701. *Conjugated Cyclic Hydrocarbons and Their Heterocyclic Analogues. Part VI.*[1] *The Condensation of Azulenes with Aliphatic Aldehydes in the Presence of Perchloric Acid.*

By E. C. Kirby and D. H. Reid.

Condensation of azulene hydrocarbons with the following classes of aliphatic aldehydes in the presence of perchloric acid is reported: simple αβ-unsaturated aldehydes; α-oxo-aldehydes; dialdehydes; β-oxo-aldehydes; α-cyano- and α-nitro-aldehydes. The nature of the products depends on the degree of alkylation of the azulene and on the type of the aldehyde. Possible pathways to the various types of products are discussed. Spectral data for the products are recorded.

In the first reported condensations of azulenes with aldehydes, guaiazulene (5-isopropyl-3,8-dimethylazulene) reacted with benzaldehyde and its derivatives in the presence of hydrogen chloride to form 3-arylmethyleneguaiazulenium chlorides.[2] These salts were unstable but could be converted into the somewhat more stable picrates. Although heterocyclic aromatic, and many aliphatic, aldehydes also condensed the unstable products could not be isolated. Subsequently, in an improved procedure,[3] with 70% (w/w) perchloric acid in place of anhydrous hydrogen chloride, ready condensation occurred with carbocyclic and heterocyclic aromatic aldehydes to give the thermally stable, crystalline perchlorates. We now describe the application of our modified procedure to the condensation of azulene hydrocarbons with simple and multifunctional aliphatic aldehydes.

The products from most reactions of azulenes with multifunctional aliphatic aldehydes do not correspond to a simple condensation of one molecule each of the azulene, the aldehyde, and perchloric acid, as in the condensations with aromatic aldehydes,[3] and are formed by a different mechanism. Also, in many condensations alkylated azulenes behave differently from azulene, owing to electron-release by the substituents which increases the electron-availability at position 1 and stabilises the methyleneazulenium structure of the primary condensation products.

Simple Aliphatic and αβ-Unsaturated Aldehydes.—Condensations with simple aliphatic

[1] Part V, *J.*, 1961, 1724.

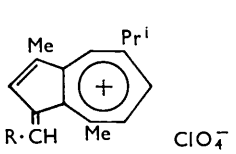
[2] (*a*) Reid, Stafford, Stafford, and (in part) McLennan and Voigt, *J.*, 1958, 1110; (*b*) Reid and Stafford, *Chem. and Ind.*, 1954, 277.

[3] (*a*) Kirby and Reid, *J.*, 1960, 494; (*b*) Reid, "Azulene and Related Substances," *Chem. Soc. Special Publ.*, No. 12, 1958, p. 69.

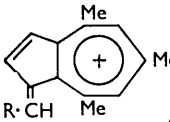
aldehydes were first examined. Acetaldehyde with guaiazulene and 4,6,8-trimethylazulene in acetic acid or tetrahydrofuran gave the stable, yellow crystalline salts (I) and (VI), whose cations are, formally, substituted vinylogues of tropylium. Though stable at room temperature they decompose partly on attempted recrystallisation from acetic acid or acetonitrile. In contrast, no useful product was isolated when perchloric acid was added to azulene and acetaldehyde in acetic acid or acetonitrile. The solutions became green, then yellow, and an intractable black solid, insoluble in the common organic solvents, was deposited.

Derivatives of acetaldehyde (propionaldehyde, butyraldehyde, isobutyraldehyde, and ethoxyacetaldehyde), in which one or more hydrogen atoms of the methyl group have been replaced by electron-releasing groups, failed to condense with guaiazulene and 4,6,8-trimethylazulene. Substituted acetaldehydes in which the methyl-hydrogen atom is replaced by electron-withdrawing substituents all condensed with azulenes. Phenylacetaldehyde with guaiazulene gave the azulenium perchlorate (II) which, however, was unstable and could not be purified. The corresponding product (VII) from 4,6,8-trimethylazulene was even less stable, decomposition preventing its isolation.

Crotonaldehyde condensed with guaiazulene in a vigorous reaction but no useful product could be isolated from the greenish-yellow solution. Cinnamaldehyde and phenylpropargylaldehyde, though formally αβ-unsaturated aldehydes, behaved like benzaldehyde,[3] and with guaiazulene readily afforded perchlorates (III) and (IV), respectively, stable salts which resemble the benzylidene salt [3] (V). The acetylenic salt (IV) absorbs at longer wavelength and more intensely than the parent (V), but at shorter wavelength and less intensely than the salt (III) (Table 1). Cinnamaldehyde also condensed with azulene but decomposition prevented the isolation of the resulting deep red salt.

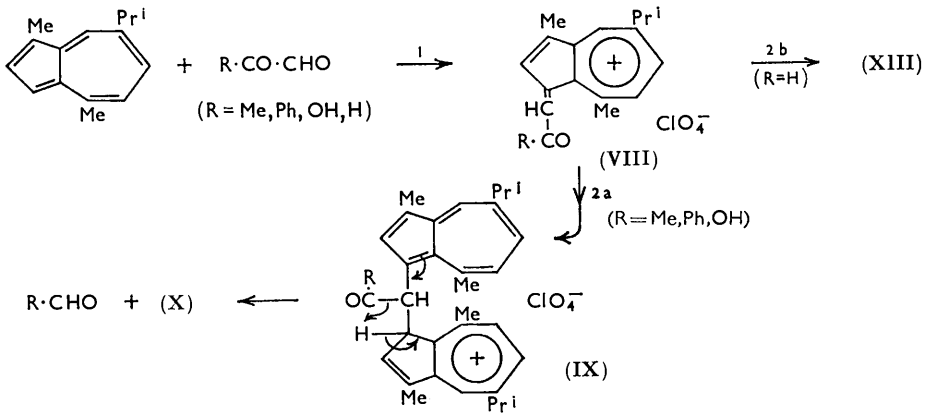


(I) R = Me
(II) R = Ph·CH$_2$
(III) R = Ph·CH=CH
(IV) R = Ph·C≡C
(V) R = Ph



(VI) R = Me
(VII) R = Ph·CH$_2$

α-*Oxo-aldehydes*.—Pyruvaldehyde, phenylglyoxal, and glyoxylic acid all condensed with guaiazulene to yield the same product, 5-isopropyl-1-(5-isopropyl-3,8-dimethylazulen-1-yl)-methylene-3,8-dimethylazulenium perchlorate [1] (X). Glyoxal behaved exceptionally among the α-oxo-aldehydes in condensing with guaiazulene at both aldehyde functions to give ethanediylidenebis-(5-isopropyl-3,8-dimethylazulenium perchlorate) (XIII) whose spectrum (Fig. 1) differs markedly from that of the dye salt (X). We suggest the annexed scheme to interpret these results.



In the primary step (1) the α-oxo-aldehyde R·CO·CHO condenses normally with guaiazulene to form a 1-acylmethylene-5-isopropyl-3,8-dimethylazulenium perchlorate (VIII). The excess of guaiazulene subsequently attacks it at the electrophilic methine carbon atom [step (2a)] to form the dye salt (X) or at the aldehyde function [step (2b)] to yield the diperchlorate (XIII). The added resonance stabilisation attending the formation of compound (X) promotes the elimination of R·CHO from the intermediate (IX).

The diperchlorate (XIV) (spectrum in Fig. 1) was obtained by condensing 4,6,8-trimethylazulene with glyoxal. In contrast, the reaction of glyoxal with azulene was similar

FIG. 1. *Diperchlorates* (XIII) *in* MeCN *containing* 0·5% (v/v) *of* $HClO_4$, (XIV) *in* MeCN *containing* 2% (v/v) *of* $HClO_4$. *Dye salt* (X) *in* AcOH.

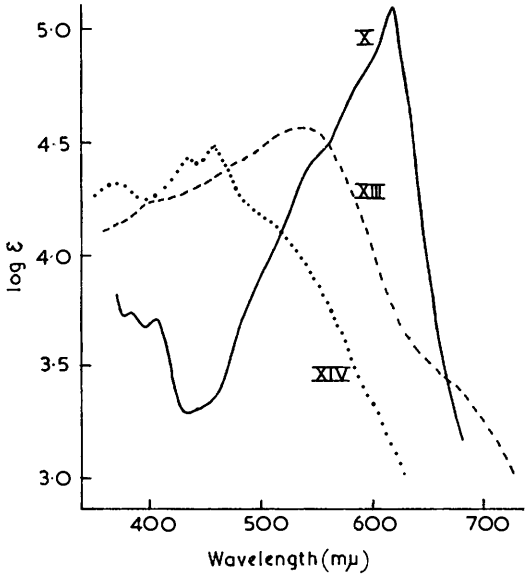
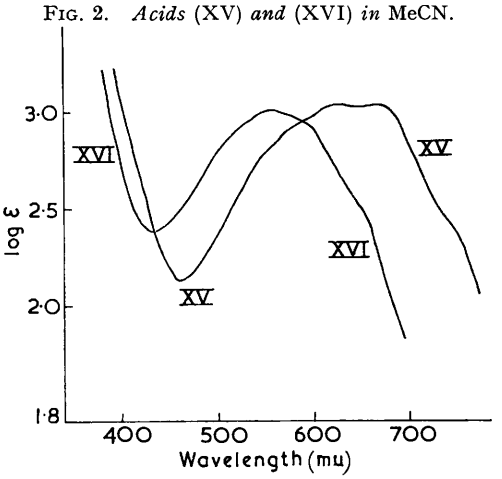


FIG. 2. *Acids* (XV) *and* (XVI) *in* MeCN.

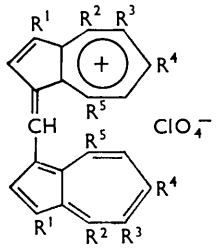


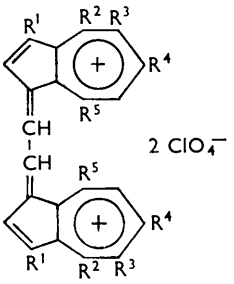
to that of methylglyoxal, phenylglyoxal, and glyoxylic acid with guaiazulene: 1-(azulen-1-yl)methyleneazulenium perchlorate [1,3a] (XI) was isolated in high yield. In this case the methine-carbon atom of the primary product is the stronger electrophilic centre. The difference in behaviour of azulene and guaiazulene with glyoxal is the result of electron-release by the alkyl substituents in the latter hydrocarbon which reduces the electrophilic activity of the methine carbon atom in (VIII; R = H).

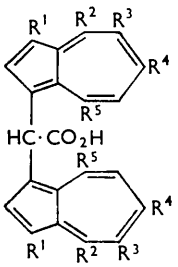
In the absence of perchloric acid glyoxylic acid reacted exothermally with guaiazulene in boiling acetonitrile, to give in high yield di-(5-isopropyl-3,8-dimethylazulen-1-yl)acetic acid (XV). This acid is not an intermediate in the formation of the dye salt (X) from guaiazulene, glyoxylic acid, and perchloric acid, since it was not converted into the salt (X) on being boiled with perchloric acid in acetic acid or acetonitrile. 4,6,8-Trimethylazulene added analogously to give di-(4,6,8-trimethylazulen-1-yl)acetic acid (XVI) with, however, a small amount of a second, unstable and unidentified acid. The assignment of structure (XVI) to the first product from 4,6,8-trimethylazulene and glyoxylic acid is based on the similarity of its visible spectrum to that of the analogue (XV) (Fig. 2). Azulene failed to react with glyoxylic acid alone, and in the presence of perchloric acid also gave an unstable and unidentified acid.

β-*Oxo-aldehydes*.—The condensation products of azulenes with β-oxo-aldehydes (2-hydroxymethylene ketones) were either 2-(azulen-1-yl)vinyl ketones or symmetrical 1-(azulen-1-yl)methyleneazulenium perchlorates. In suitable conditions all azulenes gave

products of the former type. Highly alkylated azulenes (guaiazulene, 4,6,8-trimethylazulene), however, never yielded more than traces of the symmetrical dye salts.







(X) $R^1 = R^5 = Me$; $R^2 = R^4 = H$; $R^3 = Pr^i$

(XI) $R^1 = R^2 = R^3 = R^4 = R^5 = H$

(XII) $R^1 = R^3 = H$; $R^2 = R^4 = R^5 = Me$

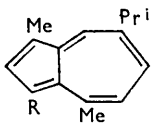
(XV) $R^1 = R^5 = Me$; $R^2 = R^4 = H$; $R^3 = Pr^i$

(XVI) $R^1 = R^3 = H$; $R^2 = R^4 = R^5 = Me$

(XIII) $R^1 = R^5 = Me$; $R^2 = R^4 = H$; $R^3 = Pr^i$

(XIV) $R^1 = R^3 = H$; $R^2 = R^4 = R^5 = Me$

Hydroxymethyleneacetophenone with guaiazulene and 4,6,8-trimethylazulene in boiling acetic acid gave, as sole products, the azulenylvinyl ketones (XVII) and (XXII),



(XVII) R = CH:CH·COPh

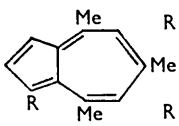
(XVIII) R = CH:CH·COMe

(XIX) R = CH:C(NO$_2$)·CHO

(XX) R = [CH:CH]$_2$·CHO

(XXI) R = CH:CPh·CN

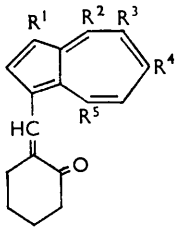
(XXII)



R = CH:CH·COPh

(XXIII)

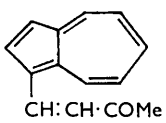
R = CH:CH·COMe



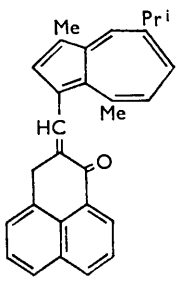
(XXIV) $R^1 = R^5 = Me$; $R^2 = R^4 = H$; $R^3 = Pr^i$

(XXV) $R^1 = R^3 = H$; $R^2 = R^4 = R^5 = Me$

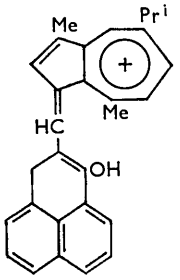
(XXVI) $R^1 = R^2 = R^3 = R^4 = R^5 = H$



(XXVII)



(XXVIII)



(XXIX)

respectively. In contrast, azulene furnished 1-(azulen-1-yl)methyleneazulenium perchlorate (XI) and, of significance for the suggested reaction mechanism, a quantity of acetophenone, isolated as its 2,4-dinitrophenylhydrazone.

2-Hydroxymethylenecyclohexanone behaved similarly. With guaiazulene it gave

the ketone (XXIV), with a small amount of the azulenium perchlorate (X); with 4,6,8-trimethylazulene it gave a ketone (XXV) with a trace of the azulenium perchlorate (XII) [1]; but with azulene it gave the dye salt (XI) as the sole azulenic product, accompanied by cyclohexanone which was isolated as its 2,4-dinitrophenylhydrazone. However, when the condensation with azulene was carried out at room temperature in methanol the main product was the ketone (XXVI), only a trace of the dye salt (XI) being formed.

The products from condensation of hydroxymethyleneacetone with guaiazulene, 4,6,8-trimethylazulene, and azulene were the three ketones (XVIII), (XXIII), and (XXVII), respectively. These were, however, isolated in very low yield, owing apparently to rapid decomposition of free hydroxymethyleneacetone; much unchanged hydrocarbon was recovered in each case.

Guaiazulene condensed with 2-hydroxymethylene-2,3-dihydrophenalen-1-one to give the perchlorate (XXIX) derived from the ketone (XXVIII); the salt crystallised from the reaction mixture.

A plausible mechanism for these condensations is illustrated in the annexed scheme. Azulene is attacked (step 1) by the ketone activated by protonation at either the terminal or the carbonyl oxygen atom, *e.g.*, by (XXX); the perchlorate (XXXI) of the 2-(azulen-1-yl)vinyl ketone (XXXII) is the primary product. Hydrolysis at this stage yields the ketone (XXXII) [step (2a)], but further reaction [step (2b)] with an excess of azulene, *e.g.*, in boiling solution, leads through the intermediate (XXXIII) to the symmetrical dye salt (XI) and the ketone $R^1 \cdot CO \cdot CH_2 \cdot R^2$. The deactivating effect of alkyl substituents on the electrophilic methine-carbon atom of the primary product determines the course of the secondary reaction and the nature of the product.

The isolation of acetophenone and cyclohexanone in the condensation of azulene with hydroxymethyleneacetophenone and 2-hydroxymethylenecyclohexanone provide evidence for the suggested mechanism. Support comes from the isolation in quantitative yield of the dye salt (XI) from a boiling solution of azulene, 2-(azulen-1-yl)methylenecyclohexanone (XXVI), and perchloric acid in acetic acid. This reaction represents a new synthesis of 1-(azulen-1-yl)methyleneazulenium perchlorates in which an azulene is condensed in the presence of perchloric acid with a 2-(azulen-1-yl)vinyl ketone. From the results of experiments described in this section the method is seen to be inapplicable to highly alkylated 2-(azulen-1-yl)vinyl ketones, and is thus complementary to the synthesis [1] of the dye salts by condensation of azulenes with 1-ethoxymethyleneazulenium salts. The visible spectra of the 2-(azulen-1-yl)vinyl ketones consist in all cases of two broad absorption bands (Table 1).

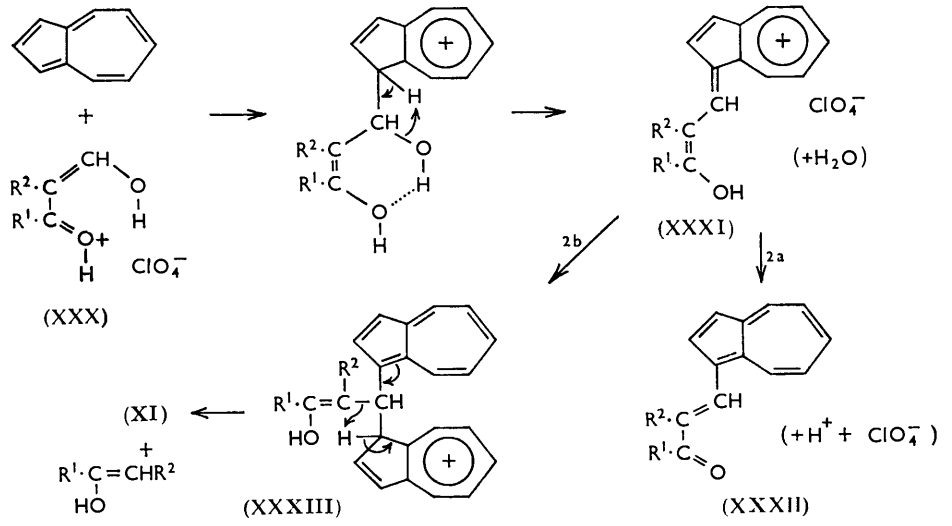
Nitromalondialdehyde and Glutacondialdehyde.—Condensations of azulenes with these aldehydes are closely related to the reactions considered in the preceding section, with respect to both the nature of the products and their mode of formation. Two products ere formed from each aldehyde in the reactions with guaiazulene. Nitromalondialdehyde gave 3-(5-isopropyl-3,8-dimethylazulen-1-yl)-2-nitropropenal (XIX), together with 5-isopropyl-1-[3-(5-isopropyl-3,8-dimethylazulen-1-yl)-2-nitropropenylidene]-3,8-dimethylazulenium perchlorate (XXXIV) which resulted from the subsequent condensation of the aldehyde (XIX) with unchanged guaiazulene. The behaviour of glutacondialdehyde was analogous. The dienal (XX) and its product of further condensation (XXXV) were isolated in comparable yields by carrying out the reaction in the cold with molecular proportions of the reactants. A boiling solution of guaiazulene and glutacondialdehyde in 2 : 1 molecular proportions gave the dye salt (XXXV) alone. This salt is vinylogous with the dye salt (X) which it resembles in showing characteristic, intense absorption in the visible region.[1,3a] The visible absorption spectra of the aldehydes (XIX), (XX), and 3-formylguaiazulene show a progressive bathochromic shift of $\lambda_{max.}$ with increase in length of the polyenal side-chain.

Attempts to cyclise the aldehyde (XIX) under basic conditions to the heptalene derivative (XXXVII) were unsuccessful.

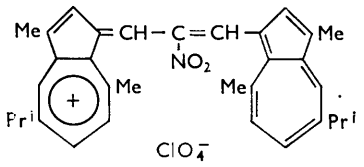
TABLE 1. *Visible absorption maxima* (mμ).

Compound	Solvent	$\lambda_{max.}$	log ε
1-Ethylidene-5-isopropyl-3,8-dimethylazulenium perchlorate (I)	A	425sh, 370	3·45, 3·75
1-Cinnamylidene-5-isopropyl-3,8-dimethylazulenium perchlorate (III)	A	513	4·63
5-Isopropyl-3,8-dimethyl-1-(3-phenylprop-2-ynylidene)azulenium perchlorate (IV)	N [a]	477	4·40
1-Benzylidene-5-isopropyl-3,8-dimethylazulenium perchlorate (V) [b]	A	456	4·09
1-Ethylidene-4,6,8-trimethylazulenium perchlorate (VI)	N	405 [c]	3·66
	A [d]	440sh, 395 [c]	3·50, 3·70
Ethanediylidenebis-(5-isopropyl-3,8-dimethylazulenium perchlorate) (XIII)	N [e]	670sh, 534, 410i	3·45, 4·56, 4·25
Ethanediylidenebis-(4,6,8-trimethylazulenium perchlorate) (XIV)	N [d]	458, 432, 370	4·48, 4·43, 4·31
Di-(5-isopropyl-3,8-dimethylazulen-1-yl)acetic acid (XV)	N	670,[c] 627 [c]	3·02, 3·03
Di-(4,6,8-trimethylazulen-1-yl)acetic acid (XVI)	N	595sh, 560 [c]	2·93, 3·00
β-(5-Isopropyl-3,8-dimethylazulen-1-yl)acrylophenone (XVII)	C	602, 441, 401	2·40, 3·94, 4·09
4-(5-Isopropyl-3,8-dimethylazulen-1-yl)but-3-en-2-one (XVIII)	B	604,[c] 426 [c]	*f*
3-(5-Isopropyl-3,8-dimethylazulen-1-yl)-2-nitropropenal (XIX)	A	527	4·51
1-Formyl-5-isopropyl-3,8-dimethylazulene	C	570	2·70
5-(5-Isopropyl-3,8-dimethylazulen-1-yl)penta-2,4-dienal (XX)	C	635, 453	2·83, 4·67
1-(2-Cyano-2-phenylvinyl)-5-isopropyl-3,8-dimethylazulene (XXI)	B	615, 448	2·87, 4·47
β-(4,6,8-Trimethylazulen-1-yl)acrylophenone (XXII)	C	563,[g] 424 [g]	2·92, 4·46
4-(4,6,8-Trimethylazulen-1-yl)but-3-en-2-one (XXIII)	C	567,[c] 405 [c]	2·89, 4·33
2-(5-Isopropyl-3,8-dimethylazulen-1-yl)methylenecyclohexanone (XXIV)	B	620,[c] 427 [c]	2·73, 4·30
2-(4,6,8-Trimethylazulen-1-yl)methylenecyclohexanone (XXV)	B	562,[c] 408 [c]	2·84, 4·24
2-(Azulen-1-yl)methylenecyclohexanone (XXVI)	B	612,[c] 410 [c]	*f*
4-(Azulen-1-yl)buten-2-one (XXVII)	B	603,[c] 436	*f*
1-(3-Hydroxyphenalen-2-yl)methylene-5-isopropyl-3,8-dimethylazulenium perchlorate (XXIX)	N [d]	502 [c]	4·27
5-Isopropyl-1-[5-(5-isopropyl-3,8-dimethylazulen-1-yl)penta-2,4-dienylidene]-3,8-dimethylazulenium perchlorate (XXXV)	A	860, 505, 430	5·49, 3·88, 3·91
5-Isopropyl-3,8-dimethyl-1-[5-(3-methylazulen-1-yl)penta-2,4-dienylidene]azulenium perchlorate (XXXVI)	A	842, 502, 423	5·37, 3·85, 3·93
1,3-Di-(2-cyano-2-phenylvinyl-1)azulene (XXXVIII)	N	605, 428	2·96, 4·58
1,3-Di-(2-cyano-2-phenylvinyl-1)-4,6,8-trimethylazulene (XXXIX)	B	560,[c] 426	3·05, 4·40

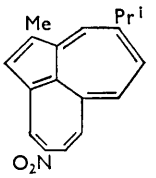
A = acetic acid, B = benzene, C = cyclohexane, N = acetonitrile.
[a] Containing 0·2% (v/v) of perchloric acid. [b] Kirby and Reid, *J.*, 1960, 494. [c] Centre of broad maximum. [d] Containing 2% (v/v) of perchloric acid. [e] Containing 0·5% (v/v) of perchloric acid. *f* log ε undetermined. [g] Hafner and Bernhard (*Annalen*, 1959, **625**, 108) give $\lambda_{max.}$ 562 (2·84) and 422 (4·44).



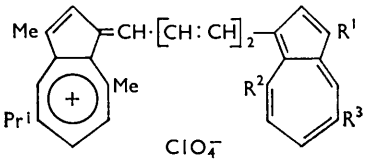
β-*Hydroxy-α-phenylacrylonitrile.*—Neutral products alone were formed in the reactions of β-hydroxy-α-phenylacrylonitrile with azulenes. Azulene and 4,6,8-trimethylazulene reacted at both the 1- and the 3-position, giving the stable, high-melting, green, crystalline 1,3-di-(2-cyano-2-phenylvinyl)azulene (XXXVIII) and 1,3-di-(2-cyano-2-phenylvinyl)-4,6,8-trimethylazulene (XXXIX), respectively. Guaiazulene gave the monosubstitution product (XXI). The presence of perchloric acid, though necessary for the condensations with azulene and 4,6,8-trimethylazulene, is not required for the formation of the salt (XXI) which is also obtained on merely boiling guaiazulene and β-hydroxy-α-phenylacrylonitrile in acetic acid.



(XXXIV)



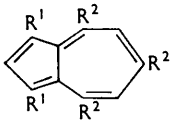
(XXXVII)



(XXXV): $R^1 = R^2 = Me$; $R^3 = Pr^i$

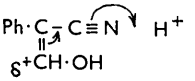
(XXXVI): $R^1 = Me$; $R^2 = R^3 = H$

The condensations with β-hydroxy·α-phenylacrylonitrile appear to involve nucleophilic attack by guaiazulene on the methine-carbon atom of β-hydroxy-α-phenylacrylonitrile or, in the reaction with azulene and 4,6,8-trimethylazulene, its *N*-protonated form (XL).



(XXXVIII) R^1 = CH:CPh·CN, R^2 = H

(XXXIX) R^1 = CH:CPh·CN, R^2 = Me



(XL)

Infrared Spectra (Table 2).—Previous studies [3a,4] have shown that the carbonyl stretching frequency of 1-acylazulenes is abnormally low. This has been correlated with the ready polarisability of the azulene nucleus which results in the significant contribution of dipolar forms to the resonance hybrid. We now find further that the insertion of one or more double bonds between the carbonyl group and the azulene nucleus at $C_{(1)}$ dampens the polarisation of the carbonyl group resulting from direct conjugation. The carbonyl stretching frequencies are shifted to normal or nearly normal values. (*a*) The relatively low frequencies of 1-formylazulene (1658 cm.$^{-1}$) and 1-formyl-5-isopropyl-3,8-dimethylazulene (3-formylguaiazulene) (1630 cm.$^{-1}$), indicative of abnormal polarisation, contrast with that of 5-(5-isopropyl-3,8-dimethylazulen-1-yl)penta-2,4-dienal (XX) (1669 cm.$^{-1}$) which lies in the region in which simple polyene aldehydes absorb.[5] Little or no electronic effect due to the polarisability of the azulene nucleus is transmitted to the carbonyl group. In agreement with the more normal character of the carbonyl group in the aldehyde (XX),

[4] Reid, Stafford, and Stafford, *J.*, 1958, 1119.
[5] Blout, Fields, and Karplus, *J. Amer. Chem. Soc.*, 1948, **70**, 194.

TABLE 2. *Infrared absorption bands* ($cm.^{-1}$).

Compound	Nujol	CCl_4
C=O stretching		
(a) *Aldehydes*		
3-(5-Isopropyl-3,8-dimethylazulen-1-yl)-2-nitropropenal (XIX)	1658	—
5-(5-Isopropyl-3,8-dimethylazulen-1-yl)penta-2,4-dienal (XX)	1668	1669
1-Formylazulene	1645 [a]	1658
1-Formyl-5-isopropyl-3,8-dimethylazulene	1616 [a]	1630
1-Naphthaldehyde	—	1700 [b, c]
$CH_3 \cdot [CH{:}CH]_n \cdot CH{:}CH \cdot CHO$ (n = 2—7)	—	1677—1664 [d]
(b) *Ketones*		
β-(5-Isopropyl-3,8-dimethylazulen-1-yl)acrylophenone (XVII)	—	1650
β-(4,6,8-Trimethylazulen-1-yl)acrylophenone (XXII)	1634	—
2-(5-Isopropyl-3,8-dimethylazulen-1-yl)methylenecyclohexanone (XXIV)	1667	1667
2-(4,6,8-Trimethylazulen-1-yl)methylenecyclohexanone (XXV)	1667	—
1-Acetyl-5-isopropyl-3,8-dimethylazulene	1642	1652
1-Benzoyl-5-isopropyl-3,8-dimethylazulene	1637	—
1-Acetylnaphthalene	—	1685 [b]
Ph·CH:CH·COMe	1680	1691m, 1667
Ph·CH:CH·COPh	—	1667
(c) *Acids*		
Di-(5-isopropyl-3,8-dimethylazulen-1-yl)acetic acid (XV)	1704	—
Di-(4,6,8-trimethylazulen-1-yl)acetic acid (XVI)	1701	—
C≡N stretching		
1-(2-Cyano-2-phenylvinyl)-5-isopropyl-3,8-dimethylazulene (XXXI)	2188	2203
1,3-Di-(2-cyano-2-phenylvinyl)azulene (XXXVIII)	2198	—
1,3-Di-(2-cyano-2-phenylvinyl)-4,6,8-trimethylazulene (XXXIX)	(2210?) 2191	(2284?) 2209
1-Cyano-5-isopropyl-3,8-dimethylazulene	2186	2201
1-Cyanonaphthalene	2212	2222
C≡C stretching		
5-Isopropyl-3,8-dimethyl-1-(3-phenylprop-2-ynylidene)azulenium perchlorate (IV)	2168	—

[a] Kirby and Reid, *J.*, 1960, 494. [b] Hunsberger, *J. Amer. Chem. Soc.*, 1950, **72**, 5626. [c] In $CHCl_3$. [d] Blout, Fields, and Karplus, *J. Amer. Chem. Soc.*, 1948, **70**, 194.

condensation took place with both guaiazulene and 1-methylazulene in the presence of perchloric acid to give the dye salts (XXXV) and (XXXVI). This is in contrast to the reported failure of 1-formyl-5-isopropyl-3,8-dimethylazulene to condense with azulenes under the same conditions.[3a] (*b*) Spectrally, the 2-(azulen-1-yl)vinyl ketones examined fall into two classes, depending on the nature of the second group attached to the carbonyl function. (i) When this is a saturated hydrocarbon residue, as in the ketones (XVIII), (XXIV), (XXV), and (XXVII), ν_{CO} is normal [cf. ν_{CO} for benzylideneacetone and 1-acetyl-5-isopropyl-3,8-dimethylazulene (3-acetylguaiazulene)]. (ii) When, however, the second group is an aromatic ring, as in (XVII) and (XXII), ν_{CO} remains close to that of the polarised 1-benzoyl-5-isopropyl-3,8-dimethylazulene (3-benzoylguaiazulene) (cf. ν_{CO} for benzylideneacetophenone).

The C≡N link in 1-cyano-5-isopropyl-3,8-dimethylazulene (3-cyanoguaiazulene) also shows considerable double-bond character resulting from appreciable contribution of polar structures of the type $Gu^+{=}C{=}N^-$ to the resonance hybrid. The C≡N frequency lowering, exemplified by a comparison of 1-cyano-5-isopropyl-3,8-dimethylazulene with 1-cyanonaphthalene, persists in the nitriles (XXI), (XXXVIII), and (XXXIX), though to a reduced extent.

EXPERIMENTAL

M. p.s were determined on a Kofler-type heating stage. Visible spectra were measured with a Unicam S.P. 600 spectrophotometer. Infrared spectra were recorded with a Grubb–Parsons Type G.S.2A instrument. Chromatography was on activated alumina. Unless otherwise stated, samples of perchlorates for analysis were dried for 6—8 hr. at 80°/0·1 mm.

Materials.—Acetic acid was of " AnalaR " grade. Acetonitrile was purified by boiling it for 30 min. with phosphoric anhydride, then distilled, and it was redistilled before use. Tetrahydrofuran was boiled over sodium wire until it no longer discoloured the fresh metal surface, and then distilled. Light petroleum was of boiling range 40—60°. Perchloric acid refers to 70—72% (w/w) perchloric acid of " AnalaR " grade.

The following aldehydes were purified by distillation immediately before use: acetaldehyde, phenylacetaldehyde, cinnamaldehyde, and phenylpropargylaldehyde. The sodium salts of hydroxymethyleneacetone,[6] hydroxymethyleneacetophenone,[7] nitromalondialdehyde monohydrate,[8] and glutacondialdehyde [9] were used in place of the corresponding unstable aldehydes. Methylglyoxal and glyoxal refer to 30% (w/w) solutions of the aldehydes in water. Phenylglyoxal and glyoxylic acid refer to the aldehyde monohydrates.

2-Hydroxymethylenecyclohexanone was prepared by Borsche's method,[10] and β-hydroxy-α-phenylacrylonitrile by Ghosh's method.[11] 2-Hydroxymethylene-2,3-dihydrophenalen-1-one was prepared by condensation at room temperature of ethyl formate with 2,3-dihydrophenalen-1-one in anhydrous benzene in the presence of sodium methoxide.[12]

Condensation of Simple Aliphatic Aldehydes with Azulenes.—Acetaldehyde with guaiazulene. The order of mixing of the reactants is critical and the following is the most satisfactory procedure. Perchloric acid (0·5 ml.) was added to a solution of guaiazulene (200 mg.) and acetaldehyde (1·5 ml.) in tetrahydrofuran (1 ml.) at room temperature. 1-*Ethylidene*-5-*isopropyl*-3,8-*dimethylazulenium perchlorate* (I) (310 mg., 96%) crystallised after 1—2 min. as yellow needles, m. p. 161—165°, which were washed with tetrahydrofuran, followed by dry ether. The salt decomposes in hot solvents and was analysed without recrystallisation after drying for 8 hr. at 70°/0·1 mm. (Found: C, 62·1; H, 6·1; Cl, 11·2. $C_{17}H_{21}ClO_4$ requires C, 62·9; H, 6·5; Cl, 10·9%).

Acetaldehyde with 4,6,8-*trimethylazulene.* Perchloric acid (1 ml.) was added to a solution of 4,6,8-trimethylazulene (763 mg.) and acetaldehyde (3 ml.) in acetic acid (10 ml.) at room temperature. 1-*Ethylidene*-4,6,8-*trimethylazulenium perchlorate* (VI) (1·17 g., 88%) crystallised as greenish-yellow needles, m. p. 148—151° (decomp.), which partly decompose in hot solvents and were analysed without recrystallisation after being washed with acetic acid, followed by dry ether (Found: C, 60·7; H, 6·0. $C_{15}H_{17}ClO_4$ requires C, 60·7; H, 5·8%).

Condensation of αβ-Unsaturated Aldehydes with Azulenes.—Cinnamaldehyde with guaiazulene. Perchloric acid (1 ml.) was added to a boiling solution of guaiazulene (200 mg.) and cinnamaldehyde (133 mg.) in acetic acid (5 ml.). The cooled solution deposited 1-*cinnamylidene*-5-*isopropyl*-3,8-*dimethylazulenium perchlorate* (III) (310 mg., 75%). Recrystallisation of the salt from acetic acid gave deep red needles, m. p. 179·5—193·5° (decomp.) (Found: C, 70·3; H, 5·9; Cl, 8·1. $C_{24}H_{25}ClO_4$ requires C, 69·8; H, 6·1; Cl, 8·6%).

Phenylpropargylaldehyde with guaiazulene. A solution of guaiazulene (600 mg.) and perchloric acid (0·5 ml.) in acetonitrile (8 ml.) was added to one of the aldehyde (400 mg.) in acetonitrile (4 ml.), all at room temperature. The orange-red solid which crystallised at once from the orange-brown solution was filtered off after 5 min. and recrystallised from acetonitrile. 5-*Isopropyl*-3,8-*dimethyl*-1-(3-*phenylprop*-2-*ynylidene*)*azulenium perchlorate* (IV) was obtained as orange-red prisms (700 mg., 57%) which melt to a black liquid on a block preheated to ⩽255°, but decompose slowly without melting on being heated from room temperature (Found: C, 69·7; H, 5·5; Cl, 8·5. $C_{24}H_{25}ClO_4$ requires C, 70·2; H, 5·6; Cl, 8·6%).

Condensation of α-Oxo-aldehydes with Azulenes.—Methylglyoxal with guaiazulene. Perchloric acid (1 ml.) was added to a solution of guaiazulene (1·0 g.) and methylglyoxal (1·2 g.) in tetrahydrofuran (15 ml.). The solution became green, then blue, and in 72 hr. at room temperature deposited 5-*isopropyl*-1-(5-*isopropyl*-3,8-*dimethylazulen*-1-*yl*)*methylene*-3,8-*dimethylazulenium perchlorate* (X) (30 mg., 2%), which recrystallised from acetic acid as flat black needles, m. p. 247—250° (decomp.) (block preheated to 240°) (Found: C, 73·3; H, 7·1; Cl, 6·9. $C_{31}H_{35}ClO_4$ requires C, 73·4; H, 7·0; Cl, 7·0%), identical (m. p., mixed m. p., and visible spectrum) with

[6] Claisen and Stylos, *Ber.*, 1888, **21**, 1144.
[7] Auwers and Schmidt, *Ber.*, 1925, **58**, 535.
[8] *Org. Synth.*, 1952, **32**, 95.
[9] Baumgarten, *Ber.*, 1924, **57**, 1622.
[10] Borsche, *Annalen*, 1910, **377**, 84.
[11] Ghosh, *J.*, 1916, **109**, 113.
[12] Aitken, Bonthrone, and Reid, unpublished results.

the product of condensation of guaiazulene with 1-ethoxymethylene-5-isopropyl-3,8-dimethylazulenium perchlorate.[1]

Phenylglyoxal with guaiazulene. Perchloric acid (1·5 ml.) was added to a solution of guaiazulene (2·4 g.) and phenylglyoxal (1·750 g.) in tetrahydrofuran (15 ml.). The solution boiled spontaneously and became deep blue. Anhydrous ether (3 ml.) was added to the cooled solution which, in 1 hr. at room temperature, deposited the salt (X) as black needles (180 mg., 6%). The salt, recrystallised from acetic acid, was identical (m. p., mixed m. p., and visible spectrum) with the product of condensation of methylglyoxal with guaiazulene (Found: Cl, 6·6%).

Glyoxylic acid with guaiazulene. The condensation was identical with the preceding, glyoxylic acid (1·15 g.) being used in place of phenylglyoxal. The product (130 mg., 4%) was identical (m. p., mixed m. p., and visible spectrum) with those from the two preceding experiments (Found: C, 73·8; H, 7·1; Cl, 6·7%).

Glyoxal with guaiazulene. A solution of guaiazulene (1·2 g.), glyoxal (600 mg.), and perchloric acid (1·5 ml.) in acetonitrile (25 ml.) was boiled for 2 min. The cooled red solution deposited *ethanediylidenebis-(5-isopropyl-3,8-dimethylazulenium perchlorate)* (XIII) (1·4 g., 75%) as brown plates with a yellow reflex, unchanged in form or composition after recrystallisation from acetonitrile (Found: C, 61·9; H, 6·0; Cl, 11·9. $C_{32}H_{36}Cl_2O_8$ requires C, 62·0; H, 5·9; Cl, 11·4%). The salt melts on a block preheated to $\lessdot$287°, and explodes on a block preheated to $\lessdot$290°.

When guaiazulene (400 mg.), glyoxal (380 mg.), and perchloric acid (1 ml.) were condensed in tetrahydrofuran (5 ml.) under the same conditions the yield of the salt (XIII) was 430 mg. (70%).

Glyoxal with 4,6,8-trimethylazulene. Glyoxal (345 mg.), 4,6,8-trimethylazulene (680 mg.), perchloric acid (0·5 ml.), and acetic acid (20 ml.) were heated to the b. p. The reddish-brown solution, on cooling, deposited a *monoperchlorate* (see below) as green needles (559 mg., 60%), m. p. 257° (decomp.) on a block preheated to $\lessdot$250°, unchanged in form, composition, or m. p. after recrystallisation from acetonitrile (100 ml./10 mg.) (Found: C, 72·6; H, 6·3; Cl, 8·2. $C_{28}H_{27}ClO_4$ requires C, 72·6; H, 5·9; Cl, 7·7%). Solutions of the salt in polar organic solvents are violet-blue. Recrystallisation of the monoperchlorate from a 20% (v/v) solution of perchloric acid in acetonitrile gave *ethanediylidenebis-(4,6,8-trimethylazulenium perchlorate)* (XIV), black needles which soften $>$250° on a block preheated to $\lessdot$250° (Found: C, 58·9; H, 7·0; Cl, 12·2. $C_{28}H_{28}Cl_2O_8$ requires C, 59·7; H, 5·0; Cl, 12·6%). Solutions of the salt (XIV) in acetonitrile containing an excess of perchloric acid are reddish-brown. The monoperchlorate $C_{28}H_{27}ClO_4$ crystallises from solutions of the diperchlorate (XIV) in acetonitrile alone. Further studies on the structure of the monoperchlorate and its relationship to the salt (XIV) are in progress.

Glyoxal with azulene. Perchloric acid (0·25 ml.) was added to a boiling solution of azulene (256 mg.) and glyoxal (200 mg.) in acetonitrile (25 ml.). The deep blue solution, which began to deposit a solid at the b. p., was boiled for 1 min., then allowed to cool to room temperature. 1-(Azulen-1-yl)methyleneazulenium perchlorate (XI) (320 mg., 87%) crystallised as black needles, identical (m. p. and visible spectrum) with the product of condensation of 1-formylazulene, azulene, and perchloric acid [1,3a] (Found: C, 68·9; H, 4·7. Calc. for $C_{21}H_{15}ClO_4$: C, 68·8; H, 4·1%).

Addition of Azulenes to Glyoxylic Acid.—Guaiazulene. A solution of glyoxylic acid (184 mg.) in acetonitrile (5 ml.) was added to one of guaiazulene (495 mg.) in acetonitrile (5 ml.), and the resulting solution was cautiously heated to the b. p. A vigorous exothermic reaction occurred and the product crystallised extensively from the boiling solution as blue needles. *Di-(5-isopropyl-3,8-dimethylazulen-1-yl)acetic acid* (XV) (520 mg., 92%) was filtered from the cooled solution, washed with acetonitrile and dry ether, and analysed without recrystallisation after drying for 5 min. at 80° (Found: C, 85·0; H, 8·4. $C_{32}H_{36}O_2$ requires C, 84·9; H, 8·0%). The acid melts $>$202° (decomp.) after becoming brown at $>$199°. It is sparingly soluble in the common organic solvents.

4,6,8-Trimethylazulene. Glyoxylic acid (183 mg.), 4,6,8-trimethylazulene (680 mg.), and acetonitrile (25 ml.) were boiled for 3 min. The solution became blue, and on cooling deposited an unidentified acid (7 mg.), blue needles which melt (decomp.) on a block preheated to $\lessdot$308°, and show infrared C=O absorption at 1701 cm.$^{-1}$. This acid decomposed when kept for 2 days in an evacuated desiccator. The filtrates were diluted with ether (400 ml.), and the ether solution was extracted exhaustively with 10% sodium carbonate solution, washed with water,

and dried (Na_2SO_4). 4,6,8-Trimethylazulene (221 mg., 33%) was recovered after evaporation of the solvent. The sodium carbonate extracts, after being acidified and extracted with ether, afforded a blue solid (250 mg.) which was readily soluble in polar solvents. Recrystallisation of the solid from light petroleum–ethanol (9 : 1) gave in low yield *di-(4,6,8-trimethylazulen-1-yl)-acetic acid* (XVI), blue, m. p. 168—171° after softening >160° (Found: C, 83·3; H, 7·5. $C_{28}H_{28}O_2$ requires C, 84·8; H, 7·1%).

Condensation of β-Oxo-aldehydes (2-Hydroxymethylene ketones) with Azulenes.—Hydroxymethyleneacetophenone with guaiazulene. Perchloric acid (1 ml.) was added to a boiling solution of guaiazulene (1995 mg.), the sodium salt of hydroxymethyleneacetophenone (1700 mg.), and acetic acid (25 ml.). The chocolate-brown solution was boiled for 2 min., cooled, and diluted with ether. The ether solution was washed until free from acetic acid with water, sodium hydrogen carbonate solution, and water before drying (Na_2SO_4) and evaporation. The residual dark, yellowish-green oil was adsorbed on a column (20 × 2·5 cm.) from a small volume of benzene. Initial development with light petroleum gave blue eluates from which guaiazulene (1365 mg., 68%) was recovered. Elution was continued with benzene, followed by ether. Evaporation of the yellowish-green ether eluates gave β-(5-isopropyl-3,8-dimethylazulen-1-yl)-acrylophenone (XVII) (996 mg., 30%) as a viscous brown oil. Attempted purification by two successive distillations in a closed system at 220°/0·1 mm. failed to give an analytically pure specimen (Found: C, 87·8; H, 7·4. Calc. for $C_{24}H_{24}O$: C, 90·2; H, 7·3%). The *2,4-dinitrophenylhydrazone* recrystallised from benzene as brown needles, m. p. 243—247° (Found: N, 11·1. $C_{30}H_{28}N_4O_4$ requires N, 11·0%).

Treatment of the ketone (XVII) (200 mg.) in acetic acid (25 ml.) with perchloric acid (1 ml.) gave *1-(γ-hydroxycinnamylidene)-5-isopropyl-3,8-dimethylazulenium perchlorate* (96 mg., 36%) which recrystallised from acetic acid as dark red needles, m. p. 209—211° (block preheated to 200°) (Found: Cl, 8·9. $C_{24}H_{25}ClO_5$ requires Cl, 8·3%).

Hydroxymethyleneacetophenone with 4,6,8-trimethylazulene. The sodium salt of hydroxymethyleneacetophenone (1·17 g.), 4,6,8-trimethylazulene (1·17 g.), and acetic acid (25 ml.) were heated to 80°. Perchloric acid (0·5 ml.) was added and the solution kept at 80° for 3 min. The reddish-brown solution was cooled, poured into water, and extracted with ether. The ether extracts, after being washed until free from acid with sodium hydrogen carbonate solution and water and dried (Na_2SO_4), were evaporated. The residue was adsorbed on a column (30 × 2·5 cm.) from the minimum volume of benzene. Elution with light petroleum gave purple eluates from which 4,6,8-trimethylazulene (932 mg., 81%) was recovered. The column was then washed with benzene, and a dark red zone was subsequently eluted with ether. The ether eluates, yellow in reflected and red in transmitted light, were evaporated, and the residual oil was allowed to crystallise from light petroleum–ethanol. Recrystallisation of the solid (269 mg., 13%) from light petroleum (b. p. 60—80°)–ethanol (20 : 1) gave β-(4,6,8-trimethylazulen-1-yl)-acrylophenone (XXII), brown needles, m. p. 142—144° (lit.,[13] m. p. 142—144°).

Hydroxymethyleneacetophenone with azulene. Perchloric acid (1 ml.) was added to a boiling mixture of azulene (1081 mg.), the sodium salt of hydroxymethyleneacetophenone (716 mg.), and methanol (25 ml.). The solution, boiled for 10 min., became deep blue. 1-(Azulen-1-yl)-methyleneazulenium perchlorate (XI) (347 mg., 22%) crystallised from the cooled solution as a blue powder, $\lambda_{max.}$ (in acetic acid) 618 mμ, identical with the product of condensation of azulene, 1-formylazulene, and perchloric acid.[1,3a]

The methanol filtrate was diluted with ether (400 ml.), and a further small quantity (14 mg., 0·9%) of precipitated salt (XI) was removed. The ether solution, after being washed successively with 10% sodium hydroxide and water and dried (Na_2SO_4), was evaporated to small volume before adsorption on a column (6 × 2·5 cm.). Initial elution was with light petroleum. The violet-blue eluates were concentrated and azulene (521 mg., 48%) was recovered from the residual liquid after further chromatography on a column (10 × 2·5 cm.) with light petroleum as solvent and eluant. Subsequent elution of the original chromatogram with benzene gave green eluates (150 ml.) which, after evaporation of solvent and treatment of the residual oil with 2,4-dinitrophenylhydrazine, gave acetophenone 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 244—246°.

When the condensation was carried out in boiling acetic acid, the dye salt (XI) was contaminated with a quantity of a sparingly soluble product of unknown structure ($\lambda_{max.}$ 693 mμ).

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

2-Hydroxymethylenecyclohexanone with guaiazulene. Guaiazulene (2440 mg.), 2-hydroxymethylenecyclohexanone (1542 mg.), perchloric acid (1·5 ml.), and acetic acid (40 ml.) were boiled for 3 min. The crimson solution was cooled and diluted with ether (500 ml.). Impure 5-isopropyl-1-(5-isopropyl-3,8-dimethylazulen-1-yl)methylene-3,8-dimethylazulenium perchlorate [1] (X) (40 mg.) was precipitated as a black solid ($\lambda_{max.}$ 683 mμ). The ether filtrate was washed exhaustively with sodium carbonate solution followed by water, dried (Na_2SO_4), and evaporated. The residual oil was adsorbed on a column (20 × 2·5 cm.) from benzene. Elution with light petroleum gave blue eluates from which guaiazulene (1279 mg., 52%) was recovered. Subsequent slow elution of a strongly adsorbed brown band with benzene–ether (1 : 1) gave green eluates. *2-(5-Isopropyl-3,8-dimethylazulen-1-yl)methylenecyclohexanone* (XXIV) (1529 mg., 41%) was obtained as a green oil which after 5 weeks formed green prisms, m. p. 116·5—119·5° (Found: C, 86·3; H, 8·5. $C_{22}H_{26}O$ requires C, 86·2; H, 8·6%). The *2,4-dinitrophenylhydrazone* recrystallised from benzene as reddish-brown needles, m. p. 212—216° after softening >209° (Found: N, 11·8. $C_{28}H_{30}N_4O_4$ requires N, 11·5%).

2-Hydroxymethylenecyclohexanone with 4,6,8-trimethylazulene. Perchloric acid (0·5 ml.), 4,6,8-trimethylazulene (1400 mg.), 2-hydroxymethylenecyclohexanone (1037 mg.), and acetic acid (25 ml.) were boiled for 2 min., the colour changing through scarlet to brownish-red. The cooled solution deposited a viscous blue tar. The supernatant liquid was decanted from the tar and diluted with ether, and the precipitate was extracted exhaustively with ether. After 12 hr. dark brown crystals (164 mg.), m. p. ~150° (decomp.), which had separated from the ether extracts were filtered off. Attempted recrystallisation failed. The material was insoluble in ether, slightly soluble in benzene, and readily soluble in acetone or ethanol, giving purple solutions.

The tar which separated from the reaction solution was dissolved in acetone. Water (1 l.) was added, then ether, and the mixture was thoroughly shaken and next morning was filtered. Recrystallisation of the solid (14 mg., 0·8%) from methanol gave 4,6,8-trimethyl-1-(4,6,8-trimethylazulen-1-yl)methyleneazulenium perchlorate (XII) ($\lambda_{max.}$ 640 mμ), identical with the product of condensation of 4,6,8-trimethylazulene with 1-ethoxymethylene-4,6,8-trimethylazulenium perchlorate.[1] The ether layer was washed with water until free from an unidentified, blue, water-soluble substance ($\lambda_{max.}$ 593 mμ); it was then reddish-brown and was combined with the ether filtrates remaining after filtration of the solid, m. p. 150°. The combined ether filtrates were washed with sodium carbonate solution and water, dried (Na_2SO_4), and evaporated. The residue was chromatographed in benzene on a column (20 × 2·5 cm.). Elution with light petroleum gave purple eluates from which 4,6,8-trimethylazulene (383 mg., 27%) was recovered. Subsequent elution of a brown band with ether gave reddish-green eluates which deposited crystals after concentration. Recrystallisation of these from cyclohexane gave *2-(4,6,8-trimethylazulen-1-yl)methylenecyclohexanone* (XXV) (599 mg., 26%), brown prisms, m. p. 151—152° (Found: C, 86·0; H, 8·2. $C_{20}H_{22}O$ requires C, 86·3; H, 7·6%).

2-Hydroxymethylenecyclohexanone with azulene. (*a*) In boiling acetic acid. Azulene (1081 mg.), 2-hydroxymethylenecyclohexanone (1061 mg.), perchloric acid (0·5 ml.), and acetic acid (25 ml.) were boiled for 30 sec. 1-(Azulen-1-yl)methyleneazulenium perchlorate (XI) (1534 mg., 99%) crystallised from the cooled solution as dark blue needles, identical spectrally ($\lambda_{max.}$ 618 mμ) with an authentic specimen.[1,3a]

In a second experiment, with azulene (1648 mg.), 2-hydroxymethylenecyclohexanone (808 mg.), perchloric acid (1 ml.), and acetic acid (25 ml.), the dye salt obtained in quantitative yield was washed several times with ether and water alternately, and the mother-liquor was shaken with the ether–water washings. The ether phase was washed with 10% sodium hydroxide solution and water, dried (Na_2SO_4), and evaporated through a short Vigreux column. Cyclohexanone distilled at <80°/15 mm. and was identified as its 2,4-dinitrophenylhydrazone, yellow plates, m. p. and mixed m. p. 154—156°.

(*b*) In methanol at room temperature. Addition of perchloric acid (0·5 ml.) to azulene (1039 mg.), 2-hydroxymethylenecyclohexanone (1020 mg.), and methanol (50 ml.) gave a reddish-brown solution which was left at room temperature for 5 min. before being poured into water (400 ml.). The emulsion was shaken with ether (500 ml.) and filtered from a trace (9 mg., 0·6%) of 1-(azulen-1-yl)methyleneazulenium perchlorate (XI) ($\lambda_{max.}$ 618 mμ). The green ether phase was washed with 10% sodium hydroxide solution and water, and dried (Na_2SO_4) before evaporation. The residue was adsorbed from benzene on a column (15 × 2·5 cm.). Azulene (54 mg., 5%) was recovered from violet-blue light petroleum eluates. Subsequent elution with

ether of a strongly adsorbed brown band gave blue-green eluates which furnished 2-(azulen-1-yl)-methylenecyclohexanone (XXVI) (353 mg., 19%) as a green oil. The 2,4-*dinitrophenylhydrazone* recrystallised from benzene as dark brown needles, m. p. 216—218° (Found: N, 12·9. $C_{23}H_{20}N_4O_4$ requires N, 13·45%).

Hydroxymethyleneacetone with guaiazulene. Perchloric acid (0·5 ml.) was added to guaiazulene (199 mg.) and the sodium salt of hydroxymethyleneacetone (112 mg.) in acetic acid (5 ml.). After 30 min. at room temperature the scarlet solution was poured into water and extracted with ether. The ether extract was worked up in the usual manner, and the residue obtained after evaporation of solvent was chromatographed. Guaiazulene (177 mg., 90%) was recovered from blue light petroleum eluates. The succeeding ether eluates yielded 4-(5-*isopropyl*-3,8-*dimethylazulen*-1-*yl*)*but*-3-*en*-2-*one* (XVIII) (18 mg., 6%) as a yellowish-green oil which could not be purified in sufficient quantity for analysis; distillation at <160°/0·1 mm. caused partial decomposition.

Hydroxymethyleneacetone with 4,6,8-*trimethylazulene.* Perchloric acid (1 ml.) was added to a solution of 4,6,8-trimethylazulene (1250 mg.) and the sodium salt of hydroxymethyleneacetone (794 mg.) in ethanol (30 ml.). The crimson solution was boiled for 5 min., a further 400 mg. of the sodium salt were added, and boiling was continued for a further 5 min. before the solution was poured into water and extracted with ether. The ether extract was worked up and chromatographed as described for the condensation of hydroxymethyleneacetophenone with guaiazulene. 4,6,8-Trimethylazulene (1238 mg., 98%) was recovered from the purple light petroleum eluates. The ether eluates, yellow in reflected and red in transmitted light, yielded 4-(4,6,8-*trimethylazulen*-1-*yl*)*but*-3-*en*-2-*one* (XXIII) (17 mg., 1%) which recrystallised from cyclohexanone as dark grey plates, m. p. 111·5—113·5° (decomp.) (Found: C, 85·7; H, 7·6. $C_{17}H_{18}O$ requires C, 87·5; H, 7·5%).

Hydroxymethyleneacetone with azulene. A mixture of azulene (2091 mg.), the sodium salt of hydroxymethyleneacetone (2095 mg.), perchloric acid (1 ml.), and ethanol (50 ml.) was boiled for 5 min., then worked up and the product chromatographed as described for the condensation of hydroxymethyleneacetophenone with guaiazulene. Azulene (2·04 g., 99%) was recovered from violet-blue light petroleum eluates. The yellowish-green ether eluates from a weak brown band afforded a yellow oil (11 mg., 0·3%) which failed to crystallise after further chromatography but was shown by its visible spectrum to be 4-(azulen-1-yl)buten-2-one (XXVII) (see Table 1).

2-*Hydroxymethylene*-2,3-*dihydrophenalen*-1-*one with guaiazulene.* A mixture of guaiazulene (600 mg.), the 2-hydroxymethylene ketone (630 mg.), perchloric acid (1 ml.), and tetrahydrofuran (10 ml.) was boiled, then allowed to cool to room temperature. 1-(3-*Hydroxyphenalen*-2-*yl*)-*methylene*-5-*isopropyl*-3,8-*dimethylazulenium perchlorate* (XXIX) (150 mg., 10%) crystallised from the red solution as brown needles, unchanged in form after recrystallisation from acetonitrile or acetic acid (Found: C, 71·2; H, 5·3. $C_{29}H_{27}ClO_5$ requires C, 70·9; H, 5·5%). A further 630 mg. (43%) of less pure product crystallised slowly from the mother liquor. The salt melts slowly to a black tar at >200°.

Condensation of 2-(*Azulen*-1-*yl*)*methylenecyclohexanone with Azulene.*—Azulene (96 mg.), 2-(azulen-1-yl)methylenecyclohexanone (177 mg.), perchloric acid (0·1 ml.), and acetic acid (10 ml.) were boiled for 2 min. 1-(Azulen-1-yl)methyleneazulenium perchlorate (XI) (100%) crystallised extensively from the boiling solution as violet-black needles, identical (m. p. and visible spectrum) with an authentic specimen.[1,3a]

Condensation of Nitromalondialdehyde with Guaiazulene.—A solution of perchloric acid (2·5 ml.) in tetrahydrofuran (10 ml.) was added to a suspension of the sodium salt of nitromalondialdehyde (800 mg.) in a solution of guaiazulene (1000 mg.) in tetrahydrofuran (10 ml.), all at 5°. The resulting red solution in which the salt dissolved immediately was swirled continuously for 5 min. at 5°, while 3-(5-*isopropyl*-3,8-*dimethylazulen*-1-*yl*)-2-*nitropropenal* (XIX) (630 mg., 36%), m. p. 197—202° (decomp.) (block preheated to 190°), crystallised as steel-blue needles, unchanged in form or m. p. after being washed with water (100 ml.) and methanol (10 ml.) and recrystallised from acetic acid (Found: C, 72·5; H, 6·5; N, 4·4. $C_{18}H_{19}NO_3$ requires C, 72·7; H, 6·4; N, 4·7%).

The yellowish-brown mother-liquor was set aside for 4 hr. at room temperature. 5-*Isopropyl*-1-[3-(5-*isopropyl*-3,8-*dimethylazulen*-1-*yl*)-2-*nitropropenylidene*]-3,8-*dimethylazulenium perchlorate* (XXXIV) (80 mg., 5%) crystallised as brown needles with a golden reflex, which did not melt <350°. The salt is almost insoluble in the common organic solvents and was analysed

without recrystallisation (Found: C, 67·9; H, 6·4; N, 2·4. $C_{33}H_{36}ClNO_6$ requires C, 68·6; H, 6·3; N, 2·4%).

Condensation of Glutacondialdehyde with Guaiazulene.—(*a*) Perchloric acid (5 ml.) was added to a solution of guaiazulene (5·94 g., 0·03 mole) and the sodium salt of glutacondialdehyde (3·60 g., 0·03 mole) in methanol (180 ml.) at room temperature. After 15 min. the purple mixture was filtered, and the violet-black solid was recrystallised from acetonitrile–methanol (2 : 1). *5-Isopropyl-1-[5-(5-isopropyl-3,8-dimethylazulen-1-yl)penta-2,4-dienylidene]-3,8-dimethylazulenium perchlorate* (XXXV) (2·063 g., 25%) crystallised to two forms: small reddish-brown needles with a copper reflex, which melt to a reddish-brown liquid on a block preheated to $<182°$; and large brown needles which do not melt but become progressively darker and finally black $>280°$. The two forms have identical visible spectra (Found: C, 73·8; H, 7·2; Cl, 7·0. $C_{35}H_{39}ClO_4$ requires C, 75·2; H, 7·0; Cl, 6·3%).

The methanol mother-liquor was poured into water (1 l.) and was extracted with ether (2 × 1 l.). A small quantity of precipitated dye salt (XXXV) was filtered off, and the ether extracts were washed with water (five times) and dried (K_2CO_3). The green solution was evaporated to 250 ml., acetone (50 ml.) was added, and the solution was further concentrated to 30 ml. On addition of ether (40 ml.) *5-(5-isopropyl-3,8-dimethylazulen-1-yl)penta-2,4-dienal* (XX) (3·01 g., 37%) crystallised as black plates. Recrystallisation from acetone–ether (2 : 1) gave brown plates, m. p. 137—139° (Found: C, 86·0; H, 7·8. $C_{20}H_{22}O$ requires C, 86·3; H, 8·0%).

(*b*) Guaiazulene (600 mg., 0·003 mole), perchloric acid (0·5 ml.), the sodium salt of glutacondialdehyde (180 mg., 0·0015 mole), and methanol (18 ml.) were boiled for 2 min. 5-Isopropyl-1-[5-(5-isopropyl-3,8-dimethylazulen-1-yl)penta-2,4-dienylidene]-3,8-dimethylazulenium perchlorate (XXXV) (475 mg., 57%) crystallised from the cooled solution as small violet-black needles, identical spectrally and, after recrystallisation, in form with the product of experiment (*a*).

Condensation of 5-(5-Isopropyl-3,8-dimethylazulen-1-yl)penta-2,4-dienal (XX) *with Azulenes.*—*With guaiazulene.* The aldehyde (XX) (278 mg., 0·001 mole), guaiazulene (200 mg., 0·001 mole), perchloric acid (0·2 ml.), and methanol (10 ml.) were boiled for 2 min. The dye salt (XXXV) (405 mg., 72%) crystallised from the cooled solution as violet-black needles, identical with the products of the two preceding experiments.

With 1-methylazulene. The aldehyde (XX) (556 mg., 0·002 mole), 1-methylazulene (284 mg., 0·002 mole), perchloric acid (0·5 ml.), and acetonitrile (15 ml.) were boiled for 1 min. *5-Isopropyl-1-[5-(3-methylazulen-1-yl)penta-2,4-dienylidene]-3,8-dimethylazulenium perchlorate* (XXXVI) (460 mg., 46%) separated from the boiling solution as black needles. Recrystallisation of the salt from acetonitrile gave violet-black needles which soften $>145°$ to a blue tar (Found: C, 71·5; H, 6·2; Cl, 6·0. $C_{31}H_{31}ClO_4$ requires C, 74·0; H, 6·2; Cl, 7·1%).

Condensation of β-Hydroxy-α-phenylacrylonitrile with Azulenes.—With guaiazulene (in the absence of perchloric acid). Guaiazulene (1431 mg.), the nitrile (1034 mg.), and acetic acid (25 ml.) were boiled for 2 min. The cooled greenish-brown solution was shaken with ether (200 ml.) and water (200 ml.). The ether extract was washed until free from acid with sodium carbonate solution and water, dried (Na_2SO_4), and evaporated. The residual oil was adsorbed from benzene on a column (20 × 2·5 cm.). Guaiazulene (793 mg., 55%) was recovered from blue light petroleum eluates. A yellowish-green band, subsequently eluted with benzene, gave an oil (1·07 g., 45%) which was purified by filtration in benzene through a column (8 × 2·7 cm.). The eluates from the second column afforded a yellowish-brown oil which was dissolved in ethanol from which *3-(2-cyano-2-phenylvinyl)-5-isopropyl-3,8-dimethylazulene* (XXI) crystallised as brown needles, m. p. 84—84·5° (Found: C, 88·4; H, 7·2; N, 4·3. $C_{24}H_{23}N$ requires C, 88·6; H, 7·1; N, 4·3%).

The nitrile (XXI) (200 mg., 62%) was also obtained from a solution of guaiazulene (198 mg.), β-hydroxy-α-phenylacrylonitrile (149 mg.), and perchloric acid (1 ml.) in acetic acid (2 ml.) which had been left at room temperature for 4 hr. and worked up in the usual manner.

With 4,6,8-trimethylazulene. Perchloric acid (0·5 ml.) was added to 4,6,8-trimethylazulene (1276 mg.) and the nitrile (1080 mg.) in hot acetic acid (25 ml.). The solution was boiled for 3 min., the colour changing through brownish-red to yellowish-brown, and on cooling deposited *1,3-di-(2-cyano-2-phenylvinyl)-4,6,8-trimethylazulene* (XXXIX) (597 mg., 19%) as brown needles (unchanged in form after recrystallisation from benzene), m. p. 227—229° (Found: C, 87·5; H, 5·9; N, 6·5. $C_{31}H_{24}N_2$ requires C, 87·7; H, 5·7; N, 6·6%). The mother-liquor,

on being diluted with ether (400 ml.), deposited 4,6,8-trimethylazulenium perchlorate (911 mg.), and on being subsequently worked up in the usual manner afforded 4,6,8-trimethylazulene (222 mg.). The total quantity of recovered hydrocarbon was thus 795 mg. (62%).

With azulene. Perchloric acid (0·5 ml.) was added to a solution of azulene (512 mg.) and the nitrile (580 mg.) in acetic acid (40 ml.). The solution was boiled for 3 min., the colour changing through yellow-brown to yellowish-green, and was diluted with benzene (1·5 l.). After filtration from a sparingly soluble precipitate, the benzene solution was washed free from acid with sodium hydroxide solution and dried (K_2CO_3) before concentration to 100 ml. 1,3-*Di*-(2-*cyano*-2-*phenylvinyl*)*azulene* (XXXVIII) (102 mg.) crystallised as yellowish-brown plates. Recrystallisation from a large volume of benzene gave plates, green in reflected and brown in transmitted light, m. p. 280—287° (Found: C, 87·1; H, 4·7; N, 7·0. $C_{28}H_{18}N_2$ requires C, 87·9; H, 4·7; N, 7·3%). The solid, filtered from the unwashed benzene solution, afforded a further 34 mg. of product. The yield was thus 136 mg. (9%). The dinitrile is sparingly soluble in the common organic solvents, including acetonitrile.

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