219. *The Azulene Series. Part III.* The Synthesis and Properties of 3-Benzylideneguaiazulenium Chloride.*

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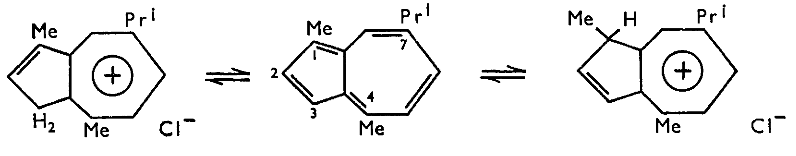
The synthesis of 3-benzylideneguaiazulenium salts is recorded and their reactions with nucleophilic reagents are discussed.

While studying the Gattermann reaction,[1] it was observed that a solution of guaiazulene (1 : 4-dimethyl-7-*iso*propylazulene) (I) in methylene chloride became colourless when saturated with hydrogen chloride. The conversion into guaiazulenium chloride (IIa and/or b) must then be complete. The methylene group in (IIa) would be expected to be reactive, by analogy with indene and 1 : 2-dialkylpyridinium salts.[2] Indeed, addition of benzaldehyde caused the rapid deposition of orange crystals. Many aromatic aldehydes readily caused this reaction but aliphatic aldehydes and ketones either did not react or gave products of a different type.



(IIa) (I) (IIb)

When ether was used as a solvent the blue colour remained at saturation but addition of the aldehyde still produced the orange precipitate. An equilibrium must exist here between (I) and (IIa and/or b), reaction with an excess of aldehyde causing eventual consumption of all the azulene. This proved to be the more convenient preparative procedure as the methylene chloride required purification on each occasion before use.

The orange substance formed by benzaldehyde was unstable. In a few hours its solubility had altered markedly and the solid had become brown, especially on the surface. It was extremely insoluble in non-hydroxylic solvents and rapidly changed to a blue material in hydroxylic solvents. Only in glacial acetic acid, and similar acids, was it reasonably stable. Analysis proved difficult owing to the instability and to failure to effect recrystallisation. In the freshly prepared material the chloride ion content was slightly high owing to apparent occlusion of hydrogen chloride. However, addition of saturated aqueous picric acid to an acetic acid solution of the chloride caused crystallisation of a picrate: this was stable for a few weeks but could not be crystallised as it was degraded by hot solvents. The crude material gave satisfactory analyses and the method was generally applicable, except to *m*-bromobenzaldehyde (here formic acid had to be used to prevent the decomposition). The analytical values showed that reaction was between one molecule each of azulene and aldehyde, giving a fulvene derivative, 3-benzylideneguaiazulenium chloride (III), or occurring at the 4-methyl group (IV).

Reduction of the blue *pseudo*-base derived from the salt by treatment with alkali gave no useful result because of complexity of the reaction with bases. Direct reduction of the salt, catalytically or with lithium aluminium hydride, gave a blue hydrocarbon. This did not crystallise or give a crystalline trinitrobenzene derivative: all the liquid hydrocarbons reported in this paper decomposed owing to oxidation, whereas related crystalline compounds were reasonably stable, presumably because of more rapid diffusion of oxygen through the liquid.

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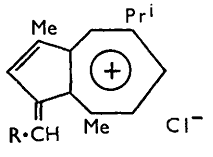
* Part II, preceding paper.

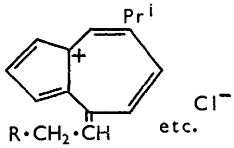
[1] Part IV, following paper.

[2] Reid and Stafford, *Chem. and Ind.*, 1954, 277.

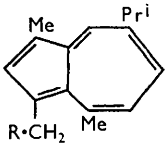
The liquid hydrocarbon showed an absorption maximum in the visible region at 630 mμ which is +25 mμ displaced from the position for the parent guaiazulene, in agreement with a new 3-alkyl substituent, as in (V). The alternative, derived from (IV), should



R = Ph (III)

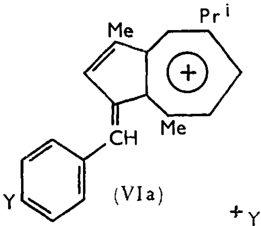


(IV) R = Ph

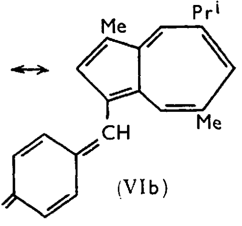


(V)

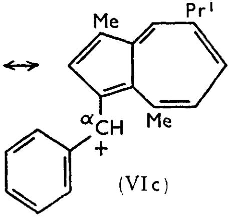
have an absorption identical with that of guaiazulene. It therefore appeared likely (but not certain) that structure (III) was correct for the salt. *m*-Bromobenzaldehyde gave a salt which on reduction with lithium aluminium hydride yielded a crystalline compound giving correct analyses for 3-*m*-bromobenzylguaiazulene (V; R = *m*-Br•C_6H_4) and having an absorption spectrum identical with that of the liquid presumed to be 3-benzylguaiazulene (Fig. 1). The molecular weight, determined by *X*-ray crystallography, confirmed its monomeric character. The bromo-compound did not form a trinitrobenzene derivative: of the several 3-alkylguaiazulenes prepared none has given a complex: this may be due to steric interaction between the 3-benzyl substituent and the 4-methyl group which forces the phenyl group out of planarity with the azulene moiety, thus preventing the required packing in the crystalline complex.



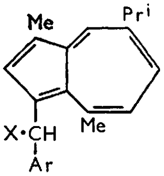
(VIa)



(VIb)



(VIc)



(VII)

These salts are formally fulvene derivatives, and the absorption spectra of derivatives from benzaldehydes possessing electron-donating substituents showed the expected shifts (Table 1). This is explained by enhanced contribution of forms analogous to (VIb), extending the molecular orbital by the assumption of an electron pair from the group Y. In agreement with this is the degree to which *o*-methoxy-, *p*-methoxy-, methylenedioxy-, and *p*-dimethylamino-groups affect the absorption and also the cancellation effect of the last group in concentrated hydrochloric acid.

TABLE 1. *The visible absorption maxima of substituted* 3-*benzylideneguaiazulenium salts.*

Guaiazulenium cation	$\lambda_{max.}$ (mμ)
3-Benzylidene	452
3-3′-Bromobenzylidene	452
3-2′-Methoxybenzylidene	496
3-4′-Methoxybenzylidene	518
3-Piperonylidene	530
3-*p*-Dimethylaminobenzylidene (in NaOAc–AcOH)	640

Salts such as (VI) should be liable to nucleophilic attack, at the α-carbon atom (cf. VIc) or at a free position in the 7-membered ring, or an alkyl group (*e.g.*, 4-methyl) might lose a proton. As the first possibility was the most likely, attack by hydroxide ion was regarded initially as giving the substance (VII; X = OH); it was assumed that the yellow colour obtained by dissolving the "*pseudo*-base" in acid was due to reversion to the salt (III). It was later shown that most of the complex hydrocarbons described below gave similar colours in acid and that the "*pseudo*-base" was an intractable and constantly changing mixture. A series of nucleophilic reagents was investigated and an extemely complex

TABLE 2. *The action of nucleophilic reagents on 3-arylideneguaiazulenium salts.*

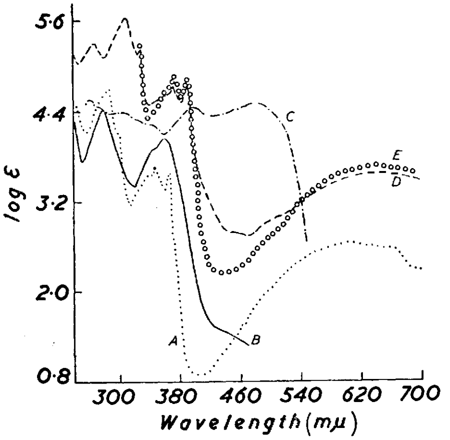
No.	Ar in Ar·CH=	Reagent	Products *
1	Ar [a]	MeMgI	Ar·CHMe·Gu
2	Ph	PhMgBr	$CH_2Ph·Gu_2$ (hydrocarbon A)
3	*m*-C_6H_4Br	PhMgBr	Ar·CHPh·Gu
4	Ph	KOEt	GuH + hydrocarbon B
5	Ar [b]	KOEt	GuH + $CH_2Ar·Gu_2$
6	Ph	KCN	GuH + NC·CHPh·Gu + hydrocarbon C
7	*m*-C_6H_4Br	KCN	GuH + $CH_2Ar·Gu$ + NC·CHAr·Gu·CHGu(CN)
8	*o*-MeO·C_6H_4	KCN	NC·CHAr·Gu
9	*p*-$NO_2·C_6H_4$	KCN	$CH_2Ar(Gu)_3$
10	Ph	Ar·NH_2 [c]	Ar·NH_3Cl + GuH + hydrocarbon D
11	*m*-C_6H_4Br	Ph·NH_2	GuH + $(CH_2Ar)_2(Gu)_7$

* Gu = guaiazulene residue. [a] Ar = Ph, 3 : 4-$(MeO)_2C_6H_3$, *p*-MeO·C_6H_4, or *m*-C_6H_4Br. [b] Ar = *m*-C_6H_4Br, 3 : 4-$(MeO)_2C_6H_4$, or *p*-MeO·C_6H_4. [c] Ar = Ph or *p*-C_6H_4Cl.

picture, summarised in Table 2, emerged. It is remarkable, however, that, in spite of this complexity, each experiment was reproducible and gave only a few products.

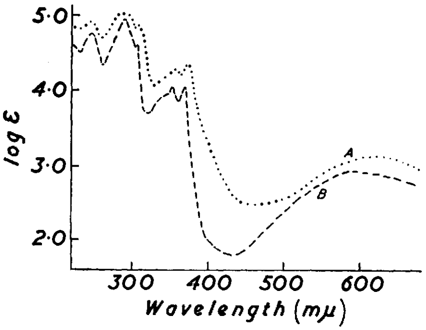
The products from the reaction with methylmagnesium iodide were all liquids of the expected composition and visible absorption ($\lambda_{max.}$ 630 mμ). Phenylmagnesium bromide with the benzylidene salt gave a crystalline product, unexpectedly composed of two guaiazulene residues per benzylidene residue (as shown by the *X*-ray molecular weight). The bromobenzylidene salt on the other hand gave a substance giving approximately the correct analysis for 3-(*m*-bromo-α-phenylbenzyl)guaiazulene, though perhaps containing a little of the diguaiazulene compound analogous to that mentioned above.

FIG. 1.



(*A*) *Guaiazulene* (*in hexane*). (*B*) *Guaiazulenium chloride* (*in methylene dichloride*). (*C*) 3-*Benzylideneguaiazulenium chloride* (*in* 10N-HCl). (*D*) 3-*Benzylguaiazulene* (*in hexane*) (log ε + 1·0). (*E*) 3-3′-*Bromobenzylguaiazulene* (*in hexane*) (log ε + 1·0).

FIG. 2.



(*A*) *Hydrocarbon and* (*B*) *dinitrile from the reaction of* 3-3′-*bromobenzylideneguaiazulenium chloride and potassium cyanide.*

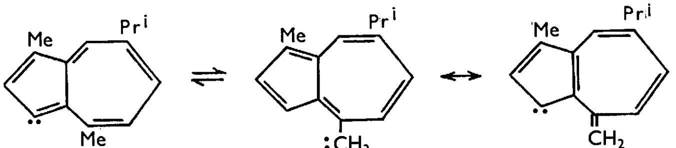
With potassium ethoxide several arylidene salts gave guaiazulene and a substance containing two guaiazulene residues for each arylidene residue. If a hydrocarbon B from the benzylidene salt conforms with the others it is an isomer of hydrocarbon A.

With potassium cyanide the benzylidene salt gave guaiazulene, a hydrocarbon C, and a nitrile, aqueous conditions favouring production of nitriles and anhydrous media that of hydrocarbons. The nitrogenous product from the benzylidene salt was the expected α-cyanobenzylguaiazulene, as shown by its analysis, *X*-ray molecular weight, and oxidation on treatment with alkali to 3-benzoylguaiazulene (cf. following paper). The hydrocarbon C did not yield a single crystal of sufficient size for an *X*-ray molecular-weight determination.

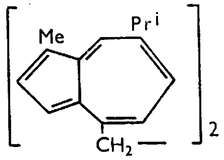
The nitrile from the bromobenzylidene salt was derived from two guaiazulene and one bromobenzylidene residue and contained two cyanide groups. Treatment with alkali again effected oxidation, to a diketone, whose absorption spectrum suggested that the dicyanide was that shown in the Table and the diketone $Br{\cdot}C_6H_4{\cdot}CO{\cdot}Gu{\cdot}CO{\cdot}Gu$; the position of linking is however uncertain. The hydrocarbon contained three guaiazulene residues for each bromobenzylidene residue, showing the critical effect of small differences in molecular structure of the arylidene salt (cf. nos. 8 and 9 in Table 2).

The action of aniline on the benzylidene salt gave a hydrocarbon D containing a little nitrogen, but use of *p*-chloraniline gave the same hydrocarbon free from nitrogen and chlorine; this substance crystallised as minute needles and it proved impossible to obtain a single crystal for a molecular-weight determination. The corresponding substance from the bromobenzylidene salt had an analysis consistent with seven guaiazulene residues for two benzylidene residues.

It is apparent that in a few instances the expected nucleophilic attack at the α-carbon atom has occurred, yielding substances of the general form (VII).



(A) (B)



(VIII)

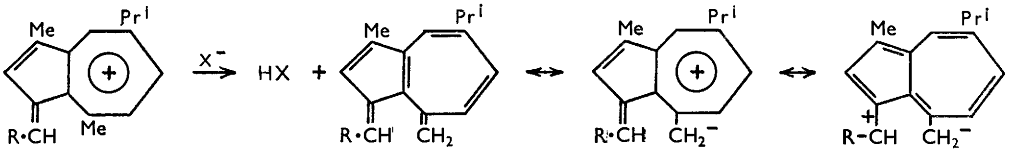
A hydrocarbon containing two guaiazulene residues and one benzylidene residue could result if a guaiazulene anion results in some way from the arylidene salt under basic attack:

$$Ar{\cdot}CH{:}Gu^+ + Gu^- \longrightarrow Ar{\cdot}CH{\cdot}Gu{\cdot}Gu$$

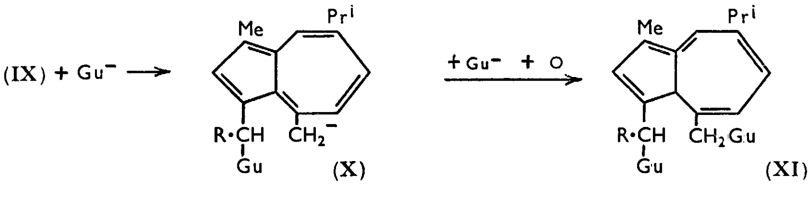
The anion may be derived by a displacement from a substance of structure (VII) by an attacking anion:

$$Ar{\cdot}CHX{\cdot}Gu + Y^- \longrightarrow Ar{\cdot}CHXY + Gu^-$$

The guaiazulene anion, by abstracting a proton from some source, would give guaiazulene, which is a product in most reactions; otherwise it could participate in the formation of a diguaiazulenylphenylmethane. Two such isomeric substances have been obtained, so two types of azulene anion may exist, *e.g.*, *A* and *B*. The form *A* would be stabilised as its magnesium derivative in the Grignard reaction, but form *B* is otherwise probably more stable.



(IXa) (IXb) (IXc)

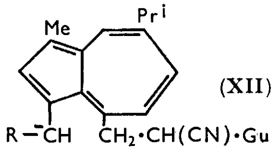


Now guaiazulene, when treated with sodamide, suffers oxidation to a dimer whose absorption spectrum is identical with that of the monomer. It appears that an anion formed by nucleophilic attack is oxidised, which might cause linking of two alkyl side-chains, as in (VIII). The oxidative linking of a complex anion with a guaiazulene anion, as in the annexed scheme, yields substances containing larger proportions of guaiazulene residues.

The initial abstraction of a hydrogen atom accounts for appearance of aniline as its hydrochloride, a mode of attack which is analogous to reaction of substances such as α-picoline methiodide.

The dicyanide from the bromobenzylidene salt would result if an anion attacking the cyanide (VII; X = CN) displaced a bromophenyl instead of a guaiazulene anion, the overall mechanism being as shown.

$R\cdot CH(CN)\cdot Gu + (IX) \longrightarrow R^- +$



(XII)

$(XII) + H^- \longrightarrow$ Dinitrile. $\quad R^- + H^+ \longrightarrow RH$

The spectra of guaiazulene, guaiazulenium chloride, 3-benzylguaiazulene, and 3-*m*-bromobenzylguaiazulene (Fig. 1) show the shifts in absorption due to a 3-alkyl substituent and the close relation between the ultraviolet absorption of the salt and of the hydrocarbons. The same figure shows the absorption of the 3-benzylideneguaiazulenium salt which is quite different. Fig. 2 shows the spectrum of one of the nitriles together with that of the accompanying hydrocarbon, to demonstrate that the cyano-group modifies the contribution of the 3-alkyl substituent.

EXPERIMENTAL

The procedure for chromatography was the following. An ether extract of the products was washed with water, dried (Na_2SO_4), and evaporated. The residue was dissolved in light petroleum (b. p. 40—60°) containing, where necessary, a little benzene, and chromatographed on alumina. The solvents used for elution were (i) light petroleum (b. p. 40—60°)–ether, (ii) mixtures of this with increasing proportions of benzene, (iii) benzene, (iv) benzene–ether, (v) ether, (vi) ether–ethanol, and (vii) ethanol. Densities of crystals were determined by the flotation method, with aqueous potassium mercuri-iodide to which it was necessary in many instances to add ethanol to " wet " the crystals.

Condensation of Guaiazulene with Aromatic Aldehydes.—General methods. Dry ether (50 ml.) was saturated with hydrogen chloride. Guaiazulene (1 g.) and the aldehyde (*ca.* 1·5 mols.) were added while the flow of hydrogen chloride was continued. A microcrystalline solid was deposited rapidly and, after the blue colour was completely dispelled, the solid was collected and washed with ether. The solid was used in this form directly for reaction. For preparation of the picrate it was usually dissolved in glacial acetic acid (formic acid was used with the *m*-bromobenzaldehyde product), and this solution was filtered. A saturated aqueous solution of picric acid was then added dropwise through a filter with continuous shaking. Crystals of the picrate were rapidly deposited. These were washed with a little aqueous acetic acid, and dried by suction and finally in a desiccator under reduced pressure. They could not be recrystallised as solutions decomposed above 50°, giving green tar. These crude materials were analysed and gave on the whole satisfactory analyses:

3-*Benzylideneguaiazulenium picrate*, orange, m. p. 101—102·5° (Found: C, 65·7; H, 5·1; N, 8·1. $C_{28}H_{25}O_7N_3$ requires C, 65·2; H, 5·0; N, 8·1%).

3-4′-*Methoxybenzylideneguaiazulenium picrate*, red-brown, m. p. 150° (decomp.) (Found: C, 64·7; H, 5·2; N, 8·4. $C_{29}H_{27}O_8N_3$ requires C, 63·8; H, 5·0; N, 7·7%).

3-2′-*Methoxybenzylideneguaiazulenium picrate*, orange, m. p. 103—106° (decomp.) (Found: C, 64·4; H, 5·2; N, 7·8%).

3-(*Piperonylidene*)*guaiazulenium picrate*, red, m. p. 104—105° (decomp.) (Found: C, 62·7; H, 4·6; N, 6·9. $C_{29}H_{25}O_9N_3$ requires C, 62·2; H, 4·5; N, 7·5%).

3-3′-*Bromobenzylideneguaiazulenium picrate*, orange (from formic acid), m. p. 74—75°

(decomp.) (Found: C, 56·6; H, 4·3; N, 7·0; Br, 12·4. $C_{28}H_{24}O_7N_3Br$ requires C, 56·6; H, 4·1; N, 7·1; Br, 13·5%).

When this method was applied to *p*-dimethylaminobenzaldehyde a mixture was always obtained of a chloride, its hydrochloride, and salts of other substances. It was best to add *p*-dimethylaminobenzaldehyde hydrochloride to guaiazulene in methylene chloride, a blue monosalt being obtained pure enough to show clearly the light absorption properties; the picrate mixture could not be resolved.

Piperonaldehyde usually formed a red chloride but in some experiments gave green needles. These were insoluble in ether, but dissolved in ethanol, concentrated hydrochloric acid, and to some extent in water to bright red solutions similar in colour and absorption to the red product (Found: C, 67·5; H, 6·6; Cl, 11·6%). They afforded a red picrate, m. p. 108° (decomp.) (Found: C, 61·9; H, 4·3; N, 7·8%), which appears identical with that from the red chloride. The green compound may be a complex of 3-piperonylideneguaiazulenium chloride with piperonaldehyde and hydrogen chloride (Calc. for $C_{31}H_{30}O_5Cl_2$: C, 67·2; H, 5·4; Cl, 12·8%).

3-3′-*Bromobenzylguaiazulene.*—3-3′-Bromobenzylideneguaiazulenium chloride, freshly prepared from guaiazulene (1·46 g.) and *m*-bromobenzaldehyde (2·04 g.), was added to dry ether (100 ml.) to which lithium aluminium hydride (0·5 g.) was added. A vigorous reaction occurred and the solution became blue. After 30 min., the complex was hydrolysed by the addition of water, and the ether layer was separated. Chromatography showed that the only product (eluted with light petroleum–ether) was 3-3′-*bromobenzylguaiazulene* which crystallised from ethanol in elongated blue plates, m. p. 77—78° (Found: C, 71·7; H, 6·5; Br, 21·9. $C_{22}H_{23}Br$ requires C, 71·9; H, 6·3; Br, 21·8%). The volume of the unit cell of this compound was found by *X*-ray methods to be 934·7 Å^3. The observed density was 1·30 g./c.c. and therefore the molecular weight must be $732/n$ where n is the number of molecules per unit cell. This is almost certainly two in this instance from the *X*-ray evidence and it follows that the molecular weight must be 366. That required is 367.

The substance did not form a trinitrobenzene derivative.

3-*Benzylguaiazulene.*—Reduction of benzylideneguaiazulenium chloride, as above and by hydrogenation, gave a hydrocarbon similar in absorption to the substance described above. It did not however crystallise or form a trinitrobenzene derivative. Analysis of liquids in this series have proved unsatisfactory as they were rapidly oxidised.

Reaction of 3-*Benzylideneguaiazulenium Chloride, etc., with Methylmagnesium Iodide.*—A paste of the chloride (from 2 g. of guaiazulene) in ether was added to a solution of methylmagnesium iodide (6 mols.) in ether (150 ml.). A vigorous reaction occurred. The solution became blue; it was boiled for 30 min. and the complex was decomposed with saturated aqueous ammonium chloride. A considerable proportion of the chlorides remained, owing to coating with the reaction complex, and this was removed by filtration before the ether phase was separated. Chromatography was used in the normal way to afford the products.

(i) From 3-benzylideneguaiazulenium chloride the major product, 3-1′-*phenylethylguaiazulene*, was blue ($\lambda_{\max.}$630 mμ), did not crystallise and decomposed within a few days (Found: C, 90·7; H, 9·1. $C_{23}H_{26}$ requires C, 91·4; H, 8·6%).

(ii) From 3-piperonylideneguaiazulenium chloride a blue green product (1 : 1 light petroleum–benzene), 3-1′-(3 : 4-*methylenedioxyphenyl*)*ethyl-guaiazulene* was obtained. It again did not crystallise but was prepared for analysis by short-path distillation (Found: C, 82·5; H, 7·9. $C_{24}H_{26}O_2$ requires C, 83·2; H, 7·6%).

(iii) After a reaction with 3-3′-bromobenzylideneguaiazulenium chloride a blue compound was eluted with light petroleum. 1-m-*Bromophenylethylguaiazulene* did not crystallise and formed a hard tar after several days (Found: C, 71·8; H, 6·8; Br, 19·4. $C_{23}H_{25}Br$ requires C, 72·4; H, 6·6; Br, 21·0%).

Reaction of 3-*Benzylideneguaiazulenium Chloride, etc., with Phenylmagnesium Bromide.*—The benzylideneguaiazulenium chloride (from 1 g. of guaiazulene) was suspended in dry benzene (20 ml.) and added to a solution of phenylmagnesium bromide (0·05 mole) in ether. The solution became green and after 30 min. was decomposed with water. The ether–benzene phase was treated in the normal way. A liquid blue hydrocarbon fraction (light petroleum–ether) was obtained. An ethanolic solution of trinitrobenzene was added and blue lozenge-shaped crystals, m. p. 179—182°, were deposited (20 mg.) (Found: C, 91·4; H, 8·1; N, 0·0. $C_{28}H_{28}$ requires C, 92·3; H, 7·8%; *M*, 364. $C_{37}H_{40}$ requires C, 91·7; H, 8·3%; *M*, 484). The *hydrocarbon* formed orthorhombic crystals of cell-volume 2919·8 Å^3. Its density was

1·10 g./c.c., hence the calculated molecular weight was 1935/*n*. The nature of the crystal suggested that *n* was 4 or, less probably, 8. The molecular weight would therefore be 484 or 242. This excludes the expected guaiazulenyldiphenylmethane and suggests instead the structure 1 : 1-di-3′-guaiazulenyl-1-phenylmethane.

The same method applied to 3-3′-bromobenzylideneguaiazulenium chloride gave a blue product (light petroleum–ether) which did not crystallise and decomposed rapidly. It appeared to be the expected 1-3′-bromophenyl-1-3′-guaiazulenyl-1-phenylmethane (Found: C, 76·3; H, 6·4; Br, 17·0. $C_{28}H_{27}Br$ requires C, 75·7; H, 6·1; Br, 18·1%).

Reaction of 3-Benzylideneguaiazulenium Chloride, etc., with Potassium Ethoxide.—To the benzylidene chloride [from the appropriate aldehyde and guaiazulene (1 g.)], suspended in benzene (30 ml.), an excess of potassium ethoxide (0·05 mole) was added. The mixture was shaken occasionally during 24 hr. at room temperature. The blue solution was filtered, to remove unchanged material, and distilled to small volume. Chromatography yielded several fractions.

(i) 3-Benzylideneguaiazulenium chloride gave a crystalline product (light petroleum–benzene, 4 : 1). Further chromatography removed traces of guaiazulene and a green impurity from it. The blue solid (42 mg.) had m. p. 155—158° (Found: C, 90·9; H, 8·1%).

(ii) 3-3′-Bromobenzylideneguaiazulenium chloride reacted almost completely. Chromatography separated guaiazulene and a blue compound (light petroleum–benzene, 2 : 1) from more strongly adsorbed material. The *product* (115 mg.), crystallised from light petroleum–ethanol, had m. p. 190° (varied with the rate of heating) (Found: C, 79·1; H, 7·0; Br, 14·7. $C_{37}H_{39}Br$ requires C, 78·8; H, 7·0; Br, 14·2%).

(iii) 3-Piperonylideneguaiazulenium chloride yielded guaiazulene and a blue compound (light petroleum–benzene, 2 : 1). This crystallised from benzene–ethanol and from ethyl acetate and had m. p. very variable with the rate of heating (Found: C, 85·8; H, 7·4. $C_{38}H_{40}O_2$ requires C, 86·3; H, 7·6%).

(iv) 3-*p*-Anisylideneguaiazulenium chloride gave a similar result. The *product* recrystallised from ethyl acetate (Found: C, 88·0; H, 8·1. $C_{38}H_{42}O$ requires C, 88·7; H, 8·2%).

Reaction of 3-Benzylideneguaiazulenium Chloride with Potassium Cyanide.—(*a*) The benzylidene salt from guaiazulene (1 g.) was suspended in benzene (40 ml.). Potassium cyanide (1 g.) in water (10 ml.) was added. The mixture immediately became blue. After 2 hr. solid matter was removed and the benzene phase was prepared for chromatography which separated guaiazulene (5 mg.), a trace of a hydrocarbon ($\lambda_{max.}$ 725 mμ), and a blue compound (benzene) which crystallised from light petroleum–ethanol as purple needles, m. p. 96—97·5° (1·2 g., 80%) (Found: C, 87·5; H, 7·3; N. 4·1. $C_{23}H_{23}N$ requires C, 88·1; H, 7·4; N, 4·5%). The substance proved to be *α-3′-guaiazulenyl-α-phenylacetonitrile.*

(*b*) The benzylidene salt was treated in benzene with dry potassium cyanide (1 g.). The mixture was milled with glass beads for 6 hr., then left overnight at room temperature, filtered, and treated as before. The products were guaiazulene (92 mg.), a blue fraction (light petroleum–benzene, 9 : 1), and another (light petroleum–benzene, 1 : 1). The second fraction (260 mg.), crystallised from light petroleum–ethanol, had m. p. 156—157° and proved to be a *hydrocarbon* (Found: C, 91·5; H, 8·8. $C_{52}H_{56}$ requires C, 91·8; H, 8·2%). The third fraction was the nitrile obtained under aqueous conditions.

The volume of the unit cell of the nitrile was 913 Å^3 and the density 1·07 g./c.c. The molecular weight was calculated to be 588/*n*. The most probable value for *n* is 2, hence the molecular weight is 294. The nitrile requires *M* 313.

Reaction of 3-3′-Bromobenzylideneguaiazulenium Chloride with Potassium Cyanide.—The same methods were applied as above. Under aqueous conditions a quantity of salt (from 1 g. of guaiazulene) yielded guaiazulene (17 mg.), a blue solid (20 mg.) eluted by light petroleum–benzene (2 : 1), and a second solid eluted by benzene (510 mg.). The first solid was a *hydrocarbon* whose m. p. varied with rate of heating (Found: C, 82·4; H, 7·6; Br, 10·3. $C_{52}H_{55}Br$ requires C, 82·2; H, 7·3; Br, 10·5%). The second was a *nitrile* (also with variable m. p.) which crystallised from light petroleum–ethanol (Found: C, 77·0; H, 6·3; N, 4·1; Br, 12·5. $C_{40}H_{39}N_2Br$ requires C, 76·5; H, 6·3; N, 4·5; Br, 12·7%).

Under anhydrous conditions the products were guaiazulene (53 mg.), the hydrocarbon (83 mg.), and the dinitrile (210 mg.).

Hydrolysis and Oxidation of Guaiazulenylphenylacetonitrile.—The nitrile was not hydrolysed by acid to a characterisable product. When phenylguaiazulenylacetonitrile (1·49 g.) was dissolved in ethanol (100 ml.), and 4% ethanolic sodium hydroxide (50 ml.) was added, the solution immediately became green (red in transmitted light). After 1 hr. the solution was diluted with water and extracted with ether. The extract was treated in the normal way and unchanged nitrile (935 mg.) was separated from an orange band (benzene–ether, 1 : 1) which gave a green solution (red in transmitted light). Dark purple crystals (230 mg.) were obtained (from light petroleum–ethanol) and had m. p. 120—122° (mixed m. p. with 3-*benzoylguaiazulene*, 119—122°) (Found: C, 87·5; H, 7·4. $C_{22}H_{22}O$ requires C, 87·5; H, 7·3%). The monoclinic crystals had a unit cell of volume 1697 Å^3 and a density of 1·19 g./c.c. The mass of the unit cell is therefore 1216 and, as *n* is probably 4, the molecular weight is probably 304. 3-Benzoylguaiazulene requires *M* 302.

Hydrolysis and Oxidation of the Dinitrile.—The method used for the dinitrile (100 mg.) gave unchanged dinitrile and a brown *compound* (80 mg.), orange on alumina, which crystallised from methanol as needles, m. p. 81—82·5° (Found: C, 75·4; H, 7·0; Br, 13·3. $C_{38}H_{37}O_2Br$ requires C, 75·3; H, 6·1; Br, 13·2%).

Reaction of 2-*Methoxybenzylideneguaiazulenium Chloride with Potassium Cyanide.*—The salt (from 0·4 g. of guaiazulene) was added to an aqueous solution of potassium cyanide. A blue colour immediately developed. An ether extract was made, washed with water, dried, and concentrated. A mixture of ethanol (25 ml.) and 10% aqueous sodium hydroxide (25 ml.) was added but there was no colour change. Air was bubbled vigorously through the solution for 30 min. and the mixture was then set aside for 12 hr. An extract was prepared for chromatography. A blue fraction (light petroleum–benzene, 1 : 1) yielded a solid material from which light petroleum extracted a green impurity. The bright blue residue (220 mg.), α-3′-*guaiazulenyl*-α-2′-*methoxyphenylacetonitrile*, crystallised from ethyl acetate, had m. p. 160° (Found: C, 84·8; H, 7·4; N, 3·8. $C_{24}H_{25}ON$ requires C, 83·9; H, 7·4; N, 4·1%). There was also an orange band (ether) which gave a blue solution (red in transmitted light); no crystals could be obtained from this.

Reaction of 3-4′-*Nitrobenzylideneguaiazulenium Chloride with Potassium Cyanide.*—The salt (from 0·5 g. of guaiazulene) was added to an aqueous solution of potassium cyanide (1 g.). The green material thus produced was extracted into ether and treated in the normal way except that benzene was required for applying the material to the chromatogram. The products included a little guaiazulene and a blue-green fraction (light petroleum–benzene, 1 : 1) which yielded a blue solid (70 mg.), m. p. 205° (Found: C, 83·1; H, 7·5; N, 3·2. $C_{59}H_{62}O_4N_2$ requires C, 82·3; H, 7·0; N, 3·3%). Other fractions yielded no crystals.

Reaction of 3-*Benzylideneguaiazulenium Chloride with* p-*Chloroaniline and Aniline.*—*p*-Chloroaniline (1·6 g.) was added to a suspension of 3-benzylideneguaiazulenium chloride (from 1 g. of guaiazulene) in benzene (50 ml.). The colour changed to blue within a few minutes and after 30 min. the solution was filtered to remove unchanged material and *p*-chloroaniline hydrochloride. The benzene solution was treated normally. The products were guaiazulene and a second blue fraction (also light petroleum) which was chromatographed again. The *hydrocarbon* (710 mg.) crystallised as pale blue needles, m. p. 125—126°, from light petroleum–ethanol (Found: C, 91·9; H, 8·3; N, 0·0; Cl, 0·0. $C_{119}H_{125}$ requires C, 91·9; H, 8·1%).

Use of aniline gave essentially the same results. The solid product was apparently identical with that above, m. p. 125—127° (Found: C, 90·8; H, 8·5; N, 0·6%).

Reaction of 3-3′-*Bromobenzylideneguaiazulenium Chloride with Aniline.*—The reaction was carried out as above. The products were guaiazulene (106 mg.) and a blue *substance* (light petroleum–benzene, 2 : 1). The latter crystallised as bright blue needles, m. p. 210° (variable with rate of heating), from light petroleum–ethanol (Found: C, 83·7; H, 7·4; N, 0·0; Br, 9·4. $C_{119}H_{123}Br_2$ requires C, 83·3; H, 7·3; Br, 9·3%).

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