# **335.** *Conjugated Cyclic Hydrocarbons and Their Heterocyclic Analogues. Part V.*[1] *1-1′-Azulenylmethyleneazulenium Salts and 1-Ethoxymethyleneazulenium Salts.*

By E. C. KIRBY and D. H. REID.

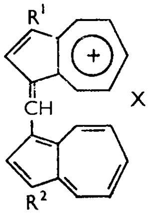
1-1′-Azulenylmethyleneazulenium salts have been synthesised by the condensation of azulenes with (A) 1-formylazulenes in the presence of strong acids and (B) 1-ethoxymethyleneazulenium salts.

Depending upon their degree of substitution, azulenes condense with ethyl orthoformate in the presence of strong acids to give either symmetrical 1-1′-azulenylmethyleneazulenium salts or substituted 1-ethoxymethyleneazulenium salts.

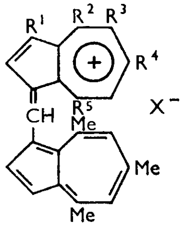
1-Ethoxymethyleneazulenium salts are hydrolysed quantitatively by water to 1-formylazulenes.

Light absorption data for the dye salts are reported.

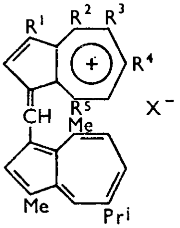
IN Part II [2] of this series it was shown that azulenes condense with aromatic aldehydes in the presence of perchloric acid to form 1-(substituted methylene)azulenium perchlorates. With 1-formylazulene, azulene and guaiazulene (7-isopropyl-1,4-dimethylazulene) gave, respectively, 1-1′-azulenylmethyleneazulenium perchlorate (II) and 1-1′-azulenylmethylene-5-isopropyl-3,8-dimethylazulenium perchlorate (XII), members of a new class of dye salts. These compounds represent the only known class of polymethine dye salts whose cations contain carbon alone. We now report further synthetic studies of this class of compounds.



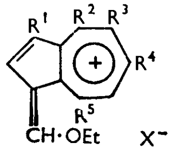
| | $R^1$ | $R^2$ | X |
|---|---|---|---|
| (I) | H | H | Cl |
| (II) | H | H | $ClO_4$ |
| (III) | Me | H | $ClO_4$ |
| (IV) | Me | Me | Br |
| (V) | Me | Me | $ClO_4$ |



| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | X |
|---|---|---|---|---|---|---|
| (VI) | H | H | H | H | H | $ClO_4$ |
| (VII) | Me | H | H | H | H | $ClO_4$ |
| (VIII) | H | Me | H | Me | Me | $ClO_4$ |
| (IX) | Me | H | Pr$^i$ | H | Me | $ClO_4$ |



| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | X |
|---|---|---|---|---|---|---|
| (X) | H | H | H | H | H | Br |
| (XI) | H | H | H | H | H | I |
| (XII) | H | H | H | H | H | $ClO_4$ |
| (XIII) | Me | H | H | H | H | Br |
| (XIV) | Me | H | Pr$^i$ | H | Me | $ClO_4$ |



| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | X |
|---|---|---|---|---|---|---|
| (XV) | H | H | H | H | H | $ClO_4$ |
| (XVI) | H | Me | H | Me | Me | Br |
| (XVII) | H | Me | H | Me | Me | I |
| (XVIII) | H | Me | H | Me | Me | $ClO_4$ |
| (XIX) | Me | H | Pr$^i$ | H | Me | Br |
| (XX) | Me | H | Pr$^i$ | H | Me | |
| (XXI) | Me | H | Pr$^i$ | H | Me | $ClO_4$ |

The method [2] of condensing an azulene with a 1-formylazulene in the presence of perchloric acid was found to be widely but not generally applicable. All condensations with 1-formylazulene and 1-formyl-3-methylazulene were successful. However, 1-formyl-4,6,8-trimethylazulene either reacted incompletely or gave products difficult to purify, while 3-formylguaiazulene (1-formyl-5-isopropyl-3,8-dimethylazulene) failed to condense (see also Kirby and Reid [2]). The desired products were obtained in certain cases by exchanging the rôles of the azulene nuclei of the reactants. Thus, while 3-formylguaiazulene failed to condense with azulene, 1-formylazulene condensed smoothly with guaiazulene to give the salt (XII).[2] This circumvention failed in the attempted preparation of salts [*e.g.*, (IX)], both of whose azulene components give rise to unreactive aldehydes.

The low reactivity of 3-formylguaiazulene and 1-formyl-4,6,8-trimethylazulene in these

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[1] Part IV, Kirby and Reid, *J.*, 1961, 163.

[2] Kirby and Reid, *J.*, 1960, 494.

condensations is undoubtedly due to deactivation of the protonated aldehyde function by the electron-releasing alkyl substituents (see also Kirby and Reid [1]).

In agreement with the formulation of these dye salts as resonance hybrids, the condensation product from azulene with 1-formyl-3-methylazulene was identical with that from 1-methylazulene with 1-formylazulene, namely, (III).

1-Formylazulene and 1-formyl-3-methylazulene condensed readily with azulenes in the presence of strong acids other than perchloric acid. The chloride (I) was isolated in high yield when azulene and 1-formylazulene were heated in acetic acid or acetonitrile saturated with hydrogen chloride. The bromides (IV), (X), and (XIII) were similarly obtained in good yield when the appropriate azulenes and azulene aldehydes (see Table 2) in acetic acid or acetonitrile were treated with 50% (w/v) hydrogen bromide in acetic acid. 1-1′-Azulenylmethyleneazulenium iodides are conveniently prepared by addition of an excess of sodium iodide to boiling solutions of the corresponding chlorides or bromides. Unexpectedly, the product thus obtained from guaiazulene and 1-formyl-3-methylazulene gave analytical data corresponding to $C_{27}H_{27}I_2$, in place of the expected $C_{27}H_{27}I$, and is probably a lattice compound containing iodide and periodide ions in equal proportions. The bromides are more stable than the chlorides; they are comparable to the corresponding perchlorates and iodides in stability and solubility in organic solvents but are much more soluble in water.

The reaction of azulenes with ethyl orthoformate in the presence of strong acids was investigated as a possible general method of synthesis of symmetrical 1-1′-azulenylmethyleneazulenium salts. This reaction was first described briefly by Aldanowa and Stepanow [3] who used it to prepare the dye salts (I) and (II). We have confirmed these results but find further that the type of product depends upon the degree of alkylation of the azulene. Azulene and 1-methylazulene with either stoicheiometric quantities or an excess of ethyl orthoformate in the presence of perchloric acid gave almost quantitative yields of the salts (II) and (V), respectively. In contrast, perchloric acid, guaiazulene, and a large excess (800%) of ethyl orthoformate in ethanol gave a 90% yield of 3-ethoxymethyleneguaiazulenium perchlorate (XXI). 4,6,8-Trimethylazulene likewise gave 1-ethoxymethylene-4,6,8-trimethylazulenium perchlorate (XVIII) in 94% yield.* Other conditions remaining the same, the proportion of ethyl orthoformate determines the yield of substituted 1-ethoxymethyleneazulenium perchlorate. Results of experiments in which the excess of ethyl orthoformate was varied are tabulated.

| Azulene (A) | % Excess of $HC(OEt)_3$ (B) | Molar ratio B/A | Yield (%) |
|---|---|---|---|
| Guaiazulene | 100 | 2 : 1 | 0 |
| ,, | 400 | 5 : 1 | 55 |
| ,, | 800 | 9 : 1 | 90 |
| 4,6,8-Trimethylazulene | 620 | 7·2 : 1 | 5 |
| ,, ,, | 800 | 9 : 1 | 94 |

3-Ethoxymethyleneguaiazulenium and 1-ethoxymethylene-4,6,8,-trimethylazulenium perchlorate react at once with azulenes in alcohols or acetonitrile to form 1-1′-azulenylmethyleneazulenium perchlorates. No appreciable reaction takes place, however, in the presence of perchloric acid. Such salts [(VI)—(IX) and (XIV)] as could not be prepared by the condensation of 1-formylazulenes with azulenes in the presence of perchloric acid were obtained by this method. Since the azulenes whose 1-aldehydes fail to condense with azulenes in the presence of perchloric acid are those which form isolable 1-ethoxymethyleneazulenium perchlorates, the two limited methods of preparation together constitute one general synthetic method.

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* Hitherto only one compound of this type has been described,[4] namely, the corresponding fluoroborate, which was formed in the reaction of triethyloxonium fluoroborate with 1-formyl-4,6,8-trimethylazulene.

[3] Aldanowa and Stepanow, *Zhur. obshchei Khim.*, 1959, **29**, 339 (*Chem. Abs.*, 1960, **54**, 462).

[4] Hafner and Bernhard, *Annalen*, 1959, **625**, 108.

The difference in behaviour of azulenes depends upon their degree of alkylation. Electron-release by the alkyl substituents reduces the electrophilic character of the methine carbon atom of 1-ethoxymethyleneazulenium salts. Thus, while 1-ethoxymethyleneazulenium perchlorate (XV) cannot be isolated but condenses at once with unchanged azulene to form the dye salt (II), 3-ethoxymethyleneguaiazulenium perchlorate (XXI) cannot further react and is itself the reaction product.

The capability of azulenes to condense with substituted 1-ethoxymethyleneazulenium perchlorates, immediately in the absence of, but to a negligible extent in the presence of an excess of perchloric acid, must be attributed to their conversion under the latter conditions into the unreactive azulenium cations. Connected with this is the dependence of the yield of alkyl-substituted ethoxymethyleneazulenium perchlorates upon the magnitude of the excess of ethyl orthoformate. This is believed to depend upon the action of the orthoester which makes available the azulene from its unreactive cation.

Guaiazulene and 4,6,8-trimethylazulene also condensed with ethyl orthoformate in the presence of 50% (w/v) hydrogen bromide in acetic acid to give the bromides (XIX) and (XVI), respectively, which are very soluble in polar organic solvents and are sensitive to atmospheric moisture. The latter salt alone could be isolated pure. When sodium iodide was present the considerably more stable and much less soluble 3-ethoxymethyleneguaiazulenium iodide (XX) and 1-ethoxymethylene-4,6,8-trimethylazulenium iodide (XVII) were obtained. These salts condense readily with azulenes to form 1-1′-azulenylmethyleneazulenium halides; *e.g.*, (XX) with azulene gives 1-1′-azulenylmethylene-5-isopropyl-3,8-dimethylazulenium iodide (XI).

1-Ethoxymethyleneazulenium salts are readily hydrolysed by water to the corresponding aldehydes, thus providing the most convenient syntheses of 1-formylazulenes. 3-Formylguaiazulene and 1-formyl-4,6,8-trimethylazulene were obtained in 89 and 92% yields through the perchlorates (XXI) and (XVIII).

In a further synthesis of symmetrical 1-1′-azulenylmethyleneazulenium salts, azulenes were treated with chloromethoxymethane and perchloric acid in methanol. Guaiazulene gave 5-isopropyl-1-(5-isopropyl-3,8-dimethyl-1-azulenylmethylene)-3,8-dimethylazulenium perchlorate (XIV), but the yield was poor, and attempts to improve and extend the method gave unpromising results.

The visible absorption spectra of all 1-1′-azulenylmethyleneazulenium salts examined consist of a single, sharp, intense absorption band and are exemplified by those of the perchlorates (II) and (XII).[2] Table 1 records the position and intensity of this band for sixteen salts. The position of $\lambda_{max.}$ for a series of salts containing the same cation, *e.g.*, (X), (XI), and (XII) [compounds 6—8 (Table 1)] is unaffected by the nature of the anion, except in the series of the 5-isopropyl-3,8-dimethyl-1-(3-methyl-1-azulenylmethylene)azulenium salts [compounds 13—15 (Table 1)] in which the complex iodide $C_{27}H_{27}I_2$ shows a small hypsochromic displacement (2 mμ) relative to the normal bromide or perchlorate. The following observations on the perchlorates are noteworthy. (*a*) Alkylation of one or both azulene nuclei always produces a bathochromic displacement of $\lambda_{max.}$ whose magnitude depends upon the position(s) and number of substituents. (*b*) For any series of 1-1′-azulenylmethyleneazulenium perchlorates $(\overset{+}{Y}{=}CH{-}Z \longleftrightarrow Y{-}\overset{+}{C}H{-}Z \longleftrightarrow Y{-}CH{=}\overset{+}{Z})ClO_4^-$ in which the nucleus Y is the same, $\lambda_{max.}$ shifts progressively to longer wavelength as Z changes in the order 1-(azulene), 1-(4,6,8-trimethylazulene), 1-(3-methylazulene), 3-(guaiazulene) [1-(5-isopropyl-3,8-dimethylazulene)]. (*c*) Definite shifts can be associated with a substituent, or group of substituents, as follows: 4,6,8-trimethyl, +9; 3-methyl, +16; 5-isopropyl-3,8-dimethyl, +26; 5-isopropyl-8-methyl, +10 mμ (calc. by difference of the immediately preceding two groups). (*d*) The shifts are additive. Agreement between calculated and observed values of $\lambda_{max.}$ is good in the case of most salts [*e.g.*, 1′-Me + 4-Me + 6-Me + 8-Me, +25 mμ; obs. for (VII), +26 mμ]. Exceptionally, in the case of the symmetrically alkylated dyes, observed values of $\Delta\lambda_{max.}$ are greater than those calculated by the additivity rule [*e.g.*, 1-Me + 4-Me + 7-Pr$^{i}$ + 1′-Me + 4′-Me + 7′-Pr$^{i}$, +52 mμ; obs. for (XIV), +62 mμ].

TABLE 1. *Visible absorption maxima* (mμ) *of* 1-1′-*azulenylmethyleneazulenium salts in acetic acid.*

| No. | | $\lambda_{max.}$ | log ε |
|---|---|---|---|
| 1 | 1-1′-Azulenylmethyleneazulenium chloride | 618 | [a] |
| 2 | ,, ,, perchlorate | 618 [b] | 5·08 |
| 3 | 1-1′-Azulenylmethylene-4,6,8-trimethylazulenium perchlorate | 627 [c] | 5·00 |
| 4 | 1-1′-Azulenylmethylene-3-methylazulenium perchlorate | 634 | 5·02 |
| 5 | 4,6,8-Trimethyl-1-(4,6,8-trimethyl-1-azulenylmethylene)azulenium perchlorate | 640 | 4·94 |
| 6 | 1-1′-Azulenylmethylene-5-isopropyl-3,8-dimethylazulenium bromide | 644 | 5·00 |
| 7 | 1-1′-Azulenylmethylene-5-isopropyl-3,8-dimethylazulenium iodide | 644 | 4·96 |
| 8 | 1-1′-Azulenylmethylene-5-isopropyl-3,8-dimethylazulenium perchlorate | 644 [d b] | 4·98 |
| 9 | 4,6,8-Trimethyl-1-(3-methyl-1-azulenylmethylene)azulenium perchlorate | 644 | 5·03 |
| 10 | 3-Methyl-1-(3-methyl-1-azulenylmethylene)azulenium bromide | 652 | 4·99 |
| 11 | 3-Methyl-1-(3-methyl-1-azulenylmethylene)azulenium perchlorate | 652 | 5·01 |
| 12 | 5-Isopropyl-3,8-dimethyl-1-(4,6,8-trimethyl-1-azulenylmethylene)azulenium perchlorate | 653 | 4·93 |
| 13 | 5-Isopropyl-3,8-dimethyl-1-(3-methyl-1-azulenylmethylene)azulenium iodide [e] | 661 | 5·00 |
| 14 | 5-Isopropyl-3,8-dimethyl-1-(3-methyl-1-azulenylmethylene)azulenium bromide | 663 | 4·94 |
| 15 | 5-Isopropyl-3,8-dimethyl-1-(3-methyl-1-azulenylmethylene)azulenium perchlorate | 663 | 4·97 |
| 16 | 5-Isopropyl-1-(5-isopropyl-3,8-dimethyl-1-azulenylmethylene)-3,8-dimethylazulenium perchlorate | 680 | 5·08 |

[a] Value uncertain owing to instability. [b] Kirby and Reid, *J.*, 1960, 494. [c] In 4% (v/v) acetonitrile in acetic acid. [d] Redetermined value; previously recorded value, 645 mμ. [e] Complex iodide $C_{27}H_{27}I_2$.

## EXPERIMENTAL

M. p.s were determined on a Kofler heating stage which, unless otherwise stated, was preheated to *ca.* 5—10° below the recorded m. p. Specimens for analysis were dried for 6—10 hr. at *ca.* 85°/0·1 mm. Visible spectra were determined with a Unicam S.P. 600 instrument.

*Materials.*—Acetic acid was of "AnalaR" grade. Acetonitrile was purified by successive distillations from phosphoric anhydride and freshly dried potassium carbonate, then redistilled before use. Ethyl orthoformate was fractionally distilled before use. Light petroleum was of boiling range 40—60°. Hydrogen bromide in acetic refers to 50% (w/v) hydrogen bromide in acetic acid. Perchloric acid refers to 70—72% (w/w) perchloric acid of "AnalaR" grade.

*Condensation* (A) *of Azulenes with* 1-*Formylazulenes in the Presence of Acids.*—Condensations were by one of the following general procedures (for details see Table 2).

*Procedure* A1. Perchloric acid (0·4 ml.) was added to the azulenealdehyde (0·002 mole) and the azulene (0·0022 mole) in acetic acid (25 ml.), and the solution was boiled for 2 min. In most cases the product crystallised extensively from the boiling blue solution. It was filtered off from the cooled solution, washed with acetic acid followed by ether, and recrystallised.

*Procedure* A2. A saturated solution of hydrogen chloride in acetic acid (1 ml.) was added to the azulenealdehyde (0·002 mole) and the azulene (0·002 mole) dissolved in acetonitrile (10 ml.), and the solution was boiled for 2 min. The product was filtered off from the cooled solution, washed with acetonitrile followed by ether, and recrystallised.

*Procedure* A3. Hydrogen bromide in acetic acid (0·5 ml.) was added to the azulenealdehyde (0·002 mole) and the azulene (0·002 mole) in boiling acetic acid (20 ml.), and the solution was boiled for 2 min. The filtered product was washed with acetic acid followed by much ether, and recrystallised.

*Procedure* A4. A saturated solution of hydrogen chloride in acetic acid (1 ml.) was added to the azulenealdehyde (0·002 mole) and the azulene (0·002 mole) in acetic acid (10 ml.). The solution was boiled for 1 min. Anhydrous sodium iodide (600 mg., 0·004 mole) was washed into the solution with acetic acid (10 ml.), and the resulting mixture was boiled for a further 2 min. In all cases the iodide partly crystallised from the boiling solution. It was filtered off from the cooled solution, washed successively with water, acetic acid, and ether, and recrystallised.

*Condensation* (B) *of Azulenes with* 1-*Ethoxymethyleneazulenium Salts.*—Condensations were by one of the following general procedures (for details see Table 2).

*Procedure* B1. A mixture of the azulene (0·002 mole), the 1-ethoxymethyleneazulenium salt (0·002 mole), and methanol (12 ml.) was boiled for 2 min., then allowed to cool slowly to room temperature. The product was washed with a small volume of methanol and recrystallised from a suitable solvent.

TABLE 2. *Preparation of* 1-1′-*azulenylmethyleneazulenium salts; condensation of azulenes with* (A) 1-*formylazulenes and strong acids,* (B) 1-*ethoxymethyleneazulenium salts.*

| Procedure | Azulene | 1-Formylazulene or 1-ethoxymethylene azulenium salt | Product no. | Yield (%) | Colour † | Solvent | M. p. * |
|---|---|---|---|---|---|---|---|
| A2 | Unsubst. | 1-Formylazulene | 1 | 82 | Black [a] | [b] | [c] |
| A1 | ,, | 1-Formylazulene | 2 [d] | 100 | Black | N | >350° [e] |
| B3 | ,, | 1-Ethoxymethylene-4,6,8-trimethylazulenium perchlorate | 3 | 50 | Black | N | >270* [g] |
| A1 | ,, | 1-Formyl-3-methylazulene | 4 | 100 | Black [h] | N | 350 [fi] |
| A1 | 1-Methyl | 1-Formylazulene | 4 | 97 | Black [h] | N | 350 [fi] |
| B2 | 4,6,8-Trimethyl | 1-Ethoxymethylene-4,6,8-trimethylazulenium perchlorate | 5 | 20 | Black | M | >300 * |
| A3 | Guaiazulene | 1-Formylazulene | 6 | 92 | Green | C | 188* [j] |
| B1 | Unsubst. | 3-Ethoxymethyleneguaiazulenium iodide | 7 | 47 | Violet-black | M2N | 180—181·5 |
| A1 | Guaiazulene | 1-Formylazulene | 8 [d] | 85 | Green | N | 199—200·5 |
| B1 | 1-Methyl | 1-Ethoxymethylene-4,6,8-trimethylazulenium perchlorate | 9 | 65 | Black | N | 274—280 [k] |
| A3 | 1-Methyl | 1-Formyl-3-methylazulene | 10 | 92 | Green [l] | N | 280 [km] |
| A1 | 1-Methyl | 1-Formyl-3-methylazulene | 11 | 100 | Green | N | 350 [fi] |
| B2 | Guaiazulene | 1-Ethoxymethylene-4,6,8-trimethylazulenium perchlorate | 12 | 20 | Blue | M | 217—219 |
| A4 | Guaiazulene | 1-Formyl-3-methylazulene | 13 | 55 | Black | N | 214 [n] |
| A3 | Guaiazulene | 1-Formyl-3-methylazulene | 14 | 75 | Green | C2N | 185—187 |
| A1 | Guaiazulene | 1-Formyl-3-methylazulene | 15 | 84 | Green | C | >265 * |
| B1 [o] | Guaiazulene | 3-Ethoxymethyleneguaiazulenium perchlorate | 16 | 3 | Black | C | 247—250 * |

| | Found (%) | | | | Required (%) | | |
|---|---|---|---|---|---|---|---|
| No. | C | H | Hal | Formula | C | H | Hal |
| 1 [p] | 85·6 | 5·6 | | $C_{21}H_{15}Cl$ | 83·3 | 5·0 | |
| 2 [d] | 68·5 | 4·0 | 9·1 | $C_{21}H_{15}ClO_4$ | 68·8 | 4·1 | 9·7 |
| 3 | 69·8 | 5·7 | 8·8 | $C_{24}H_{21}ClO_4$ | 70·5 | 5·2 | 8·7 |
| 4 | 69·8 | 4·4 | 9·1 | $C_{22}H_{17}ClO_4$ | 69·4 | 4·5 | 9·3 |
| 5 | 72·2 | 6·2 | 8·5 | $C_{27}H_{27}ClO_4$ | 71·9 | 6·0 | 7·9 |
| 6 | 73·3 | 6·4 | | $C_{26}H_{25}Br$ | 74·8 | 6·0 | |
| 7 | 67·4 | 5·5 | | $C_{26}H_{25}I$ | 67·3 | 5·4 | |
| 8 [d] | 71·1 | 5·6 | 8·2 | $C_{26}H_{25}ClO_4$ | 71·5 | 5·8 | 8·1 |
| 9 | 71·3 | 5·9 | 8·2 | $C_{25}H_{23}ClO_4$ | 71·0 | 5·5 | 8·4 |
| 10 | 73·5 | 5·5 | 21·2 | $C_{23}H_{19}Br$ | 73·6 | 5·1 | 21·3 |
| 11 | 70·6 | 5·1 | 9·5 | $C_{23}H_{19}ClO_4$ | 70·0 | 4·9 | 9·0 |
| 12 | 72·1 | 6·7 | 7·3 | $C_{29}H_{31}ClO_4$ | 72·8 | 6·5 | 7·4 |
| 13 | 54·8 | 4·6 | 41·7 | $C_{27}H_{27}I_2$ | 53·6 | 4·5 | 41·9 |
| 14 | 74·9 | 6·4 | | $C_{27}H_{27}Br$ | 75·2 | 6·3 | |
| 15 | 71·5 | 5·9 | 8·5 | $C_{27}H_{27}ClO_4$ | 71·9 | 6·0 | 7·9 |
| 16 | 73·3 | 7·1 | 6·9 | $C_{31}H_{35}ClO_4$ | 73·4 | 7·0 | 7·0 |

* With decomp. † Needles unless otherwise stated.

Recrystn. solvents: C = acetic acid. M = methanol. N = acetonitrile. C2N = acetic acid (once), then from acetonitrile (twice). M2N = methanol (once), then from acetonitrile (twice).

[a] Powder. [b] Decomp. during attempted recrystn. from acetonitrile. [c] Does not melt <340°. [d] Kirby and Reid, *J.*, 1960, 494. [e] Decomp. without melting. [f] Block preheated to $\nless$350. [g] Block heated from room temperature. [h] Green reflex. [i] Explodes. [j] Block preheated to $\nless$188°. [k] Decomp. with partial melting. [l] Prisms. [m] Block preheated to $\nless$280°. [n] Block preheated to $\nless$214°. [o] Reaction solution diluted with dry ether (3 ml.), then set aside for 3 hr. [p] No satisfactory analysis.

*Procedures* B2 *and* B3. These were identical with the preceding except that the volumes of methanol used were, respectively, 20 and 30 ml.

*Condensation of Ethyl Orthoformate with Azulenes and Strong Acids.*—(a) *With azulene and perchloric acid.* Perchloric acid (2·5 ml.) in ethanol (15 ml.) at room temperature was added to a solution of azulene (1·28 g., 0·01 mole) and ethyl orthoformate (15 ml., 0·09 mole) in ethanol (30 ml.), also at room temperature. 1-1′-Azulenylmethyleneazulenium perchlorate (II) (1·80 g., 98%) separated at once from the resulting blue solution as black needles, identical spectrally and in physical properties with the product from azulene, 1-formylazulene, and perchloric acid.[3] The formation of 1-ethoxymethyleneazulenium perchlorate (XV) could not be detected.

(b) *With 1-methylazulene and perchloric acid.* The condensation was carried out as described for the preceding experiment, but with 1-methylazulene (1·42 g., 0·01 mole) in place of azulene. Recrystallisation of the product (3·83 g., 97%) from acetonitrile gave 3-methyl-1-(3-methyl-1-azulenylmethylene)azulenium perchlorate (V), identical (m. p. and visible spectrum) with the product of condensation of 1-methylazulene, 1-formyl-3-methylazulene, and perchloric acid. No trace of 1-ethoxymethylene-3-methylazulenium perchlorate was detected.

(c) *With guaiazulene and perchloric acid.* Perchloric acid (2·5 ml., 0·03 mole, 200% excess) in dry ethanol (15 ml.) at room temperature was added all at once to a solution of guaiazulene (1·98 g., 0·01 mole) and ethyl orthoformate (15 ml., 0·09 mole, 800% excess) in dry ethanol (30 ml.), also at room temperature. Orange-yellow plates began to separate almost immediately in the orange-yellow solution. After 5 min. dry ether (15 ml.) was added with swirling to complete the crystallisation. The filtered product (3·23 g., 90%) was washed with anhydrous ethanol (15 ml.), followed by dry ether (100 ml.), and was thus satisfactory for further reactions. For analysis a specimen was dissolved in the minimum volume of boiling acetone and an equal volume of dry ether was subsequently added. 3-*Ethoxymethyleneguaiazulenium perchlorate* (XXI) crystallised as orange needles which became green >155° and melted at 161—163° (decomp.) (Found: C, 60·9; H, 6·9; Cl, 10·4. $C_{18}H_{23}ClO_5$ requires C, 60·9; H, 6·5; Cl, 10·0%). When the quantity of ethyl orthoformate was 8·3 ml. (0·05 mole, 400% excess) the yield fell to 1·960 g. (55%); the use of 3·32 ml. (0·02 mole, 100% excess) gave no crystalline product at all. Attempts to prepare the symmetrical dye salt (XIV) by the condensation of guaiazulene with a stoicheiometric amount or with a large excess of ethyl orthoformate in the presence of perchloric acid, either in boiling solution or at room temperature, were unsuccessful.

(d) *With* 4,6,8-*trimethylazulene and perchloric acid.* (i) The condensation was carried out as in (c), with 4,6,8-trimethylazulene (1·70 g., 0·01 mole) in place of guaiazulene. 1-*Ethoxymethylene*-4,6,8-*trimethylazulenium perchlorate* (XVIII) (3·05 g., 94%) crystallised at once as greenish-yellow needles, unchanged in form after recrystallisation from acetonitrile. It does not melt but slowly becomes grey and finally black above 180° without losing shape (Found: C, 58·8; H, 6·1; Cl, 10·8. $C_{16}H_{19}ClO_5$ requires C, 58·8; H, 5·9; Cl, 10·9%).

(ii) The condensation was repeated with 4,6,8-trimethylazulene (3·40 g., 0·02 mole), ethyl orthoformate (24 ml., 0·144 mole, 620% excess), perchloric acid (5 ml., 0·06 mole, 200% excess), and absolute ethanol (90 ml.). The mixture became bluish-purple and a small quantity of solid separated. The mixture was hydrolysed with water (1 l.) and extracted exhaustively with ether. The ether extract was worked up in the usual manner, and the residue obtained on evaporation of solvent was dissolved in light petroleum for chromatography on alumina. Elution with light petroleum gave 4,6,8-trimethylazulene (2·99 g., 88% recovery). Subsequent elution with ether gave 1-formyl-4,6,8-trimethylazulene (196 mg., corresponding to 5% conversion of 4,6,8-trimethylazulene into 1-ethoxymethylene-4,6,8-trimethylazulenium perchlorate).

Attempts to prepare the symmetrical dye (VIII) by condensing 4,6,8-trimethylazulene with ethyl orthoformate in the presence of perchloric acid were unsuccessful.

(e) *With* 4,6,8-*trimethylazulene and hydrogen bromide.* Hydrogen bromide in acetic acid (0·5 ml.), dissolved in dry ethanol (3 ml.), was added to a solution of 4,6,8-trimethylazulene (340 mg., 0·002 mole), ethyl orthoformate (5 ml., 0·03 mole, 1400% excess), and dry ethanol (3 ml.) at room temperature. 1-*Ethoxymethylene*-4,6,8-*trimethylazulenium bromide* (XVI) (308 mg., 50%) crystallised at once from the green solution. It was filtered off, washed with ethanol followed by ether, and dried at 100° for 5 min. Work must be as rapid as possible since hydrolysis occurs in air, especially in the presence of solvents. Recrystallisation from acetonitrile gave green prisms, m. p. 146—150° (decomp.) (Found: C, 62·1; H, 5·7. $C_{16}H_{19}BrO$ requires C, 62·55; H, 6·2%).

3-*Ethoxymethyleneguaiazulenium Iodide.*—Hydrogen bromide in acetic acid (4 ml.), dissolved in dry ethanol (30 ml.) at room temperature, was added to a solution of guaiazulene (4 g., 0·02 mole), anhydrous sodium iodide (6 g., 0·04 mole), ethyl orthoformate (30 ml.), and dry ethanol (30 ml.), also at room temperature. 3-*Ethoxymethyleneguaiazulenium iodide* (XX) (6·16 g., 81%) crystallised at once as garnet-red needles which were washed with ethanol, followed by ether, and dried *in vacuo* (Found: C, 55·8; H, 6·1; I, 31·8. $C_{18}H_{23}IO$ requires C, 56·6; H, 6·1; I, 33·2%). The salt, when freshly prepared, has m. p. 128—130° (decomp. to black liquid), but slowly changes at room temperature into orange-brown needles which decompose slowly with partial melting >135° and melt completely to a green liquid at 152°. The change is accelerated by heat and occurs during recrystallisation from acetonitrile.

1-*Ethoxymethylene*-4,6,8-*trimethylazulenium Iodide*.—Hydrogen bromide in acetic acid (0·5 ml.), when dissolved in dry ethanol (4 ml.) and added to a cold solution of 4,6,8-trimethylazulene (340 mg., 0·002 mole), ethyl orthoformate (5 ml., 0·03 mole), and anhydrous sodium iodide (700 mg.) in dry ethanol (10 ml.), gave directly 1-ethoxymethylene-4,6,8-trimethylazulenium iodide (XVII) (700 mg., 100%), brown needles, m. p. 145—150° (decomp.), which was analysed without recrystallisation owing to decomposition in hot solvents (Found: C, 53·3; H, 5·3. Calc. for $C_{16}H_{19}IO$: C, 54·3; H, 5·4%).

*Hydrolysis of* 1-*Ethoxymethyleneazulenium Salts*.—3-*Ethoxymethyleneguaiazulenium perchlorate*. Cold water (100 ml.) was added slowly with swirling to an initially boiling solution of 3-ethoxymethyleneguaiazulenium perchlorate (2·84 g.) in acetone (30 ml.). 3-Formylguaiazulene crystallised at once as brown needles (1·795 g., 99%), identical in m. p. and mixed m. p. with an authentic specimen.

1-*Ethoxymethylene*-4,6,8-*trimethylazulenium perchlorate*. This salt (3·05 g.), acetone (200 ml.), and water (200 ml.) were shaken together for several minutes, or until hydrolysis was complete. The mixture was diluted with water and extracted with ether (2 × 350 ml.), and the combined extracts were worked up in the usual manner. Evaporation left 1-formyl-4,6,8-trimethylazulene (1·83 g., 99%) which after one recrystallisation from ethanol had m. p. 105—106° (lit.,[4] m. p. 106—107°).

*Condensation of Guaiazulene, Chloromethoxymethane, and Perchloric Acid*.—Guaiazulene (2400 mg.), chloromethoxymethane (245 mg.), and anhydrous ethanol (10 ml.) were heated to the b. p., perchloric acid (1·5 ml.) was added, and the solution was boiled for 30 sec. Dry ether (5 ml.) was added with swirling to the cooled solution which was then left at room temperature for 1·5 hr. 5-Isopropyl-1-(5-isopropyl-3,8-dimethyl-1-azulenylmethylene)3,8 dimethylazulenium perchlorate (XIV) (75 mg., 5%) crystallised as flat, black needles which, after one recrystallisation from acetic acid, was identical (m. p., mixed m. p., and visible spectrum) with the product of condensation of guaiazulene with 3-ethoxymethyleneguaiazulenium perchlorate. Addition of dry ether (20 ml.) to the filtrate afforded a further 80 mg. of slightly less pure material, bringing the total yield to 155 mg. (10%).

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DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY, ST. ANDREWS, SCOTLAND.

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