tautomer of a *cyclo*pentadienotropone, *e.g.*, (XV); its instability is not due to an equilibrium favouring (XV), but rather to oxidation. The stability of the system is enhanced by the addition of a carboxylic acid group and Fig. 5 records the absorption spectra of 4-hydroxyazulene-6-carboxylic acid in ethanol and alkali. The change in absorption may in part be due to ionisation of the hydroxyl group as well as of the carbonyl group, but acidification always restores the azulene and there is no evidence of tropone formation. The amino-compound in acid is colourless. It is to be expected that proton addition to the amino-group (cf. XVI) would give a blue or violet compound as this would remove electronic interaction with the azulene moiety. As this does not occur, it follows that proton addition is to carbon, giving an aminotropylium compound, *e.g.*, (XVII).



(XIIIa) (XIIIb) (XIV) (XV) (XVI) (XVII)

The general picture for these absorption spectra conforms to the findings of Plattner and his co-workers [14] for the alkylazulenes and their ester derivatives, and of Heilbronner and his associates [15] for the alkoxytropylium and tropylium derivatives. The absorption spectra of 6-hydroxymethylene- and 4-ethoxy-azulene are given in Fig. 6.

[13] Hafner and Weldes, *Angew. Chem.*, 1955, **67**, 302.
[14] Plattner and Pfau, *Helv. Chim. Acta*, 1937, **20**, 224; Plattner, Fürst, and Schmid, *ibid.*, 1945, **28**, 1647.
[15] Rennhard, di Modica, Simon, Heilbronner, and Eschenmoser, *ibid.*, 1957, **40**, 961.

Experimental

Ligroin refers to the fraction of b. p. 40—60°.

Thermal Decomposition of Ethyl Diazoacetate in Alkoxyindanes.—General method. The alkoxyindane (30—40 g.) was heated at 140°, with stirring, under an air-condenser drawn to a capillary. Ethyl diazoacetate (10—15 g.) was added dropwise during 3 hr. The mixture was then heated at 200° for a further 2 hr. and distilled under reduced pressure.

Isomeric Ethyl 4-Methoxyazulenecarboxylates.—4-Methoxyindane (30·0 g.; b. p. 127—128°/31 mm.) was treated with ethyl diazoacetate (13 g.). Distillation yielded fractions, (i) a colourless liquid (3·0 g.; b. p. 72—75°/47 mm.), (ii) unchanged 4-methoxyindane (17·0 g., b. p. 133°/50 mm.), (iii) unchanged 4-methoxyindane (2·0 g., b. p. 85°/1·5 mm.), (iv) a mobile oil, green in reflected light, red in transmitted light (4·5 g., b. p. up to 150°/0·3 mm.), and (v) a viscous red oil (2·4 g., b. p. 180°/0·3 mm.). A residual brown tar accounted for the balance. Fractions (ii) and (iii) were combined and recycled.

The fraction (iv) from two cycles (7·0 g.) was heated with sulphur (2·0 g.) for 5 min. in a preheated oil-bath at 200°. The colour changed to dark blue-green and hydrogen sulphide was evolved. No advantage is served in prolonging the reaction. The mixture was cooled, dissolved in the minimum quantity of benzene, and chromatographed on neutral alumina, yielding (i) a broad blue band eluted with benzene–ligroin (1 : 1) and (ii) a green band eluted with benzene.

The blue eluate was diluted with ligroin (250 ml.) and extracted with successive portions (50 ml.) of cold syrupy phosphoric acid until no further orange colour appeared in the acid layer. Sulphur and a little green material were retained in the organic layer. The combined acid layers were washed with 1 : 1 benzene–ligroin (250 ml.) and poured into ice-water. An ether extract of the resulting blue precipitate, dried (Na_2SO_4) and evaporated, yielded a mobile blue oil (510 mg.).

The green eluate gave an oil (2·1 g.), which contained a little sulphur, yielded 4-indanyloxyacetic acid on hydrolysis, and gave no more blue material on further dehydrogenation.

Dehydrogenation of a further quantity of fraction (iv) by 20% palladium–charcoal for 8 min. at 240° gave a blue oil (130 mg.) (recovered from phosphoric acid) and a green oil (0·7 g.). Dehydrogenation of fraction (v) (2 g.) with sulphur gave a small amount of the blue oil (30 mg.).

The combined blue oils (650 mg.) were chromatographed, giving the following products: (A) On elution with benzene–ligroin (1 : 9), a blue oil (380 mg.) which yielded a crystalline *s*-trinitrobenzene derivative. This was recrystallised until pure and was then decomposed on an alumina column with elution by the same solvent mixture. *Ethyl 4-methoxyazulene-6-carboxylate* crystallised from ligroin as dark blue blades with a green reflection, m. p. 63·5—64·5° (Found: C, 73·1; H, 6·2. $C_{14}H_{14}O_3$ requires C, 73·0; H, 6·1%). The *trinitrobenzene complex* crystallised as brown needles (from ethanol), m. p. 90—92° (Found: C, 53·7; H, 3·7; N, 10·0. $C_{20}H_{17}O_9N_3$ requires C, 54·2; H, 3·9; N, 9·5%). (B) On elution with 1 : 1 ligroin–benzene, a violet eluate which gave a violet oil (200 mg.). This was rechromatographed until an ethanolic solution deposited pure *ethyl 4-methoxyazulene-7-carboxylate* as violet needles, m. p. 76·5—77·5° (Found: C, 73·2; H, 6·1%). The *trinitrobenzene complex* formed orange needles (from ethanol), m. p. 102—103° (Found: C, 53·7; H, 3·6; N, 9·4%). (C) On elution with benzene, a blue eluate yielding a blue oil (8 mg.). *Ethyl 4-methoxyazulene-8-carboxylate* formed a trinitrobenzene complex, brown plates, m. p. 123° (Found: C, 54·1; H, 4·0; N, 9·2%).

4-Ethoxyazulene-6-carboxylic Acid.—Ethyl 4-methoxyazulene-6-carboxylate (125 mg.) was boiled in ethanol (25 ml.) containing potassium hydroxide (1·0 g.) for 2 hr., then diluted with water (150 ml.). The neutral material was separated by ether-extraction, and the acidic product recovered from the violet aqueous layer by acidification and further extraction. The blue extract yielded a green solid (100 mg.). *4-Ethoxyazulene-6-carboxylic acid* crystallised from benzene–ethanol as green needles, m. p. 234—236° (decomp.) (Found: C, 72·1; H, 5·4. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·6. $C_{12}H_{10}O_3$ requires C, 71·3; H, 5·0%).

4-Hydroxyazulene-6-carboxylic Acid.—Ethyl 4-methoxyazulene-6-carboxylate (30 mg.) was treated as above, but with aqueous potassium hydroxide, and yielded *4-hydroxyazulene-6-carboxylic acid* (20 mg.), green needles (from benzene–ethanol), m. p. 236° (decomp.) (admixture with the previous acid gave a depression to 195—230°) (Found: C, 69·6; H, 4·8. $C_{11}H_8O_3$ requires C, 70·2; H, 4·3%).

4-Ethoxyazulene.—Unseparated isomeric esters (190 mg.) were hydrolysed with ethanolic

potassium hydroxide as above, to give acids (140 mg.), which were heated with copper bronze (1 g.) in quinoline (20 ml.) at 240° for 45 min., then dissolved in ether. The decarboxylation product was freed from quinoline by extraction with dilute hydrochloric acid and from unchanged acids by extraction with sodium hydrogen carbonate solution. The neutral material was chromatographed on alumina, to give: (i) On elution with ligroin, a blue oil (4 mg.) which showed some tendency to crystallise. It was converted into a trinitrobenzene complex, m. p. 166—167°, identical with that of azulene. (ii) On elution with benzene–ligroin (1 : 3), a violet oil (12 mg.); this ether formed a *trinitrobenzene derivative*, red-brown needles, m. p. 143°, from ethanol (Found: C, 56·2; H, 4·0; N, 10·4. $C_{18}H_{15}O_7N_3$ requires C, 56·1; H, 3·9; N, 10·9%). The ether was volatile in organic solvents.

4-*Methoxyazulene*.—Mixed esters (110 mg.) were converted by methanolic potassium hydroxide into acids (80 mg.) which were decarboxylated as above. Chromatography gave a trace of azulene and a violet oil (7 mg.) which was converted into its *trinitrobenzene derivative*, red-brown needles (from ethanol), m. p. 163° (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 co-distils with organic solvents. Reducing the time of the decarboxylation by one half gave a better yield (90 mg. of acid gave 14 mg. of ether) and no azulene. Further reduction of the time led to a lower yield and recovery of most of the starting acid.

4-*Indanyloxyacetic Acid*.—Fraction (iv) (720 mg.) with ethanolic potassium hydroxide (3%) for 2 hr. gave an acid (600 mg.) which formed prisms, m. p. 184° (480 mg.), from benzene. This was identical (mixed m. p.) with 4-*indanyloxyacetic acid* prepared from 4-hydroxyindane in the normal manner (Found: C, 68·6; H, 6·4. $C_{11}H_{12}O_3$ requires C, 68·7; H, 6·3%). The benzene mother-liquors contained a green acidic oil. Similarly, fraction (v) gave a small portion of the phenoxyacetic acid and a quantity of the oil. The combined oils gave no azulenic materials on dehydrogenation.

Ethyl 5-Methoxyazulene-7-carboxylate.—5-Methoxyindane (40 g.) (prepared from the phenol and dimethyl sulphate in the normal manner; b. p. 143—145°/60 mm.) was treated with ethyl diazoacetate in the usual way. Distillation yielded fractions: Unchanged 5-methoxyindane (i) 25·5 g., b. p. 132°/39 mm.; (ii) 1·9 g., b. p. 95°/0·6 mm.; (iii) a mobile green oil (6·8 g.), b. p. up to 145°/0·6 mm.; (iv) a viscous green oil (2·3 g.), boiling up to 190°/0·6 mm. There was a residual tar (12·5 g.). Fractions (i) and (ii) were recycled.

Fraction (iii) (8·0 g.) was heated with sulphur (2·0 g.) in a preheated oil-bath at 200° for 5 min. The mixture was cooled, taken into benzene, and chromatographed on alumina. Elution with benzene–ligroin (1 : 3) gave a blue eluate, and with benzene a green eluate. The blue eluate was diluted with ligroin and extracted with phosphoric acid. The acid extract was washed with ligroin and diluted with water. An ether-extract of the resulting blue precipitate was dried (Na_2SO_4) and gave a blue oil (710 mg.) which was rechromatographed. No separation into fractions was achieved and only one blue band was eluted. *Ethyl 5-methoxyazulene-carboxylate* did not crystallise even when recovered from its *trinitrobenzene derivative*, brown needles (from ethanol), m. p. 70° (Found: C, 53·9; H, 3·8; N, 9·7. $C_{20}H_{17}O_9N_3$ requires C, 54·2; H, 3·9; N, 9·5%). This ester was hydrolysed to the acid by ethanolic potassium hydroxide; the acid was treated with diazomethane but the methyl ester thus obtained did not crystallise. It (methyl 5-methoxyazulene-7-carboxylate) gave a *trinitrobenzene complex*, brown needles (from ethanol), m. p. 118° (Found: C, 53·3; H, 3·7; N, 9·8. $C_{19}H_{15}O_9N_3$ requires C, 53·2; H, 3·5; N, 9·8%).

5-*Methoxyazulene*.—Ethyl 5-methoxyazulene-7-carboxylate (180 mg.) was hydrolysed with ethanolic potassium hydroxide to an acid (140 mg.). This was decarboxylated as usual and chromatography of the neutral material, freed from quinoline and unchanged acid, gave on elution with benzene–ligroin a single blue band, yielding a blue oil (18 mg.). This oil did not crystallise but gave a *trinitrobenzene derivative*, black needles (from ethanol), m. p. 125° (Found: C, 55·0; H, 3·4; N, 11·3. $C_{17}H_{13}O_7N_3$ requires C, 55·0; H, 3·5; N, 11·3%). 5-Methoxyazulene was volatile in organic solvents.

5-*Indanyloxyacetic Acid*.—A portion of fraction (iii) (1·0 g.) was hydrolysed with boiling 3% ethanolic potassium hydroxide (30 ml.) for 2 hr. The acidic product was a green oil (0·8 g.) which deposited colourless plates (580 mg.), m. p. 157°, from benzene (Found: C, 68·7; H, 6·6. Calc. for $C_{11}H_{12}O_3$: C, 68·7; H, 6·3%). Kruber gives m. p. 157°. No depression was observed in a mixed m. p. with a sample made by his method.

Reaction of 2-Methoxyindane with Ethyl Diazoacetate.—2-Hydroxyindane (42 g.) with methyl

iodide and silver oxide gave 2-*methoxyindane* (32 g.), b. p. 100—103°/14—15 mm. (Found: C, 81·0; H, 8·1. $C_{10}H_{12}O$ requires C, 81·0; H, 8·2%). This (32 g.), treated with ethyl diazoacetate (12·0 g.) and distilled, yielded: Unchanged 2-methoxyindane (i) (27·2 g.), b. p. 98—100°/12 mm., (ii) (1·8 g.), b. p. 70°/0·3 mm., (iii) a deep blue oil (6·2 g.), b. p. 180°/0·3 mm., and (iv) a viscous green oil (1·5 g.), b. p. 180—200°/0·3 mm.

Fraction (iii) (3·3 g.) was chromatographed on alumina, to give fractions: (A) On elution with benzene–ligroin (1 : 3) a blue oil (1·8 g.). (B) On elution with ethanol a green oil (1·5 g.). The latter was heated with sulphur (0·5 g.) for 5 min. at 200° and the product chromatographed on alumina, to give a further quantity (160 mg.) of the blue oil. The combined blue oils were taken into ligroin and extracted with phosphoric acid. The acid extract was diluted and the blue precipitate was taken into ether and dried (Na_2SO_4). The blue oil obtained from this extract was chromatographed. Only a single band was obtained and it appeared to be homogeneous. The compound was distilled in a short-path still (bath 120°/10^{-5} mm.) (Found: C, 77·8; H, 6·7. Calc. for $C_{13}H_{12}O_2$: C, 78·0; H, 6·1%). It appeared to be ethyl azulene-6-carboxylate which is known. It did not form a trinitrobenzene complex.

The blue oil (1·0 g.) was hydrolysed with 3% ethanolic potassium hydroxide and the resulting acid was decarboxylated in quinoline with copper bronze. Chromatography of the neutral product gave a single blue-violet eluate which gave a crystalline residue of azulene (85 mg.). The trinitrobenzene derivative of this had m. p. and mixed m. p. 166—167°.

6-*Hydroxymethylazulene*.—The blue oil (300 mg.) was reduced with lithium aluminium hydride (60 mg.) in dry ether (50 ml.). The deep blue colour of the ester was replaced within a few minutes by the less intense colour of the reduction complex. On the addition of water the blue colour reappeared. The product was chromatographed on alumina, giving several bands: (i) On elution with combinations of ligroin–benzene–ether faint pink, blue, and green bands which contained insignificant quantities of material. (ii) On elution with 1 : 9 ethanol–ligroin a blue substance (190 mg.) which crystallised from benzene as violet-blue plates, m. p. 116—118°. The *alcohol* (Found: C, 83·3; H, 6·8. $C_{11}H_{10}O$ requires C, 83·5; H, 6·4%) failed to give a trinitrobenzene complex.

The use of 1-methoxyindane gave the same results as that of 2-methoxyindane.

4-*Aminoazulene*.—Sodamide was formed in liquid ammonia (200 ml.) from sodium (2·0 g.) and ferric nitrate (0·1 g.). When the blue colour was completely dispelled, azulene (240 mg.) in ether (10 ml.) was added. The mixture was agitated several times during 5 hr. Excess of ammonia was expelled and moist ether was added to decompose the complex. Ethanol and finally water were employed to decompose the sodamide. The violet ether layer was separated, washed with water, and extracted with 4N-hydrochloric acid. Azulene (40 mg.) was retained in the ether, and addition of sodium hydroxide to the acid layer precipitated red material. This was taken into ether and after this extract had been dried (Na_2SO_4) the ether was removed, leaving a bright red crystalline residue (120 mg.). Within a few minutes a brown crust had been formed which was insoluble in warm ethanol. Solutions of this red compound appeared stable, and from ethanol a crystalline trinitrobenzene derivative was isolated as brown needles, m. p. 218° (decomp.). Analyses of this derivative from several preparations proved unsatisfactory. The carbon–hydrogen values were reasonable but the nitrogen value was very low and variable, probably owing to oxidation or hydrolysis (Found on 2 samples: C, 54·4, 53·9; H, 3·6, 3·4; N, 13·9, 12·9. Calc. for $C_{16}H_{12}O_6N_4$: C, 53·9: H, 3·4; N, 15·7%).

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THE CHEMISTRY DEPARTMENT,
THE UNIVERSITY, EDINBURGH, 9.

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