269. *Conjugated Cyclic Hydrocarbons and Their Heterocyclic Analogues. Part VII.*[1] *Cationic Allenes in the Azulene and Indolizine Series.*

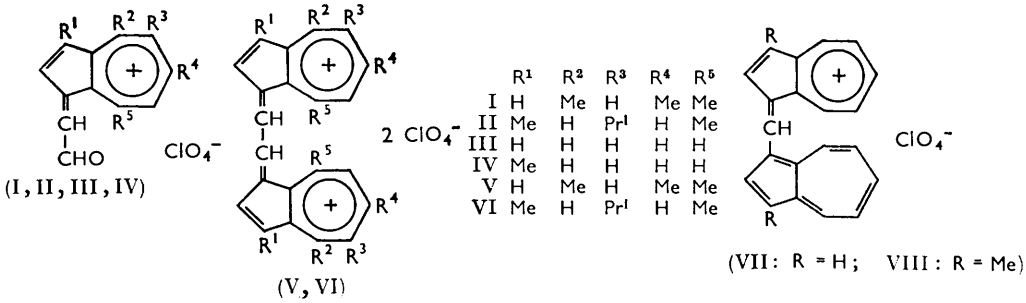
By M. Fraser and D. H. Reid.

The condensation of azulenes and indolizines with glyoxal in the presence of perchloric acid has been studied. The nature of the products has been elucidated and shown to depend on the degree of alkylation of the azulene or indolizine and on the solvent employed.

It has been shown[1] that azulenes condense with α-oxo-aldehydes in the presence of perchloric acid to give ethanediylidenebis(azulenium perchlorates) or symmetrical 1-(azulen-1-ylmethylene)azulenium perchlorates. With glyoxal, 4,6,8-trimethylazulene and guaiazulene (7-isopropyl-1,4-dimethylazulene) gave ethanediylidenebis-(4,6,8-trimethylazulenium perchlorate) (V) and ethanediylidenebis-(5-isopropyl-3,8-dimethylazulenium perchlorate) (VI), respectively, while azulene afforded 1-(azulen-1-ylmethylene)azulenium perchlorate (VII). A possible mechanism was advanced which takes into account the electronic effects of substituents in the azulene. The primary step is similar in all condensations. A 1-formylmethyleneazulenium perchlorate (I), (II), or (III) is formed by the condensation of one molecule of each of the azulene, glyoxal, and perchloric acid. The intermediate (I) from 4,6,8-trimethylazulene is attacked by an excess of the hydrocarbon at the aldehyde group, giving the diperchlorate (V). Similarly, the intermediate

[1] Part VI, Kirby and Reid, *J.*, 1961, 3579.

(II) from guaiazulene yields the diperchlorate (VI), but the intermediate (III) from azulene reacts at the electrophilic methine-carbon atom to form the dye salt (VII) with simultaneous elimination of formaldehyde.



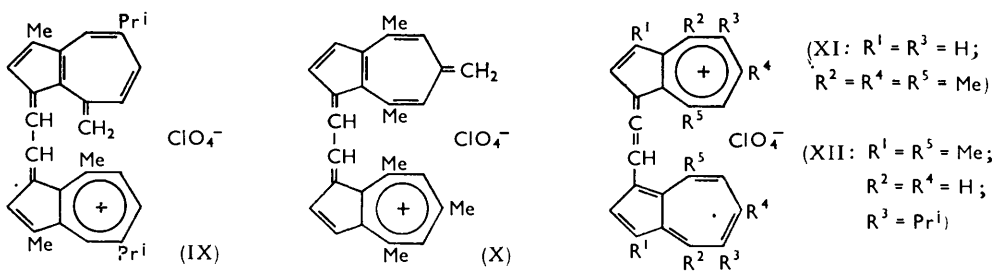
	R¹	R²	R³	R⁴	R⁵
I	H	Me	H	Me	Me
II	Me	H	Pr^i	H	Me
III	H	H	H	H	H
IV	Me	H	H	H	H
V	H	Me	H	Me	Me
VI	Me	H	Pr^i	H	Me

(VII: R = H; VIII: R = Me)

We have since found that 1-methylazulene condenses with glyoxal analogously to azulene, forming azulenylmethyleneazulenium perchlorate (VIII). The difference in behaviour of azulene and 1-methylazulene from that of 4,6,8-trimethylazulene and guaiazulene is the result of electron-release by the several alkyl substituents in the latter pair of hydrocarbons. The electrophilic activity of the methine-carbon atom in the 1-formylmethyleneazulenium perchlorates (I) and (II) is thereby reduced below that of the more remote formyl group.

We have reported also [1] that ethanediylidenebis-(4,6,8-trimethylazulenium perchlorate) (V) could be recrystallised from acetonitrile only in the presence of an excess of perchloric acid. Attempted recrystallisation from acetonitrile alone gave a compound of unknown structure, whose composition corresponded to that of the diperchlorate (V) minus $1HClO_4$. This monoperchlorate regenerated the diperchlorate (V) when treated with an excess of perchloric acid. We have now found that ethanediylidenebis-(5-isopropyl-3,8-dimethylazulenium perchlorate) (VI), though stable in acetonitrile, also forms a monoperchlorate on attempted recrystallisation from a mixture of ethanol and acetonitrile. The present paper discusses the formation, structure, and reactions of these monoperchlorates and of those formed analogously from indolizines.

It seemed likely that the loss of a proton from the diperchlorates (V) and (VI) had occurred at a substituent or the ethanediylidene bridge. Reversible proton-transfer from the azulene nucleus is improbable. Loss of a proton from a methyl substituent appeared an attractive possibility in view of the known acidity of methyl groups [2] when situated in the 4(8)- or 6-position of azulene. Also, the cationic charge would enhance this acidity. Such a process would convert ethanediylidenebis-(5-isopropyl-3,8-dimethylazulenium perchlorate) (VI) into compound (IX). Ethanediylidenebis-(4,6,8-trimethylazulenium

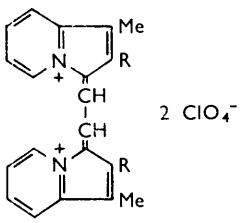


perchlorate) (V) would give one or more of three similar structures, for example (X), depending on the relative acidities of the 4-, 6-, and 8-methyl groups. Alternatively, loss

[2] Hafner, Pelster, and Patzelt, *Annalen*, 1961, **650**, 80; Hafner and Schneider, *ibid.*, 1959, **624**, 37.

of a proton from the ethanediylidene bridge in (V) and (VI) would give the allenes (XI) and (XII).

In order to decide whether the acidity of a methyl group at position 4, 6, or 8 is involved in the reversible loss of a proton, it would be necessary to examine the behaviour of diperchlorates from azulenes which are highly alkylated but do not carry the substituents at positions 4, 6, and 8. Such azulenes are unavailable. The structure of the mono-



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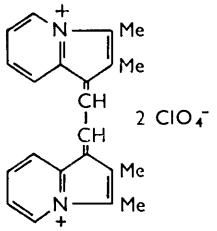

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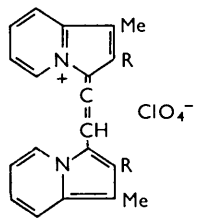

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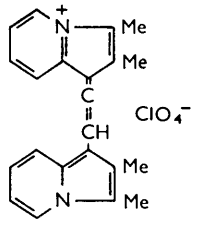


ClO_4^-

(XIII: R = Me) (XIV: R = Ph) (XV) (XVI: R = Me) (XVII: R = Ph) (XVIII)

(XIX) $(p\text{-MeO}\cdot C_6H_4)_2C{:}C{:}CH\cdot CH{:}C(p\text{-MeO}\cdot C_6H_4)_2$

(XX) $[(p\text{-MeO}\cdot C_6H_4)_2C{:}CH\cdot CH\cdot CH{:}C(p\text{-MeO}\cdot C_6H_4)_2]^+ClO_4^-$

perchlorates was settled indirectly, however, by comparative studies of analogous salts in the indolizine series. The close similarity in chemical behaviour between the azulenes and indolizines prompted us to examine the condensation of glyoxal with indolizines in the presence of perchloric acid. In fact, glyoxal condensed smoothly with 1,2-dimethyl-3*H*-indolizinium perchlorate * in acetonitrile to give ethanediylidenebis-(1,2-dimethyl-indolizinium perchlorate) (XIII) which in ethanol loses a molecule of perchloric acid reversibly to form a monoperchlorate. Similar behaviour was shown by the perchlorates of other 1,2- and 2,3-disubstituted indolizines, namely, 2,3-dimethyl- and 1-methyl-2-phenyl-indolizine. Indolizines in which positions 1 and 3 are both unsubstituted reacted differently. 2-Methyl-, 2,6- and 2,8-dimethyl-, and 2-phenyl-indolizine gave green solutions from which intractable greenish-black amorphous solids, insoluble in the common organic solvents, were deposited.

1,2,3-Trimethyl-3*H*-indolizinium perchlorate [3] failed to react with glyoxal. Condensation of indolizines with glyoxal can, therefore, take place only at an unsubstituted 1- or 3-position. The structures of the diperchlorates from 1,2-dimethyl-3*H*-, 2,3-dimethyl-1*H*-, and 1-methyl-2-phenyl-3*H*-indolizinium perchlorate are thereby established as (XIII), (XV), and (XIV), respectively.

In view of the great similarity in chemical behaviour between azulenes and indolizines it seemed reasonable to assume that reversible proton loss had occurred at chemically analogous sites in the diperchlorates of both series. Azulene [4] and indolizine [5] are polarised so that the five-membered rings carry an excess of π-electron density at positions 1 and 3. Position 1 of azulene corresponds in the type of its reactivity to positions 3 and 1 of

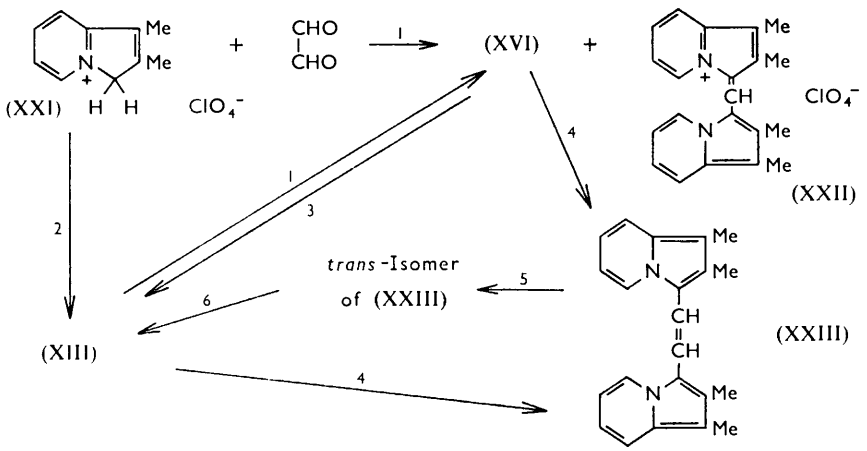
* Protonation of 1,2-dimethyl- and 1-methyl-2-phenyl-indolizine with perchloric acid gives the 3*H*-indolizinium salts. 2,3-Dimethylindolizine gives a mixture of 2,3-dimethyl-3*H*- and -1*H*-indolizinium perchlorate.[3]

[3] Fraser, Melera, Molloy, and Reid, *J.*, 1962, 3288 and unpublished results.

[4] Brown, *Trans. Faraday Soc.*, 1948, **44**, 984; Coulson and Longuet-Higgins, *Rev. Sci. Instr.*, 1947, **85**, 929; Julg, *Compt. rend.*, 1954, **239**, 1498; Pullman and Bertier, *Compt. rend.*, 1948, **227**, 677; Pullman, Mayot, and Bertier, *J. Chem. Phys.*, 1950, **18**, 257.

[5] Coulson and Longuet-Higgins, *Trans. Faraday Soc.*, 1947, **43**, 87; Fukui, Yonezawa, Nagata, and Shingu, *J. Chem. Phys.*, 1954, **22**, 1433.

indolizine. A methyl group at position 1 or 3 of azulene [6] or indolizine [7] tends to lose hydrogen as a hydride ion, while the methyl group of 4- or 6-methylazulenes [2] and 5-methylindolizines [8] is acidic. On the basis of these facts and the following observations on the diperchlorates of the two series considered jointly, we conclude that reversible



Reagents: 1, EtOH. 2, MeCN. 3, $HClO_4$. 4, $NaBH_4$—EtOH. 5, Alumina. 6, Chloranil—$HClO_4$.

proton loss does not occur at a methyl substituent. First, a methyl group at position 2 of the indolizine nucleus cannot be involved since the diperchlorate (XIV) forms a monoperchlorate. Secondly, acidic methyl substituents, though present in the seven-membered ring of the diperchlorates (V) and (VI), are not present in the chemically analogous six-membered ring of (XIII), (XIV), or (XV). Finally, a methyl group at position 1 or 3 of the azulene or indolizine nucleus cannot be involved since ethanediylidenebis-(4,6,8-trimethylazulenium perchlorate) (V) carries no substituents at these sites. We conclude that reversible proton-transfer occurs at the structural feature common to all the diperchlorates, the ethanediylidene bridge. The monoperchlorates from 4,6,8-trimethylazulene, guaiazulene, 1,2- and 2,3-dimethylindolizine, and 1-methyl-2-phenylindolizine therefore possess the structures (XI), (XII), (XVI), (XVIII), and (XVII), respectively. It is noteworthy that the ready interconversion of the allenic monoperchlorates and the corresponding diperchlorates now described bears a resemblance to the reversible protonation of the neutral colourless allene (XIX) to give the blue perchlorate (XX).[9]

Condensation of 1,2-dimethyl-3*H*-indolizinium perchlorate (XXI) with glyoxal in acetonitrile gave ethanediylidenebis-(1,2-dimethylindolizinium perchlorate) (XIII) alone, but in ethanol solution afforded the sparingly soluble violet-black monoperchlorate (XVI) (89% yield) along with 1,2-dimethyl-3-(1,2-dimethylindolizin-3-ylmethylene)indolizinium perchlorate (XXII) (5·5% yield). For comparison the monomethine dye salt (XXII) [10] was also prepared, unambiguously, by condensing 3-formyl-1,2-dimethylindolizine with 1,2-dimethyl-3*H*-indolizinium perchlorate. The diperchlorate (XIII) is undoubtedly an intermediate in the condensation in ethanol, being at once converted into the monoperchlorate by the action of the solvent. The condensation of glyoxal with 1,2- or 2,3-disubstituted indolizines thus appears to occur by a mechanism similar to that formulated for its condensation with the azulenes.[1]

The readiness with which the diperchlorates (V), (VI), (XIII), (XIV), and (XV) are

[6] Kirby and Reid, *Tetrahedron Letters*, 1960, No. 15, 1.
[7] Fraser and Reid, unpublished results.
[8] Boekelheide, Saunders, and Windgassen, *J. Amer. Chem. Soc.*, 1959, **81**, 1459.
[9] Cookson, Rosenbaum, and Symons, *Proc. Chem. Soc.*, 1960, 353.
[10] Stepanov and Lukashina, *Zhur. obshchei Khim.*, 1959, **29**, 2792.

converted into the corresponding monoperchlorates is probably due to electrostatic repulsion of adjacent positive charges on the carbon atoms of the ethanediylidene bridge.

Formation of the monomethine dye salt (XXII) occurs to a limited extent in ethanol solution but is completely suppressed in acetonitrile. We suggest that hydrogen bonding of the intermediate (XXIV) with ethanol shields the formyl group and thereby promotes reaction at the methine-carbon atom, whereas nucleophilic addition of acetonitrile to the methine-carbon atom, as in (XXV), leaves the formyl group free for reaction.

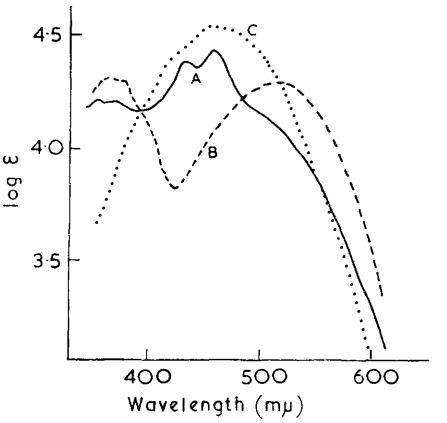


FIG. 1. Absorption spectra of diperchlorates (V) (curve A) in MeCN containing 4% (v/v) of $HClO_4$, and of (XIII) (curve B) and (XV) (curve C) in MeCN containing 2% (v/v) of $HClO_4$.

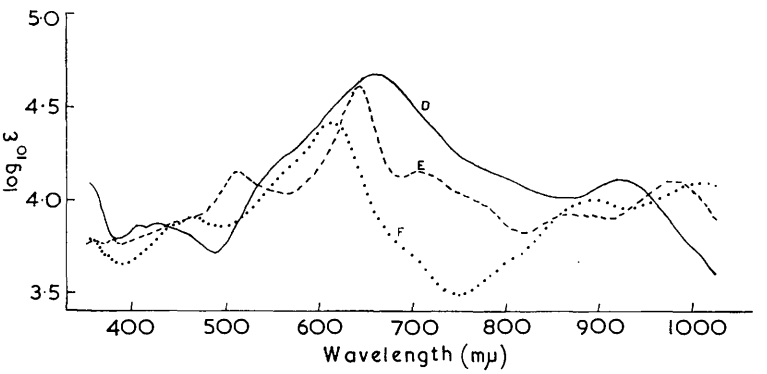
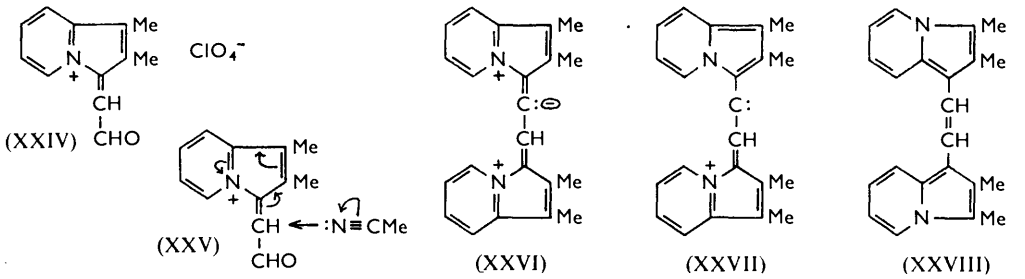


FIG. 2. Absorption spectra of perchlorates (XI) (curve D), (XVI) (curve E), and (XVIII) (curve F).

The monoperchlorates (XI), (XII), (XVI), (XVII), and (XVIII) are interesting cases of compounds showing molecular asymmetry of the allene type, in which one of the double bonds of the allene group possesses a low bond order and high polarisability owing to its conjugation with the polarisable azulene or indolizine nucleus. Resolution is therefore likely to be difficult or impossible.

The diperchlorates of both series show a single broad absorption band in the visible region below 550 mμ (Fig. 1) with little (azulene series) or no fine structure (indolizine series). The spectra of the monoperchlorates (Fig. 2) are all similar above 350 mμ and are characterised by three regions of broad absorption: (i) Below 550 mμ a broad or flat band occurs (log ε 3·7—4·2), on which a number of smaller peaks is in certain cases superimposed. (ii) Between 600 and 750 mμ there occurs an intense band (log ε 4·4—4·8) which with the salts of the indolizine series is just resolved into two peaks. This is the most intense absorption band in the electronic spectrum of the salts of both series. (iii) All the monoperchlorates show strong absorption in the near-infrared region between 850 and 1050 mμ

(log ε 4·0—4·2). The monoperchlorates of the azulene series show a single peak, those of the indolizine series two peaks. The intense absorption extending throughout the visible region and into the near-infrared cannot be explained in terms of extended π-electron delocalisation in structures such as (XI) and (XVI). Conjugation is interrupted at the central carbon atom of the allene group as the axes of the π-orbitals are orthogonal. We suggest that other polar structures may be important in the ground or excited states, for example (XXVI) and (XXVII) in the case of the monoperchlorate (XVI).



The behaviour of the monoperchlorates (XVI) and (XVIII) towards hydride donors was examined. Sodium borohydride in ethanol produced 1,1′,2,2′-tetramethylvinylene-3,3′-di-indolizine (XXIII) and 2,2′,3,3′-tetramethylvinylene-1,1′-di-indolizine (XXVIII), respectively, in quantitative yield, both as mixtures of the *cis*- and *trans*-isomers. One isomer from each of the *cis*–*trans*-mixtures was isolated by chromatography, the other being destroyed or isomerised on the alumina. The isomers which were isolated are tentatively assigned the *trans*-structure in view of the usually greater stability of *trans*- than of *cis*-polyenes. Though stable orange crystalline solids in the dark, they are slowly altered by the action of air and light.

The *trans*-ethylenes (XXIII) and (XXVIII) readily lost a hydride ion to quinones in the presence of perchloric acid,[11] giving the diperchlorates (XIII) and (XV), respectively. These salts result from the action of the excess of the acid on the monoperchlorates (XVI) and (XVIII), the primary products of the dehydrogenation. These results are further evidence for the allenic structures deduced for the monoperchlorates.

Experimental

M.p.s were determined on a Kofler-type heating stage. Visible spectra were measured with a Unicam S.P. 600, ultraviolet spectra with a Unicam S.P. 700, spectrophotometer. Light-absorption data refer to solutions in acetonitrile, unless otherwise stated. The following abbreviations are used: b = broad; sh = shoulder; infl = inflection.

Materials.—Acetic acid was of " AnalaR " grade. Acetonitrile was purified by boiling it for 1 hr. over phosphoric anhydride, then distilled, and it was redistilled through a Vigreux column (50 cm.) before use. Ethanol was redistilled commercial absolute ethanol. Light petroleum was of boiling range 40—60°. Glyoxal refers to a 30% (w/w) solution of the aldehyde in water. Perchloric acid refers to 70—72% (w/w) perchloric acid of " AnalaR " grade.

Condensation of Glyoxal with Azulenes in the Presence of Perchloric Acid.—(i) The condensations of glyoxal (*a*) with azulene in acetonitrile, giving 1-(azulen-1-ylmethylene)azulenium perchlorate (VII), $\lambda_{max.}$ (in acetic acid) 618 mμ (log ε 5·0), (*b*) with guaiazulene in acetonitrile. giving ethanediylidenebis-(5-isopropyl-3,8-dimethylazulenium perchlorate) (VI), $\lambda_{max.}$ [in MeCN containing 2% (v/v) of $HClO_4$] 670sh, 534, 466sh, 410sh, 318, and 258 mμ (log ε 3·45, 4·56, 4·46, 4·25, 4·25, and 4·63), and (*c*) with 4,6,8-trimethylazulene in acetic acid, giving 4,6,8-trimethyl-1-(4,6,8-trimethylazulen-1-ylvinylidene)azulenium perchlorate (V), were carried out as already described.[1]

[11] Reid, Fraser, Molloy, Payne, and Sutherland, *Tetrahedron Letters*, 1961, 530.

(ii) *With* 1-*methylazulene in acetonitrile.* Perchloric acid (0·25 ml., 3 mmoles) was added to a boiling solution of 1-methylazulene (280 mg., 2 mmoles) and glyoxal (200 mg., 1·04 mmoles) in acetonitrile (25 ml.). Black needles separated at once from the boiling deep-blue solution. The product (quantitative yield) was filtered from the cooled solution, washed with ether, and recrystallised from acetonitrile. 3-Methyl-1-(3-methylazulen-1-ylmethylene)azulenium perchlorate (VIII) was obtained as green prismatic needles, identical (visible spectrum) with the product of condensation of 1-methylazulene, 3-formyl-1-methylazulene, and perchloric acid.[12]

(iii) *With* 4,6,8-*trimethylazulene in acetonitrile.* A boiling solution of glyoxal (380 mg., 2 mmoles) in acetonitrile (5 ml.) was added to one of 4,6,8-trimethylazulene (540 mg., 3 mmoles) and perchloric acid (1 ml., 12 mmoles) in acetonitrile (10 ml.), also boiling. The mixture became reddish-brown and was boiled for 1 min. The solid which had crystallised from the cooled solution was filtered off and added to boiling acetonitrile (40 ml.). Boiling ethanol (40 ml.) was added and the violet mixture was boiled for 1 min., then cooled. Filtration followed by washing with ethanol gave 4,6,8-trimethyl-1-(4,6,8-trimethylazulen-1-ylvinylidene)azulenium perchlorate (XI) (372 mg., 54%), m. p. 257° (decomp.) on block preheated to 250°, $\lambda_{max.}$ 920, 660, 430b, 405b, 321sh, 292b, and 249 mμ (log ε 4·13, 4·67, 3·87, 3·87, 4·30, 4·39, and 4·65), identical (m. p., visible and ultraviolet spectrum) with the product of condensation of glyoxal, 4,6,8-trimethylazulene, and perchloric acid in acetic acid.[1]

5-*Isopropyl*-1-(5-*isopropyl*-3,8-*dimethylazulen*-1-*ylvinylidene*)-3,8-*dimethylazulenium Perchlorate* (XII).—Ethanol (125 ml.) was added to a boiling solution of ethanediylidenebis-(5-isopropyl-3,8-dimethylazulenium perchlorate) (1·930 g.) in acetonitrile (125 ml.), and the resulting solution was boiled for 1 min. The solution became violet-blue and was cooled to 5°. The *perchlorate* (XII) (657 mg., 41%) crystallised as dark green needles, readily soluble in acetonitrile and methylene chloride. For recrystallisation it was dissolved in boiling acetone and the filtered solution was evaporated to low volume. The salt melts on a block preheated to <205°, but decomposes slowly on being heated from room temperature (Found: C, 74·1; H, 7·1; Cl, 7·0. $C_{32}H_{35}ClO_4$ requires C, 74·0; H, 6·8; Cl, 6·8%); it has $\lambda_{max.}$ 990, 702, 556infl, 485b, 395, 326sh, 285b, 257, and 243 mμ (log ε 4·20, 4·81, 4·03, 3·98, 3·80, 4·16, 4·35, 4·52, and 4·52).

3-(1,2-*Dimethylindolizin*-3-*ylmethylene*)-1,2-*dimethylindolizinium Perchlorate* (XXII).—A mixture of 3-formyl-1,2-dimethylindolizine [7] (1·73 g., 10 mmoles), 1,2-dimethyl-3*H*-indolizinium perchlorate (1·45 g., 10 mmoles), and methanol (50 ml.) was boiled for 4 min. The deep blue solution was cooled, ether (30 ml.) was added, and the filtered product was recrystallised from methanol. The perchlorate (XII) (3·3 g., 85%) was obtained as green needles with a golden reflex which decompose >260° and have $\lambda_{max.}$ (in MeOH) 629 mμ (log ε 4·62) (lit.,[10] 629 mμ).

Condensation of Glyoxal with Indolizinium Perchlorates in Acetonitrile.—(i) *With* 1,2-*dimethyl*-3H-*indolizinium perchlorate.* Glyoxal (24 ml., 120 mmoles) was added to a hot solution of 1,2-dimethyl-3*H*-indolizinium perchlorate (19·68 g., 80 mmoles) in acetonitrile (120 ml.). The solution became red at once, and was boiled for 2 min. before the addition of 60% (w/w) perchloric acid (12 ml.). Dry ether (50 ml.) was added with swirling to the cooled solution which, in 1 hr. at 10°, deposited *ethanediylidenebis*-(1,2-*dimethylindolizinium perchlorate*) (XIII) (6·17 g., 30%) as reddish-brown prisms with a golden reflex, unchanged in form or m. p. after recrystallisation from acetonitrile. It melts gradually with decomp. >225° (Found: C, 51·6; H, 4·5; N, 5·3. $C_{22}H_{22}Cl_2N_2O_8$ requires C, 51·5; H, 4·3; N, 5·5%) and has $\lambda_{max.}$ [in MeCN containing 2% (v/v) of $HClO_4$] 516, 365b, 289, and 234infl mμ (log ε 4·29, 4·31, 4·24, and 4·10).

(ii) *With* 2,3-*dimethyl*-1H-*indolizinium perchlorate.* The condensation was carried out in the same manner as the preceding one, with glyoxal (3 ml., 15 mmoles), 2,3-dimethyl-1*H*-indolizinium perchlorate (2·46 g., 10 mmoles), 60% (w/w) perchloric acid (2 ml.), and acetonitrile (10 ml.). *Ethanediylidenebis*-(2,3-*dimethylindolizinium perchlorate*) (XV) (540 mg., 21%) crystallised from the cooled solution without the addition of ether. Recrystallisation from acetonitrile containing 1% (v/v) of perchloric acid gave small brown prismatic needles which slowly decompose >260° (Found: C, 51·8; H, 4·6; N, 5·1. $C_{22}H_{22}Cl_2N_2O_8$ requires C, 51·5; H, 4·3; N, 5·5%) and have $\lambda_{max.}$ [in MeCN containing 2% (v/v) of $HClO_4$] 458, 303, and 255 mμ (log ε 4·54, 3·89, and 4·24).

(iii) *With* 1-*methyl*-2-*phenyl*-3H-*indolizinium perchlorate.* Glyoxal (3 ml., 15 mmoles) was added to a hot solution of 1-methyl-2-phenyl-3*H*-indolizinium perchlorate (3·07 g., 10 mmoles) in acetic acid (40 ml.). The dark red solution was boiled for 2 min., then cooled, and perchloric

[12] Kirby and Reid, *J.*, 1961, 1724.

acid (2 ml.) was added. The solution, cooled at 10° for 30 min., deposited *ethanediylidenebis-(1-methyl-2-phenylindolizinium perchlorate)* (XIV) (1·34 g., 42%) which recrystallised from acetic acid as ruby-red prisms, m. p. 243—255° with slight decomp. >210° (Found: C, 60·5; H, 4·1; N, 4·1. $C_{32}H_{26}Cl_2N_2O_8$ requires C, 60·3; H, 4·1; N, 4·4%), $\lambda_{max.}$ [in MeCN containing 2% (v/v) of $HClO_4$] 505, 368b, and 248b mμ (log ε 4·20, 4·16, and 4·40).

Condensation of Glyoxal with Indolizinium Perchlorates in Ethanol.—(i) *With 1,2-dimethyl-3H-indolizinium perchlorate.* Glyoxal (6 ml., 30 mmoles) was added to a boiling solution of 1,2-dimethyl-3*H*-indolizinium perchlorate (4·92 g., 20 mmoles) in ethanol (120 ml.). Black needles began to separate from the deep-blue boiling solution, which was boiled for a further 30 sec. before being allowed to cool spontaneously to room temperature. The solid was filtered off and washed with ethanol (60 ml.), and the combined ethanol filtrates were filtered, diluted with dry ether (100 ml.), and set aside for 24 hr. 3-(1,2-Dimethylindolizin-3-ylmethylene)-1,2-dimethylindolizinium perchlorate (XXII) (220 mg., 5·5%) crystallised as violet-black rosettes of needles which melt with decomp. >260°, $\lambda_{max.}$ (in MeOH) 629 mμ (log ε 4·61), identical (m. p. and visible spectrum) with the product of condensation of 1,2-dimethyl-3*H*-indolizinium perchlorate with 3-formyl-1,2-dimethylindolizine in methanol.

The black solid was extracted exhaustively with boiling ethanol (6 × 150 ml.) until the colour of the extracts had changed from deep blue to pale violet-blue. Removal of traces of the soluble dye salt (XXII) was then complete. Elemental analysis showed the crude product (3·49 g., 89%) to be virtually pure. A sample, recrystallised from a large volume of methanol, gave 3-(1,2-*dimethylindolizin*-3-*ylvinylidene*)-1,2-*dimethylindolizinium perchlorate* (XVI) as fine violet-black needles, m. p. 222—224° (decomp.) on a block preheated to 215° (Found: C, 64·5; H, 5·7; N, 6·7. $C_{22}H_{21}ClN_2O_4$ requires C, 64·0; H, 5·1; N, 6·8%), $\lambda_{max.}$ 980, 870, 705, 642, 514, 378b, 358b, 324infl, 290, and 246 mμ (log ε 4·09, 3·91, 4·19, 4·62, 4·16, 3·78, 3·78, 3·93, 4·17, and 4·28). The salt is almost insoluble in the common polar organic solvents except nitromethane in which, however, it slowly decomposes.

(ii) *With 2,3-dimethyl-1H-indolizinium perchlorate.* The condensation was analogous to the preceding one. The crude product from glyoxal (3 ml., 15 mmoles), 2,3-dimethyl-1*H*-indolizinium perchlorate (2·46 g., 10 mmoles), and ethanol (60 ml.), which had begun to crystallise from the boiling solution as black needles, was washed with hot ethanol (3 × 150 ml.) and recrystallised from acetonitrile. 1-(2,3-*Dimethylindolizin*-1-*ylvinylidene*)-2,3-*dimethylindolizinium perchlorate* (XVIII) (1·26 g., 61%) formed small dark brown needles, m. p. 228—228·5° (Found: C, 63·9; H, 5·5; Cl, 8·5; N, 6·9. $C_{22}H_{21}ClN_2O_4$ requires C, 64·0; H, 5·1; Cl, 8·6; N, 6·8%), $\lambda_{max.}$ 1010, 895, 612, 468b, 334, 255sh, and 233 mμ (log ε 4·13, 4·04, 4·48, 3·97, 3·91, 4·27, and 4·42).

(iii) *With 1-methyl-2-phenyl-3H-indolizinium perchlorate.* Glyoxal (1·5 ml., 7·5 mmoles) was added to a boiling solution of 1-methyl-2-phenyl-3*H*-indolizinium perchlorate (1·54 g., 5 mmoles) in ethanol (25 ml.). The resulting greenish-blue mixture was boiled for 30 sec. The product (1·0 g., 92%) which had partly crystallised from the boiling solution as black needles, was filtered off from the cooled solution, washed with boiling ethanol (2 × 150 ml.), and recrystallised from ethanol. 1-*Methyl*-3-(1-*methyl*-2-*phenylindolizin*-3-*ylvinylidene*)-2-*phenylindolizinium perchlorate* (XVII) was obtained as brownish-black crystals which gradually decompose >230° (Found: N, 4·5. $C_{32}H_{25}ClN_2O_4$ requires N, 5·2%) and have $\lambda_{max.}$ 1070sh, 706, 647, 518, and 242 mμ.

1,1′,2,2′-*Tetramethyl*-(cis + trans)-*vinylene*-3,3′-*di-indolizine*.—Sodium borohydride was added portionwise to a boiling suspension of 3-(1,2-dimethylindolizin-3-ylvinylidene)-1,2-dimethylindolizinium perchlorate (4·13 g., 10 mmoles) in ethanol (240 ml.) until the black solid had disappeared (1—1·2 g. of the reagent were required). Towards the end of the reduction orange crystals separated from the deep-yellow boiling solution. Water was added to the cooled solution, and the precipitated product was extracted in ether (1200 ml.). The extract was washed with water (5 × 300 ml.) before being dried (K_2CO_3). Owing to the sensitivity of the product to traces of acid subsequent operations in this experiment and in the reduction of the monoperchlorate (XVIII) were carried out in apparatus which had been washed with aqueous ammonia followed by distilled water. Evaporation of the solvent left a mixture of *cis*- and *trans*-1,1′,2,2′-tetramethylvinylene-3,3′-di-indolizine (XXIII) in almost quantitative yield; this recrystallised from acetonitrile as flat orange needles, m. p. 165—180° (decomp.), becoming brown >155° (Found: C, 83·8; H, 6·9; N, 8·9. Calc. for $C_{22}H_{22}N_2$: C, 84·0; H, 7·1; N, 8·9%).

The same product (985 mg., 63%), m. p. 165—180° (decomp.), after recrystallisation from acetonitrile, was obtained by the reduction of ethanediylidenebis-(1,2-dimethylindolizinium perchlorate) (2·57 g., 5 mmoles) with sodium borohydride (800—1000 mg.) in boiling ethanol (120 ml.).

A solution of the *cis–trans* mixture (3 g.), m. p. 165—180°, in the minimum volume of benzene–light petroleum (1 : 1) was chromatographed on alumina (30 × 5·5 cm.). Elution with the same solvent mixture brought through yellow eluates which were collected in 200-ml. fractions. Each fraction was evaporated at reduced pressure and the residue was crystallised from acetonitrile. The following crops were obtained (numbers refer to the eluate fractions): (i) yellow-orange needles, 350 mg., m. p. 179—183°; (ii) thick orange needles, 700 mg., m. p. 180—183°; (iii) as in (ii), 250 mg.; (iv) thick orange needles, 110 mg., m. p. 178·5—181·5°; (v) a negligible quantity of orange needles which were discarded. Recrystallisation of the combined crops (ii) and (iii) from acetonitrile gave 1,1′,2,2′-*tetramethyl*-trans-*vinylene*-3,3′-*di-indolizine* (XXIII) as orange needles, m. p. 180—183° (Found: C, 83·6; H, 7·0; N, 9·2. $C_{22}H_{22}N_2$ requires C, 84·0; H, 7·1; N, 8·9%), $\lambda_{max.}$ 410, 299, 290, 245, and 223 mμ (log ε 4·45, 4·39, 4·39, 4·45, and 4·51).

2,2′,3,3′-*Tetramethyl*-(cis + trans)-*vinylene*-1,1′-*di-indolizine*.—1-(2,3-Dimethylindolizin-1-ylvinylidene)-2,3-dimethylindolizinium perchlorate (2·06 g., 5 mmoles) was reduced with sodium borohydride (0·5 g.) in ethanol (60 ml.), and the mixture was worked up as in the preceding experiment. A mixture of *cis*- and *trans*-2,2′,3,3′-tetramethylvinylene-1,1′-di-indolizine (XXVIII) (1·31 g., 83%) was obtained as orange needles, m. p. 193—210°.

A solution of the foregoing mixture (2 g.) in the minimum volume of benzene–light petroleum (1 : 2) was adsorbed on alumina (28 × 4·2 cm.). Elution was with benzene–light petroleum (2 : 1). The eluates were collected in 100-ml. fractions which were worked up as described for the preceding experiment. The following crops of yellow-orange needles were obtained (numbers refer to the eluate fractions; all m. p.s were with decomposition): (i) and (ii) 700 mg., m. p. 193—197·5°; (iii) 89 mg., 206—210·5°; (iv) 120 mg., 208·5—211·5°; (v) 119 mg., 210·5—213°; (vi) and (vii) 147 mg., m. p. 208·5—213°; (viii) and (ix) 27 mg., m. p. 208·5—213°. The combined crops (v)—(ix) were rechromatographed on alumina (10 × 2·7 cm.) with benzene–light petroleum (2 : 1) as solvent and eluant. The eluates gave 2,2′,3,3′-*tetramethyl*-trans-*vinylene*-1,1′-*di-indolizine* (XXVIII) as yellow-orange needles, m. p. 210·5—214° (decomp.) after one recrystallisation from acetonitrile, unchanged by further crystallisation (Found: C, 83·4; H, 7·4; N, 8·9. $C_{22}H_{22}N_2$ requires C, 84·0; H, 7·1; N, 8·9%), $\lambda_{max.}$ 413b, 362, 347sh, 300infl, 255, and 229 mμ (log ε 4·14, 4·30, 4·27, 4·10, 4·62, and 4·46).

Oxidation of 1,1′,2,2′-*Tetramethyl*-trans-*vinylene*-3,3′-*di-indolizine with Chloranil–Perchloric Acid*.—The *trans*-ethylene (XXIII) (314 mg., 1 mmole), m. p. 180—183°, was added all at once to a boiling mixture of chloranil (246 mg., 1 mmole), 60% (w/w) perchloric acid (0·45 ml.), and acetonitrile (5 ml.). The mixture became red immediately and was boiled for 2 min., or until all the chloranil had dissolved. The cooled solution deposited ethanediylidenebis-(1,2-dimethylindolizinium perchlorate) (XIII) (110 mg., 21%) as dark brown prisms which were washed with dry ether, identical (m. p. and visible spectrum) with the product of condensation of glyoxal with 1,2-dimethyl-3*H*-indolizinium perchlorate in acetonitrile.

Oxidation of 2,2′,3,3′-*Tetramethyl*-trans-*vinylene*-1,1′-*di-indolizine with Chloranil–Perchloric Acid*.—The procedure was identical with that of the preceding experiment; the *trans*-ethylene (XXVIII) (105 mg., 0·33 mmole), m. p. 210·5—214°, chloranil (89 mg., 0·33 mmole), 60% (w/w) perchloric acid (0·15 ml.), and acetonitrile (3 ml.) were used. Dry ether (3 ml.), added slowly to the cooled mixture, precipitated ethanediylidenebis-(2,3-dimethylindolizinium perchlorate) (XV) in quantitative yield as brown prismatic needles which, after being washed with dry ether, were identical (m. p. and visible spectrum) with the product of condensation of glyoxal with 2,3-dimethyl-1*H*-indolizinium perchlorate in acetonitrile.

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