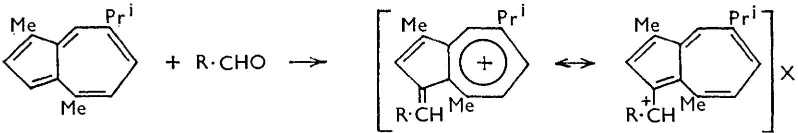
102. *Conjugated Cyclic Hydrocarbons and Their Heterocyclic Analogues. Part II.*[1] *The Condensation of Azulenes with Homocyclic and Heterocyclic Aromatic Aldehydes in the Presence of Perchloric Acid.*[2]

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

Homocyclic and heterocyclic aromatic aldehydes, and certain azulene aldehydes, condense with azulenes in the presence of 70% perchloric acid to form 1-(R-methylene)azulenium perchlorates. The influence of alkyl substituents in the azulene nucleus on (i) the stability of the perchlorates, (ii) the reactivity of the azulene aldehydes, is noted.

The preparation of several 1-hydroxymethyleneazulenium perchlorates is described.

In a previous paper[3] it was shown that guaiazulene (1,4-dimethyl-7-isopropylazulene) (I) condenses with many aromatic aldehydes in ether containing anhydrous hydrogen chloride to give arylmethyleneguaiazulenium chlorides (II; X = Cl). The products (II) are salt-like substances, soluble in polar solvents, *e.g.*, acetone and acetic acid, insoluble in ether and hydrocarbons, and notable chemically for their marked reactivity towards nucleophilic reagents.[3]



(I) (IIa) (IIb)

However, the chlorides (II; X = Cl) are unstable, and, depending on the aldehyde moiety, decompose more or less rapidly at room temperature. Satisfactory analyses could not be obtained but treatment of the freshly prepared chlorides in acetic acid with saturated aqueous picric acid afforded the corresponding picrates (II; X = $C_6H_2O_7N_3$) which were stable for considerably longer periods and gave satisfactory analyses. Neither they nor the chlorides could be recrystallised from hot solvents without decomposition, and the intensities of absorption in the visible and ultraviolet regions could not be measured.

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[1] Part I, *J.*, 1956, 3487.

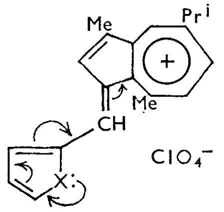
[2] For a preliminary account see Reid, "Azulene and Related Substances," Chem. Soc. Special Publ. No. 12, 1958, p. 69.

[3] Reid, Stafford, Stafford, and (in part) McLennan and Voigt, *J.*, 1958, 1110.

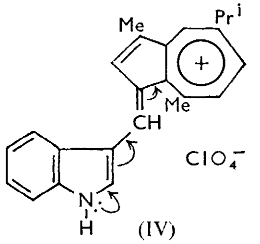
A more serious objection is that the products of condensation of guaiazulene with heterocyclic and aliphatic aldehydes could not be isolated, although in many cases reaction was made evident by consumption of guaiazulene, appearance of the expected colours, and the behaviour of the solutions containing the condensation products.

We now report a superior modification of our previous procedure. This consists in allowing the homocyclic or heterocyclic aromatic aldehyde, guaiazulene, and an excess of 70% perchloric acid to interact in acetic acid, tetrahydrofuran, or acetonitrile. Reaction usually occurs at room temperature but a short boiling is sometimes expedient. The perchlorates (II; X = ClO_4) produced are beautifully crystalline, readily isolated in high yield, and capable of repeated recrystallisation without decomposition (best from acetic acid or acetonitrile). For the twenty perchlorates thus prepared, the effect of the radical R on the intensity and position of the long-wave absorption band is illustrated in Table 1. The visible spectra (Figs. 1—4) consist in most cases of a single, broad band devoid of fine structure, with in some cases a second maximum in the near-visible region (360—380 mμ).

Extension of the molecular orbital of the benzylideneguaiazulenium cation in (II; R = Ph) by annelation or by the introduction of electron-releasing substituents into the benzene ring (Fig. 1) produces a bathochromic shift in $\lambda_{max.}$ and increases the intensity. In the latter case the variations are in agreement with theory. For a hydroxyl group the order of effectiveness of electron-release is *p* > *o* > *m*, and the shifts are almost additive (*e.g.*, *o*- + *p*-, 110 mμ; obs. for 2′,4′-, 107 mμ). The *p*-dialkylamino-group causes a greater shift (90 mμ) in the same direction and a nine-fold increase in intensity. Halogen hardly changes the position or intensity of maximum absorption, but the electron-attracting nitro-group brings about a hypsochromic displacement and slightly lowers the intensity.



(III)



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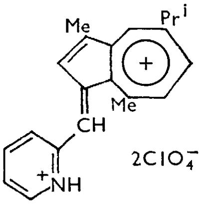


(V)

TABLE 1. *The visible absorption maxima of* 1-(R-*methylene*)*guaiazulenium perchlorates in acetic acid.*

No.	R	$\lambda_{max.}$ (mμ)	log ε	No.	R	$\lambda_{max.}$ (mμ)	log ε
1	Ph	456	4·09	11	*p*-Cl·C_6H_4	454	4·00
2	1-$C_{10}H_7$	503	4·30	12	*m*-O_2N·C_6H_4	438	3·97
3	3-Pyrenyl	597	4·41	13	*p*-O_2N·C_6H_4	~435 sh	3·74
4	*o*-HO·C_6H_4	499	4·28	14	2′-Furyl	505	4·56
5	*m*-HO·C_6H_4	475	4·18	15	2′-Thienyl	505	4·53
6	*p*-HO·C_6H_4	523	4·51	16	3′-Indolyl	582	4·10
7	*p*-MeO·C_6H_4	515	4·45	17	2′-Pyridyl *	410	3·8
8	2′,4′-$(HO)_2C_6H_3$	563	4·67	18	4′-Pyridyl *	420 infl	3·7
9	3′,4′-CH_2O_2:C_6H_3	531	4·43	19	2′-Quinolyl *	425	4·15
10	*p*-Me_2N·C_6H_4	647	4·98	20	4′-Quinolyl *	~435 sh	3·88

* Diperchlorates.

m-Nitrobenzylideneguaiazulenium perchlorate has typically a maximum at 438 mμ ($\Delta\lambda_{max.}$ —18 mμ); *p*-nitrobenzylideneguaiazulenium perchlorate, however, shows only a shoulder at *ca.* 435 mμ, the absorption rising to the near visible maximum at 370 mμ (Fig. 3). Furan, thiophen, and indole nuclei function qualitatively in the same way as a phenyl group carrying an electron-releasing substituent [cf. (III) and (IV): the spectra of the furfurylidene (III; X = O) and the thenylidene perchlorate (III; X = S) both resemble closely that of *p*-hydroxybenzylideneguaiazulenium perchlorate (Fig. 2)].

The products from 2- and 4-formyl-pyridine and -quinoline are diperchlorates (cf. V), in which a proton has added to the ring-nitrogen atom, enhancing the electron-attracting character of the heterocyclic nucleus so that their spectra resemble those of the *m*- and *p*-nitrobenzylideneguaiazulenium perchlorate (Figs. 3 and 4) in showing a hypsochromic displacement of $\lambda_{max.}$.

All the aldehydes which condensed with guaiazulene also condensed with azulene itself; nevertheless only those containing electron-releasing groups gave products (VI) capable of

FIGS. 1—4. *Absorption spectra for acetic acid solutions of the perchlorates listed in Table* 1. (*Numbers refer to Table* 1.)

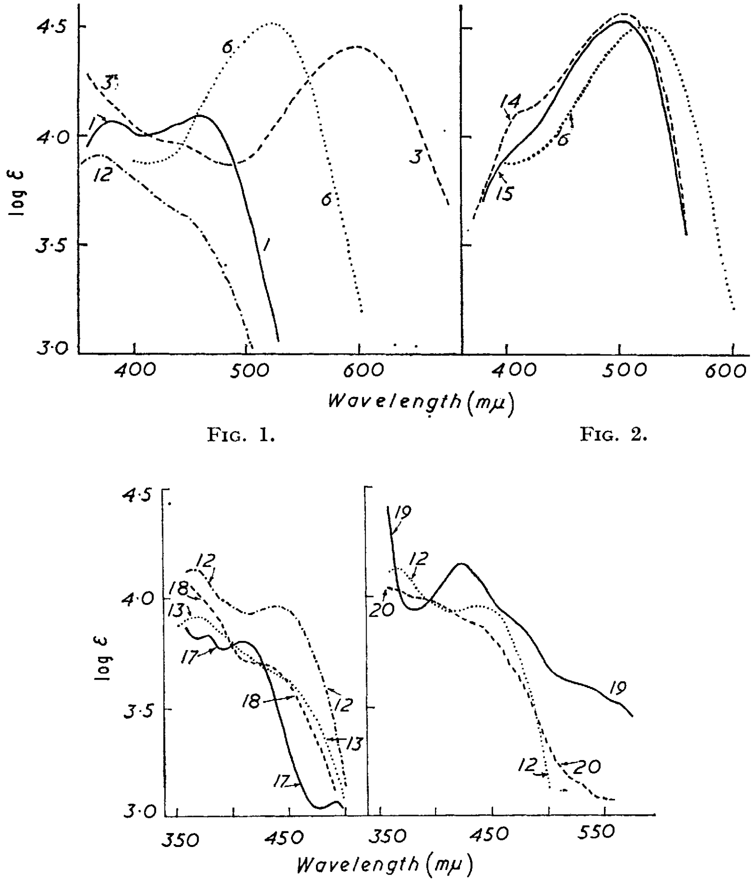


FIG. 1. FIG. 2.

FIG. 3. FIG. 4.

isolation (Table 2), and these, moreover, decomposed on attempted recrystallisation. Benzaldehyde, its ring homologues and derivatives carrying electron-attracting substituents, and the pyridine and quinoline aldehydes gave appropriately coloured solutions which yielded no perchlorate and rapidly became green. The electrophilic character of the arylmethyleneazulenium cation is therefore decreased, and the stability increased, by the inductive and hypercongugative effects of alkyl substituents. It will be shown that the products from many aldehydes are diazulenylmethane derivatives (VII) formed by an electrophilic substitution of unchanged azulene by the methyleneazulenium cation in (VI).

TABLE 2. *Visible absorption maxima* (mμ) *of some* 1-(R-*methylene*)*azulenium perchlorates* (*in acetonitrile*).

R	p-HO·C$_6$H$_4$	p-Me$_2$N·C$_6$H$_4$	2-Furyl	3-Indolyl
$\lambda_{max.}$	500	635	496	560

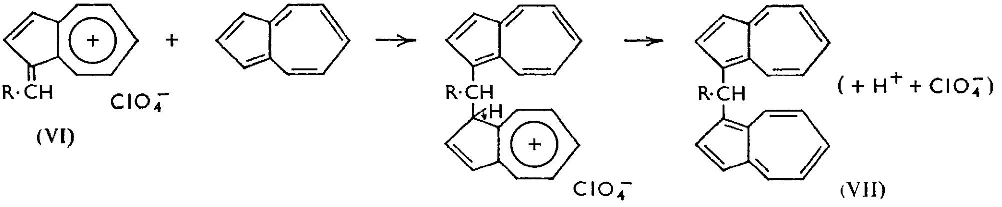
(log ε were uncertain owing to instability)

TABLE 3. *Infrared* C=O *stretching frequencies* (*cm.*$^{-1}$) *of azulene aldehydes.*

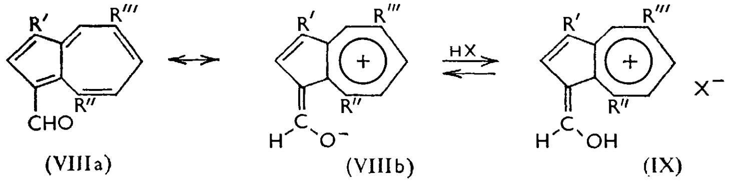
Aldehyde	Nujol	CCl$_4$	CS$_2$
1-Formylazulene	1645 [a]	—	—
1-Formylguaiazulene	1610 [a]	1634 [b]	—
1,3-Diformylazulene	1647 [a]	—	—
1-Formyl-7-isopropenyl-4-methylazulene (lactoroviolin)	—	—	1658 [c]
6-Formyl-4,8-dimethylazulene	—	—	1705 [c, d]
1-Naphthaldehyde	—	—	1700 [e]
2-Naphthaldehyde	—	—	1698 [e]

[a] Present work. [b] Reid, Stafford, and Stafford, *J.*, 1958, 1118. [c] Heilbronner and Schmid, *Helv. Chim. Acta*, 1954, **37**, 2018. [d] Arnold and Pahls, *Chem. Ber.*, 1954, **87**, 257. [e] Hunsberger, *J. Amer. Chem. Soc.*, 1950, **72**, 5626.

Owing to the ready polarisability of the azulene nucleus, interaction between the carbonyl group and the π-electrons of the nucleus is greater in 1-acylazulenes than in acylated benzenoid hydrocarbons. Azulene-1-aldehydes (VIII) are best represented in the ground state as resonance hybrids to which the dipolar forms (VIIIb) make important contribution.[5] The abnormally low infrared stretching frequency of 1-formylazulenes supports this view [cf. ν_{CO} of 6-formyl-4,8-dimethylazulene, which is considered normal in view of the varied conditions under which the frequency measurements were made (Table 3)].



ν_{CO} is further lowered in passing from 1-formyl- (VIII; R′ = R″ = R‴ = H) and 1,3-diformyl-azulene (VIII; R′ = CHO, R″ = R‴ = H) to 3-formylguaiazulene (VIII; R′ = R″ = Me, R‴ = Pr^i) owing to enhancement of the ground-state polarisation by the electron-releasing alkyl substituents.



(VIIIa) (VIIIb) (IX)

Further polarisation takes place readily when 1-formylazulenes are placed in a suitable environment. Azulene aldehydes dissolve readily in dilute acids; the resulting solutions contain the hydroxymethyleneazulenium cation. We have isolated these as their crystalline perchlorates (IX; X = ClO$_4$) by treating the appropriate azulene aldehyde with 70% perchloric acid in acetic acid. The salts vary in their stability towards water. 3-Formylguaiazulene gave a stable, yellow crystalline perchlorate. 1-Formyl- and 1,3-diformyl-azulene also formed yellow crystalline perchlorates but atmospheric moisture reconverted them into the parent aldehyde. Alkylated azulene-1-aldehydes are thus

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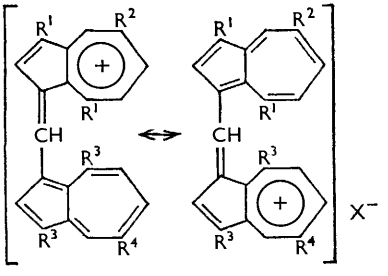
[4] Plattner, Heilbronner, and Weber, *Helv. Chim. Acta*, 1949, **32**, 574.

more basic than 1-formylazulene for the same reason that alkylazulenes are more basic than azulene.[4]

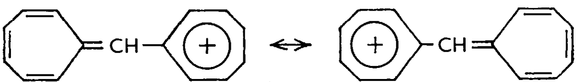
3-Formylguaiazulene has been reported [5] to condense with guaiazulene in ether containing anhydrous hydrogen chloride to form 3-3′-guaiazulylmethyleneguaiazulenium chloride (Xa), which was not, however, isolated. Our procedure gave smoothly the perchlorates (Xb and c). These are stable substances, members of a new class of all-carbon polymethine dyestuffs based formally on the hypothetical cation (XI) for which we predict considerable stability. The salts (Xb and c) have very intense absorption (ε ~ 10^5) at long wavelengths ($\lambda_{max.}$ >615 mμ) (Fig. 5).



(Xa) $R^1 = R^3 = Me; R^2 = R^4 = Pr^i; X = Cl$

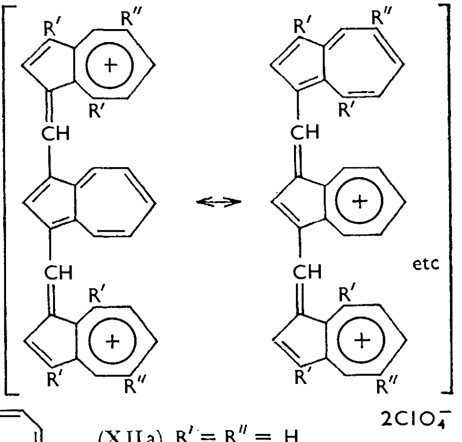
(Xb) $R^1 = R^2 = R^3 = R^4 = H; X = ClO_4$

(Xc) $R^1 = R^2 = H; R^3 = Me; R^4 = Pr^i; X = ClO_4$



(XI)

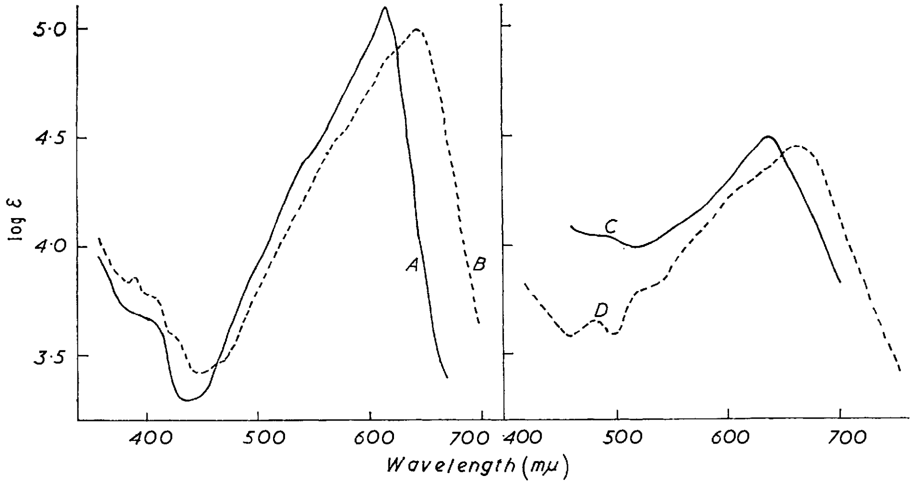
Fig. 5.



(XIIa) $R' = R'' = H$

(XIIb) $R' = Me; R'' = Pr^i$

Fig. 6.



Absorption spectra for acetic acid solutions of perchlorates: (*A*) *compound* (Xb), (*B*) *compound* (Xc), (*C*) *compound* (XIIa), *and* (*D*) *compound* (XIIb).

$\lambda_{max.}$ *A* 618, *B*, 645, *C* 638, *D* 664 mμ.
log ε *A* 5·08, *B* 4·98, *C* 4·49, *D* 4·45.

1,3-Diformylazulene underwent double condensation with azulene and guaiazulene to

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[5] Reid, Stafford, and Stafford, *J.*, 1958, 1118.

form the trinuclear diperchlorates (XIIa and b) whose spectra (Fig. 6) are structurally similar to those of (Xb and c) (the maxima also lie at >615 mμ but the intensities are much lower).

3-Formylguaiazulene failed to condense with azulene or guaiazulene under our conditions, owing to its more complete conversion into the salt (IX; R′ = R = Me, R‴ = Prⁱ) by the stronger perchloric acid and/or the presence of the electron-releasing alkyl substituents which lower to an ineffective level the electrophilic character of the aldehydic carbon atom, already considerably attenuated by interaction with the nucleus.

EXPERIMENTAL

M. p.s were determined on a Kofler-type heating stage. Visible spectra were determined with a Unicam S.P.600 instrument. Specimens for analysis were dried for 6—10 hr. at 90°/0·1 mm.

Materials.—Acetic acid was of " AnalaR " grade. Acetonitrile was purified by successive distillations from phosphoric anhydride and freshly dried potassium carbonate. Tetrahydrofuran was boiled over sodium wire until it no longer discoloured the fresh metal surface, and then distilled.

All aldehydes used except 2- and 4-formylpyridine and 2- and 4-formylquinoline were purified immediately before use, liquids by distillation at reduced pressure (~15 mm.) and solids, if necessary, by recrystallisation.

Perchloric acid refers to 70—72% (w/w) perchloric acid of " AnalaR " grade.

Condensation of Guaiazulene with Aldehydes (Table 4).—Condensations were by one of the following general procedures (for details see Table 4).

Procedure A. Perchloric acid was added to a solution of the aldehyde and guaiazulene at room temperature. In most cases the product crystallised at once but if necessary the solution was left at room temperature until crystallisation was complete. The product was filtered off, washed with a small volume of the solvent, and, unless otherwise stated, recrystallised from acetic acid.

Procedure B. A solution of the aldehyde, guaiazulene, and perchloric acid was heated to the b. p., then allowed to cool to room temperature. If necessary it was left at room temperature until crystallisation was complete. Further treatment of the product was then as in procedure A.

Condensations of Azulene with Aldehydes.—The perchlorates of this series decompose more or less rapidly on attempted recrystallisation from hot solvents. Analyses were carried out on samples taken directly from the reaction product without further purification, and tended to be unsatisfactory.

p-*Hydroxybenzaldehyde.* A solution of the aldehyde (122 mg.) and perchloric acid (0·5 ml.) in acetic acid (15 ml.), at room temperature, was added to a solution of azulene (128 mg.) in acetic acid (15 ml.), also at room temperature. The blood-red solution deposited after several minutes a reddish-brown solid. 1-p-*Hydroxybenzylideneazulenium perchlorate* (VI; R = *p*-HO·C_6H_4) (205 mg., 61%), m. p. 210—215° (decomp.), was filtered off after 2 hr., washed with acetic acid followed by much ether, and dried for analysis for 3 days over phosphoric anhydride–potassium hydroxide (Found: Cl, 9·3. $C_{17}H_{13}O_5Cl$ requires Cl, 10·7%).

p-*Dimethylaminobenzaldehyde.* This aldehyde (150 mg.) as above gave a green solution, and green 1-*p*-dimethylammoniumbenzylideneazulenium diperchlorate separated at once from solution. This was collected, washed with acetic acid, and on being suspended in water (25 ml.) immediately became blue. After being shaken for 30 min. to complete hydrolysis, the blue solid was filtered off, washed with water until free from acid, and dried for analysis *in vacuo* as above for 10 days. 1-p-*Dimethylaminobenzylideneazulenium perchlorate* was thus obtained as blue crystals which melt to a blue tar on a block preheated to ≮210° (Found: C, 66·4; H, 5·4; N, 4·7. $C_{19}H_{18}O_4NCl$ requires C, 63·4; H, 5·0; N, 3·9%).

Furfuraldehyde. The aldehyde (144 mg.), azulene (192 mg.), and perchloric acid (0·5 ml.) in acetic acid (8 ml.) gave a bright red solution. 1-2′-*Furfurylideneazulenium perchlorate* (415 mg., 90%) crystallised as orange-red needles, m. p. 179—181° (block preheated to 175°). It was washed with acetic acid followed by much ether and dried for 20 min. at 110° (Found: C, 56·1; H, 3·9; Cl, 12·4. $C_{15}H_{11}O_5Cl$ requires C, 58·8; H, 3·6; Cl, 11·6%).

3-*Formylindole.* Mixing azulene (128 mg.), perchloric acid (0·5 ml.), and the aldehyde

TABLE 4. *Condensation of guaiazulene with homocyclic and heterocyclic aromatic aldehydes.*

Procedure, solvent (ml.)		Aldehyde, R·CHO		Guaiazulene (mg.)	$HClO_4$ (ml.)	Product	Yield (%)	Colour ‡	M. p.
		R	mg.						
AD	10	Ph	200	400	0·5	1	75	Orange	195—200° *
BC[a]	10	1-$C_{10}H_7$	0·35 †	400	1	2	33	Red	195—220 *
AD	5	3-Pyrenyl	230	200	0·5	3	85	Green	>230 *
BD	10	*o*-HO·C_6H_4	370	600	1	4	57	Reddish-brown	220—225 *
AD	2	*m*-HO·C_6H_4	122	200	0·5	5	60	Orange-red	203—211 *
BD	10	*p*-HO·C_6H_4	370	600	1	6	45	Brown	>230 *
BC[b]	5	*p*-MeO·C_6H_4	1360	2000	1	7	36	Reddish-brown[c]	201—203
AD	2	2,4-$(HO)_2C_6H_3$	140	200	0·5	8	20	Dark red	207—210 *
AD	2	3,4-$CH_2O_2{:}C_6H_3$	150	200	0·5	9	41	Crimson	236—240 *
BD[d]	7	*p*-Me_2N·C_6H_4	300	400	0·5	10	42	Copper[m]	159—160·5
AD	10	*p*-Cl·C_6H_4	280	400	1	11	80	Orange[n]	212—220 *
AD	2	*m*-O_2N·C_6H_4	150	200	0·5	12	71	Orange	195—200 *
AD	5	*p*-O_2N·C_6H_4	150	200	0·5	13	76	Orange	195—201 *
BD	10	2-Furyl	0·17 †	400	1	14	89	Red	236·5—241 *
AD	2	2-Thienyl	112	200	0·5	15	27	Dark red	222—226 *
BC	10	3-Indolyl	290	400	1	16	66	Violet-black	242 *
AD	2	2-Pyridyl	107	200	0·5	17	23[e,f]	Orange[g]	188—190·5 *
AD	2	4-Pyridyl	107	200	0·5	18	69[f]	Yellow-brown[h]	195—198 *
AD	2	2-Quinolyl	157	200	0·5	19	97[f]	Orange-red[g]	>210[i]
AD[j]	2	4-Quinolyl[k]	175	200	0·5	20	78[f]	Yellow[l]	>203[i]

A = procedure A. B = procedure B. C = acetic acid. D = tetrahydrofuran. * With decomp. † Vol. (ml.). ‡ Needles unless otherwise stated.

[a] Boiled for 2 min., then left at room temp. for 2 days. [b] Boiled for 1 min. [c] Recryst. from acetonitrile. [d] Solution left at room temp. for 90 min. [e] Scratching for crystn.; solution left for 30 min. [f] Diperchlorate. [g] Recryst. from acetonitrile–ethyl methyl ketone (1 : 2). [h] Recryst. from acetonitrile–ethyl methyl ketone (1 : 5). [i] Decomp. without melting. [j] Solution left at room temp. for 5 hr. [k] Hydrate. [l] Recryst. from acetonitrile–ethyl methyl ketone (1 : 1). [m] Prisms. [n] Indefinite form.

No.	Found (%)				Formula	Required (%)			
	C	H	N	Hal		C	H	N	Hal
1	68·2	6·1		9·7	$C_{22}H_{23}O_4Cl$	68·3	6·0		9·2
2	71·1	5·6		8·6	$C_{26}H_{25}O_4Cl$	71·5	5·8		8·1
3	75·2	5·5		6·9	$C_{32}H_{27}O_4Cl$	75·2	5·3		6·9
4[o]	65·1	6·0		8·9	$C_{22}H_{23}O_5Cl$	65·6	5·8		8·8
5[p]	64·5	5·8		7·4	$C_{22}H_{23}O_5Cl$	65·6	5·8		8·8
6[o]	65·5	5·9		8·9	$C_{22}H_{23}O_5Cl$	65·6	5·8		8·8
7	66·6	6·2		8·2	$C_{23}H_{25}O_5Cl$	66·3	6·1		8·5
8	62·7	5·4		9·2	$C_{22}H_{23}O_6Cl$	63·1	5·5		8·5
9	63·6	5·6		9·1	$C_{23}H_{23}O_6Cl$	64·1	5·4		8·2
10[o]	67·2	6·7	3·4	8·2	$C_{24}H_{28}O_4NCl$	67·1	6·6	3·3	8·3
11	63·0	5·4		16·5	$C_{22}H_{22}O_4Cl_2$	62·7	5·3		16·9
12	61·2	5·2	3·2	8·3	$C_{22}H_{22}O_6NCl$	61·2	5·1	3·2	8·2
13	60·7	4·8	3·3	7·6	$C_{22}H_{22}O_6NCl$	61·2	5·1	3·2	8·2
14	63·6	6·1		10·2	$C_{20}H_{21}O_5Cl$	63·7	5·6		9·4
15	61·2	5·3		9·1	$C_{20}H_{21}O_4ClS$[r]	61·1	5·4		9·0
16	67·8	5·8	3·0	7·9	$C_{24}H_{24}O_4NCl$	67·7	5·9	3·3	8·3
17[q]	51·9	5·2	2·6	14·8	$C_{21}H_{23}O_8NCl_2$	51·6	4·8	2·9	14·5
18[q]	51·6	5·2	3·2	14·0	$C_{21}H_{23}O_8NCl_2$	51·6	4·8	2·9	14·5
19[q]	55·5	4·7	1·9	13·3	$C_{25}H_{25}O_8NCl_2$	55·8	4·7	2·6	13·2
20[q]	55·1	4·5	2·4	13·2	$C_{25}H_{25}O_8NCl_2$	55·8	4·7	2·6	13·2

[o] Analysed without recrystn. [p] No satisfactory analysis. [q] Diperchlorate. [r] Found: S, 8·5. Reqd.: S, 8·2%.

(145 mg.) in acetic acid (10 ml.) afforded 1-3′-*indolylmethyleneazulenium perchlorate* (305 mg., 89%) as violet-black needles which were washed with acetic acid and then ether before drying for 20 min. at 110° (Found: N, 3·6; Cl, 9·6. $C_{18}H_{14}O_4NCl$ requires N, 4·1; Cl, 10·3%). It melts to a violet liquid on a block preheated to $\nless 270°$, but on being heated from room temperature decomposes slowly to a black tar.

1-*Hydroxymethyleneazulenium Perchlorate*.—Perchloric acid (0·5 ml.) was added to a cold solution of 1-formylazulene (173 mg.) in acetic acid (5 ml.). On addition of dry ether (5 ml.) 1-*hydroxymethyleneazulenium perchlorate* crystallised as golden-yellow plates in quantitative yield. Recrystallisation was from acetonitrile. The compound melts to a clear yellow liquid on a block preheated to $\nless$123°. When heated from room temperature it decomposes slowly $>$140°. Work must be as rapid as possible since hydrolysis rapidly occurs in air (Found: C, 48·1; H, 4·1; Cl, 12·4. $C_{11}H_9O_5Cl$ requires C, 51·5; H, 3·5; Cl, 13·3%).

3-*Formyl*-1-*hydroxymethyleneazulenium Perchlorate*.—Treatment of a solution of 1,3-diformylazulene (100 mg.) in acetic acid (5 ml.) with perchloric acid (0·5 ml.) as described in the last paragraph gave directly 1-*formyl*-3-*hydroxymethyleneazulenium perchlorate* in quantitative yield. On recrystallisation from acetonitrile it formed yellow plates, decomp. slowly $>$150° (colour changes through greenish-yellow and greenish-blue to black at ~230°) (Found: C, 51·45; H, 4·1; Cl, 11·8. $C_{12}H_9O_6Cl$ requires C, 50·6; H, 3·2; Cl, 12·4%). It readily reverts to 1,3-diformylazulene.

3-*Hydroxymethyleneguaiazulenium Perchlorate*.—Perchloric acid (1 ml.) was added to 3-formylguaiazulene (211 mg.) in acetic acid (5 ml.). Bright yellow needles separated at once quantitatively. Recrystallisation from acetonitrile–ethyl methyl ketone (1 : 2) gave 3-*hydroxymethyleneguaiazulenium perchlorate* as yellow needles, m. p. 158—160° to a green liquid (Found: C, 58·8; H, 6·1; Cl, 11·0. $C_{16}H_{19}O_5Cl$ requires C, 58·8; H, 5·9; Cl, 10·9%). In contrast to the salts from 1-formylazulene and 1,3-diformylazulene, 3-hydroxymethyleneguaiazulenium perchlorate is stable.

Condensations of Azulenealdehydes with Azulenes.—1-*Formylazulene and azulene*. Perchloric acid (0·5 ml.), added to 1-formylazulene (330 mg.) and azulene (300 mg., 5% excess) in boiling acetic acid (10 ml.), gave a deep blue solution. A solid began to separate from the boiling solution as black needles. The product (770 mg., 100%), separated from the cooled solution, was dissolved in an excess of acetonitrile. The solution was filtered, and solvent was evaporated on a water-bath until solid had just begun to separate from the boiling solution. On being cooled slowly to room temperature, the solution deposited 1-1′-*azulylmethyleneazulenium perchlorate* (Xb), black needles, decomp. $>$350° (block preheated to 350°), sparingly soluble in acetone and acetonitrile but readily soluble in cold dimethylformamide (Found: C, 68·5; H, 4·0; Cl, 9·1. $C_{21}H_{15}O_4Cl$ requires C, 68·8; H, 4·1; Cl, 9·7%).

1-*Formylazulene and guaiazulene*. Perchloric acid (0·3 ml.) was added to a boiling solution of 1-formylazulene (170 mg.) and guaiazulene (0·24 ml., 5% excess) in acetic acid (6 ml.). Black needles began to separate from the deep-blue boiling solution. The product, on recrystallisation from acetonitrile as described for the preceding condensation, afforded 3-1′-*azulylmethyleneguaiazulenium perchlorate* (Xc) (405 mg., 85%), green needles, m. p. 199—200·5° (block preheated to 195°) (Found: C, 71·1; H, 5·6; Cl, 8·2. $C_{26}H_{25}O_4Cl$ requires C, 71·5; H, 5·8; Cl, 8·1%).

1,3-*Diformylazulene and azulene*. A boiling solution of 1,3-diformylazulene (92 mg.) in acetonitrile (20 ml.) was added to azulene (140 mg.) and perchloric acid (0·3 ml.) in acetonitrile (20 ml.) at room temperature. When the deep blue solution was heated to the b. p., a black solid began to separate. The black solid (270 mg. 85%), 1,3-*azulenylenedi*-αα′-(1-*methyleneazulenium perchlorate*) (XIIa), was filtered off after 2 hr., washed with ether (100 ml.), dried, and analysed without recrystallisation (Found: C, 63·3; H, 4·0; Cl, 11·9. $C_{32}H_{22}O_8Cl_2$ requires C, 63·5; H, 3·7; Cl, 11·7%). It did not melt $<$325°. It is very insoluble in the common organic solvents except dimethylformamide.

1,3-*Diformylazulene and guaiazulene*. Perchloric acid (0·5 ml.) was added to a boiling solution of 1,3-diformylazulene (184 mg.) and guaiazulene (440 mg., 10% excess) in acetic acid (10 ml.). The deep blue solution, which had begun to deposit a solid at the b. p., was boiled for 1 min., then allowed to cool to room temperature. The product, recrystallised from acetonitrile as described for 1-1′-azulylmethyleneazulenium perchlorate, gave 1,3-*azulenylenedi*-αα′-(3-*methyleneguaiazulenium perchlorate*) (XIIb) (550 mg., 75%), black needles which decompose violently when placed on a block preheated to $\nless$325°, but decompose slowly on being heated from room temperature (Found: C, 67·8; H, 5·8; Cl, 9·2. $C_{42}H_{42}O_8Cl_2$ requires C, 67·6; H, 5·7; Cl, 9·5%). It is sparingly soluble in the common organic solvents with the exception of dimethylformamide in which it is fairly soluble.

Acetonitrile was employed successfully as solvent in place of acetic acid for the above condensations of azulenes with azulene aldehydes.

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