633. *The Substitution of Azulene by Benzyl Radicals.*

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Direct substitution of azulene by benzyl radicals yields 1- and 2-benzylazulene in comparable amounts and a small quantity of a pentabenzylazulene. The structures of the products have been established by direct comparison with synthetic specimens; each possible monobenzylazulene has been synthesised. For 2-benzylazulene evidence of structure was also provided by measurements of proton magnetic resonance spectra.

The production of 1- and 2-benzylazulene by homolytic substitution of azulene is not in accord with published predictions based on quantum-mechanical calculations, but is not inconsistent with previously published experimental work.

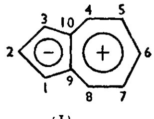
HOMOLYTIC bimolecular reactions do not involve major charge displacements, but polar effects are quite absent only if the formation of the transition state between the neutral radical and the substrate involves no net displacement of valency electrons with respect to the approaching nuclear centres. It is of interest therefore to investigate the degree to which polar effects may influence reactions between free hydrocarbon radicals and hydrocarbon molecules and already in the homolytic substitution of benzene derivatives, C_6H_5R, appreciable differences between the actions of methyl and phenyl radicals have been discerned.[1]

TABLE 1. *Theoretical calculations for azulene.*

Position	1	2	4	5	6	9
Electron density *	1·049	0·997	0·908	1·034	0·938	1·042
Electron density †	1·090	1·042	0·933	0·970	0·943	1·014
Atom localisation energy [2a] (units of β), for:						
Nucleophilic attack (*N*)	2·60	2·36	1·93	2·34	1·99	—
Electrophilic attack (*E*)	1·92	2·36	2·55	2·34	2·73	—
Free-radical attack (*R*)	2·26	2·36	2·24	2·34	2·36	—

* Calc. by the self-consistent field method (Julg, *J. Chim. phys.*, 1955, **52**, 377).
† Values calculated by the molecular orbital method (Berthier and Pullman, *Compt. rend.*, 1949, **229**, 761.

Unsubstituted alternant hydrocarbons, such as naphthalene, have unit π-electron density at all positions, and reactions of all types (electrophilic, nucleophilic, and homopolar) take place predominantly at the point of highest polarisability so that, though isomer ratios may vary, similarly substituted products result from all types of substitution. In contrast, non-alternant hydrocarbons, such as azulene, do not have a uniform π-electron density and different predominant positions of attack are to be expected with reagents of different types.



(I)

Theoretical computations of π-electron density and of atom localisation energies of azulene (I) for free-radical, nucleophilic, and electrophilic attack are given in Table 1.

According to theoretical approaches,[2] position 4 has the lowest calculated atom localisation energy for free radical attack, but it is closely followed by the 1-position. There is only a relatively small difference in atom localisation energies at all positions, though 2 and 6, which are the most remote from the ring-linking bond (9,10), would seem to be the least probable points of attack. Position 1 is clearly favoured for electrophilic attack and position 4 for nucleophilic attack.

To predict the reaction path for the attack on azulene of a radical having some degree of dipolar character one would have to use some combination of the data on the last line (*R*) of Table 1 with that of one of the preceding lines (*E*, *N*), according to the sense and magnitude of the electrical dipole associated, in the transition state, with the new developing

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[1] Cowley, Norman, and Waters, *J.*, 1959, 1799.
[2] (*a*) Peters, *J.*, 1958, 1028; (*b*) Brown, *Trans. Faraday Soc.*, 1948, **44**, 984.

bond: the figures show that less than 10% of electrophilic character in the addition process would suffice to favour attack on the 5-membered ring.

The early, naive view that free radicals are essentially electrophilic with respect to olefinic bonds (Waters [3]) indicates that free-radical substitution of azulene should occur in the 5-membered ring, and probably in position 1. It has been verified experimentally that nucleophilic attack takes place at position 4 [4,5] and electrophilic attack at position 1.[5] In regard to homolytic substitution, previous workers [6,7] have shown that phenyl radicals substitute azulene to give 1-phenylazulene, but only in low yield, and that benzoyloxy-radicals yield 1-benzoyloxyazulene.[7] Study of the attack on azulene by radicals of still more different character being desirable, we have investigated its substitution by benzyl radicals, which can be regarded as alkyl radicals almost devoid of any intrinsic dipolar character.

RESULTS

Free-radical Substitution.—Preliminary tests showed that azulene reacts immediately with 2-cyano-2-propyl radicals with loss of colour. Presumably this is due to the formation of an unstable adduct of two radicals to azulene with destruction of the fully conjugated system. With benzyl radicals, generated by the decomposition of t-butyl peroxide in boiling toluene under nitrogen,[8] some substitution did occur. In this case an initial radical addition to give $Ph{\cdot}CH_2{\cdot}C_{10}H_8{\cdot}$ can be followed by hydrogen abstraction by benzyl or t-butoxy-radicals as in the substitution of aromatic hydrocarbons by this reagent.

It was found necessary to work on a small scale and overall yields of substituted azulenes were not over 10%, but chromatography through alumina separated three products with spectra of azulene type. One of these substituted azulenes, m. p. 73—75°, was at once identified as 1-benzylazulene by its m. p., the m. p. of its 1,3,5-trinitrobenzene complex, and by the correspondence of its spectrum in the visible and the ultraviolet region with data published by Anderson and Cowles.[9] Later, through the kindness of Dr. A. G. Anderson in sending us a record of his infrared spectrum, we have been able to check the identity of our product by means of its infrared spectrum also.

The second product, m. p. 46—47°, which was separated only with difficulty, though in comparable yield, from 1-benzylazulene, was rigorously proved to be an isomer. From the study of its proton magnetic resonance spectrum by Dr. R. E. Richards and Mr. P. Higham (see Appendix) and finally by unequivocal synthesis, it was identified as 2-benzylazulene. During substantiation of this structure all the monobenzylazulenes were synthesised.

The third product, m. p. 83·5—84·5°, appears, from the analysis of its 1,3,5-trinitrobenzene adduct, to be a pentabenzylazulene.

Methylation of the sodium adduct of azulene was also investigated: this probably yields 1,3-dimethylazulene.

Whilst theoretical conclusions that can be adduced from all studies of azulene substitution must be viewed with reserve, since chemical attack always leads to extensive destruction of this ring system, the present results show that benzyl radicals attack azulene in both the 1- and the 2-position. Thus, from three different groups of workers comes evidence that three different organic radicals (alkyl, aryl, acyl) attack azulene in the negatively polarised 5-membered ring: there is as yet no clear evidence of radical attack in position 4 as predicted by certain theorists.[2]

Synthesis of the Isomeric Benzylazulenes.—2-Benzylazulene was prepared from 2-benzylindane by expanding the 6-membered ring with ethyl diazoacetate and dehydrogenating

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[3] Waters, *Trans. Faraday Soc.*, 1941, **37**, 770; "The Chemistry of Free Radicals," Oxford, 1946, p. 183.

[4] Hafner and Weldes, *Angew. Chem.*, 1955, **67**, 302; *Annalen*, 1957, **606**, 90.

[5] Hafner, *Angew. Chem.*, 1958, **70**, 419.

[6] Arnold and Pahls, *Chem. Ber.*, 1956, **89**, 121.

[7] Anderson and Chang, *J. Org. Chem.*, 1958, **23**, 151.

[8] Beckwith and Waters, *J.*, 1957, 1001; Waters and Watson, *J.*, 1957, 253.

[9] Anderson and Cowles, *J. Amer. Chem. Soc.*, 1955, **77**, 4617.

the product with palladised charcoal, following the general procedure of Plattner and Wyss.[10] The 2-benzylindane was synthesised from dibenzylacetic acid by ring closure to the indanone and then Clemmensen reduction. 4-Benzylazulene was prepared by addition of benzylsodium to azulene followed by dehydrogenation of the intermediate benzyldihydroazulene with chloranil. The method is a modification of that used by Hafner and Weldes[4] for the preparation of 4-alkyl- and 4-aryl-azulenes from azulene and lithium alkyls or aryls. Hafner[5] has listed 4-benzylazulene, with physical properties corresponding to our reaction product, but has given no experimental details of his work.

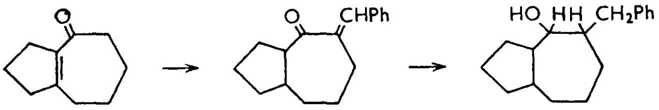
6-Benzylazulene was prepared by the type of synthesis due to Hafner.[11] Treatment of 4-benzylpyridine with cyanogen bromide and *N*-methylaniline yielded the anil (II).

$$[\mathrm{PhMeN{\cdot}CH{:}CH{\cdot}C(CH_2Ph){:}CH{\cdot}CH{:}NPhMe}]^+\mathrm{Br}^- \quad \text{(II)}$$

This yielded 6-benzylazulene when treated with cyclopentadiene by a procedure similar to that[12] for the preparation of azulene.

Attempts to prepare 5-benzylazulene by a route similar to that employed for the synthesis of 6-benzylazulene were unsuccessful. The reaction between 3-benzylpyridine, cyanogen bromide, and *N*-methylaniline yielded 3-benzylpyridine hydrobromide instead of the expected anil (III), and the reaction between *N*-methylaniline and 3-benzyl-1-(2,4-dinitrophenyl)pyridinium chloride likewise failed to give this anil. Eventually 5-benzylazulene was synthesised from 2-decalol. This was converted by standard methods *via* Δ^9-octalin into the ketone (IV), which was reduced catalytically to a saturated ketone and then condensed with benzaldehyde to give the benzylidene-ketone (V). Thence catalytic reduction followed by treatment with lithium aluminium hydride yielded the alcohol (VI) together with a small proportion of a hydrocarbon. Dehydration of the alcohol and dehydrogenation of the product in the vapour phase with palladised charcoal gave a small yield of 5-benzylazulene.

$$[\mathrm{MePhN{\cdot}CH{:}CH{\cdot}CH{:}C(CH_2Ph){\cdot}CH{:}NPhMe}]^+\mathrm{Br}^- \quad \text{(III)}$$



(IV) (V) (VI)

TABLE 2. *Visible spectra of the benzylazulenes: shift of the absorption maximum of longest wavelength.*

Compound	Shift (mμ)	Compound	Shift (mμ)
1-Benzylazulene	+31·5	2-Benzylazulene	−20·5
5-Benzylazulene	+14·5	4-Benzylazulene	−26·0
—	—	6-Benzylazulene	−10·5
Pentabenzylazulene	+4·5		

Absorption Spectra of the Benzylazulenes.—The visible and ultraviolet absorption spectra of the isomeric benzylazulenes have been measured in hexane solution on a Cary recording spectrophotometer. Data concerning the absorption maxima are given in Table 3. Table 2 gives the shifts of the absorption maxima of longest wavelength with respect to that of azulene, and shows that Plattner's rule,[13] developed for the methylazulenes, is also applicable to the benzylazulenes. The spectral correlations, however, are not assured enough for the identification of the probable pentabenzylazulene. The infrared spectra are rather too complicated for diagnostic use without further systematic study of both band positions and intensities.

[10] Plattner and Wyss, *Helv. Chim. Acta*, 1940, **23**, 907.

[11] Hafner, *Annalen*, 1957, **606**, 79.

[12] Ziegler and Hafner, *Angew. Chem.*, 1955, **67**, 301; improved by A. G. Anderson (personal communication).

[13] Plattner, *Helv. Chim. Acta*, 1936, **19**, 858; 1941, **24**, 283; Gordon, *Chem. Rev.*, 1952, **50**, 185.

EXPERIMENTAL

Azulene was prepared in 32% overall yield by Anderson's modification of the synthesis by Ziegler and Hafner.[12]

Reaction of Azulene with 2-Cyano-2-propyl Radicals.—Azulene (2·0 g.) and azoisobutyronitrile (7·7 g., 3 equiv.) were heated at 100° for 2½ hr. in toluene (100 ml.) under nitrogen. The solution soon lost its blue colour. After removal of the solvent the residue was chromatographed through deactivated alumina and yielded unchanged azulene (0·1 g.) and tetramethylsuccinonitrile (2·1 g., 33%), together with a gum which failed to give any azulene derivative with chloranil in hot benzene.

Reaction of Azulene with Benzyl Radicals.—Azulene (4·0 g.), t-butyl peroxide (11 g.), and toluene (250 ml.) were refluxed together under nitrogen for 70 hr. After removal of the solvent the residue was passed in light petroleum (b. p. 40—60°) through alumina (type H) and gave unchanged azulene (0·5 g.) and then a blue oil (0·6 g.). Crystallisation of the latter from light petroleum yielded 1-benzylazulene (0·095 g.), m. p. 73—75°, identified by means of its visible, ultraviolet, and infrared spectra and as 1,3,5-trinitrobenzene adduct, m. p. 96—97° [5,9] (Found: C, 64·5; H, 4·4; N, 9·3. Calc. for $C_{23}H_{17}O_6N_3$: C, 64·0; H, 4·0; N, 9·7%).

Crystallisation of the more soluble portions of the blue oil gave dark blue needles (0·080 g.), m. p. 46—47°, of *2-benzylazulene* [Found: C, 93·2; H, 7·0%; *M* (isothermal distillation [14]), 216, 220. $C_{17}H_{14}$ requires C, 93·5; H, 6·5%; *M*, 218]. Its *1,3,5-trinitrobenzene adduct* had m. p. 125—126° (Found: C, 64·0, 64·3; H, 4·7, 3·9; N, 9·4. $C_{23}H_{17}O_6N_3$ requires C, 64·0; H, 4·0; N, 9·7%). The absorption spectrum of this compound was identical with that of synthesised 2-benzylazulene.

The uncrystallised portion of the blue oil was collected together and analysed spectrophotometrically [15] in hexane; it contained 37% of 1-benzylazulene, 40% of 2-benzylazulene, and 23% of material that did not absorb in the visible region. Elution of the alumina with 5% of benzene in light petroleum gave blue needles, m. p. 83·5—84·5° (0·08 g.) (Found: C, 92·9; H, 6·3. $C_{45}H_{38}$ requires C, 93·1; H, 6·9%), which gave a chocolate-coloured trinitrobenzene adduct, m. p. 79—80° (Found: C, 77·3; H, 5·2; N, 5·2. $C_{51}H_{41}O_6N_3$ requires C, 77·4; H, 5·2; N, 5·3%); this corresponds to a *pentabenzylazulene.*

Reaction of Sodium with Azulene.—Azulene (0·5 g.) was shaken for 3½ days at room temperature with sodium (0·4 g.), 1,2-dimethoxyethane (7 ml.), and a little powdered glass. The mixture, under nitrogen, was then treated with methyl iodide (1·9 ml.), benzene was added, and the filtered solution was refluxed for 3 hr. with chloranil (1 g.). After removal of the solvent the residue, in light petroleum, was chromatographed through alumina. It gave 0·08 g. of a blue gum which, after treatment with trinitrobenzene (0·12 g.) in boiling ethanol gave black needles (0·06 g.), m. p. 162—164° (Found: C, 58·9; H, 4·2; N, 12·1. Calc. for $C_{18}H_{15}O_6N_3$: C, 58·6; H, 4·1; N, 11·4%). This corresponds to the *adduct* of a dimethylazulene. Passage of this adduct in ethanol through alumina regenerated a blue oil (0·02 g.), which by crystallisation from light petroleum at $-50°$ gave a trace of solid, m. p. 39—48°. The visible spectrum, in ethanol has maxima at wavelengths corresponding to that of 1,3-dimethylazulene, m. p. 54° (cf. Gordon [13]):

Peak positions found (mμ)	780	742	697	666	633	611	585
Δλ from that of azulene (mμ)	88	86	68	68	56	55	44
Δλ for 1,3-dimethylazulene	73	89	72	69	58	53	45

Synthesis of 2-Benzylazulene.—Dibenzylacetic acid, m. p. 88—89°, was prepared in 83% yield (3 stages) from benzyl chloride and ethyl malonate. The acid (200 g.) was converted, with thionyl chloride, into its acyl chloride which, in light petroleum (b. p. 80—100°; 1 l.), was treated with aluminium chloride (200 g.) and heated at 100° until reaction ceased. After decomposition with ice *2-benzylindan-1-one* (75%), b. p. 154—160°/0·4 mm., was isolated in the usual manner [*2,4-dinitrophenylhydrazone*, m. p. 195—197° (decomp.) (Found: C, 65·1; H, 4·4; N, 14·2. $C_{22}H_{18}O_4N_4$ requires C, 65·7; H, 4·5; N, 13·9%)]. Reduction of 2-benzylindan-1-one with amalganated zinc and hydrochloric acid gave a 77% yield of 2-benzylindane, b. p. 104—106°/0·2 mm. (Found: C, 91·8; H, 7·8. Calc. for $C_{16}H_{16}$: C, 92·2; H, 7·8%). Ethyl diazoacetate (6·4 g.) was added dropwise in 20 min. to 2-benzylindane (59 g.) at 130°. The mixture was then heated during 30 min. to 160°, kept thereat for 1½ hr., and distilled through a column. The unchanged 2-benzylindane, b. p. up to 125°/0·1 mm., was treated, as before, with a further

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[14] Niederl, Kasanov, Kisch, and Subba Rao, *Mikrochem.*, 1949, **34**, 132.

[15] Dewar and Urch, *J.*, 1957, 345.

equal portion of ethyl diazoacetate, and the whole process was repeated a further 3 times. The combined distillation residues were then distilled at 130—190°/0·2 mm., yielding a brown oil (26·3 g.), 44·5 g. of 2-benzylindane being recovered.

This oil was refluxed for 2 hr. with potassium hydroxide (10 g.) in water (20 ml.) and ethanol (50 ml.). The acid was separated, by ether, as a dark viscous oil (10·5 g.). This was distilled rapidly from 10% palladised charcoal (1·1 g.), yielding a deep blue liquid, chromatography of which, in light petroleum, through alumina gave some azulene and crude 2-benzylazulene (0·7 g.) which, on further crystallisation from light petroleum (40—60°), formed intensely blue crystals, m. p. 48° (0·37 g.), mixed m. p. 46—47° with the benzylation product of azulene. The residue from the crystallisation of the authentic material gave, with trinitrobenzene in ethanol, an adduct, m. p. 121—124°, identical with that of the benzylation reaction. The infrared, visible, and ultraviolet absorption spectra of the two 2-benzylazulenes were, in similar solvents, identical.

Synthesis of 4-*Benzylazulene.*—A mixture of toluene (1 ml.) and chlorobenzene (0·9 ml.) was added slowly, with vigorous stirring, to powdered sodium (0·5 g.), suspended in toluene (2·9 ml.) at 30—40° under dry nitrogen. After 1 hour's stirring, the mixture was refluxed for 2 hr. to convert phenylsodium into benzylsodium,[16] then treated with azulene (0·5 g.) in toluene (3 ml.), stirred at 100° for another 10 min., cooled, and decomposed with ice-water. The organic layer was separated, washed with dilute acid, dried ($MgSO_4$), and refluxed for 90 min. with chloranil (1·5 g.) in benzene (50 ml.). After removal of the solvent, chromatography of the residue gave 4-benzylazulene (0·14 g.), m. p. 54—55°, after crystallisation from light petroleum (b. p. under 40°) at $-30°$ (Hafner [5] gives m. p. 55—57°) (Found: C, 93·4; H, 6·5. Calc. for $C_{17}H_{14}$: C, 93·5; H, 6·5%). Its trinitrobenzene complex had m. p. 125—126° (from ethanol) (Found: C, 64·2; H, 4·1; N, 9·9. Calc. for $C_{23}H_{17}O_6N_3$: C, 64·0; H, 4·0; N, 9·7%).

Synthesis of 6-*Benzylazulene.*—4-Benzylpyridine [17] (6·15 g.) and *N*-methylaniline (7·8 g.) in dry ether (30 ml.) at 0° were treated, with stirring, during 20 min., with cyanogen bromide (3·9 g.) in ether (20 ml.). After the mixture had been stirred overnight, ether was decanted from the red gum which had been formed. This crude 3-*benzyl*-N-*methyl*-5-(N-*methylanilino*)-N-*phenylpenta*-2,4-*dienylideneammonium bromide* (II) was dissolved in a little ethanol, precipitated with ether, and further purified in the same way; it formed pink crystals, m. p. 101° (decomp.) (6·64 g.), containing 1 mol. of ethanol of crystallisation (evident from the infrared spectrum) (Found: C, 67·6; H, 6·4. $C_{26}H_{27}N_2Br,C_2H_5{\cdot}OH$ requires C, 67·6; H, 6·7%).

Cyclopentadiene (1·83 g.) was stirred with sodium methoxide (0·96 g.) in diethylene glycol (80 c.c.) under nitrogen for 5 min., then the above salt (6·25 g.) was added. After a further hour's stirring at room temperature the mixture was diluted with diethylene glycol (240 ml.), heated to 220°, and distilled with superheated steam. The distillate was diluted with a large bulk of water, and the precipitate of 6-*benzylazulene* was collected. A further quantity was obtained by diluting the distillation residue with water and extracting it with light petroleum (total yield, 0·58 g.). After crystallisation from light petroleum the 6-benzylazulene had m. p. 99—100° (Found: C, 92·9; H, 6·6. $C_{17}H_{14}$ requires C, 93·5; H, 6·5%). Its *trinitrobenzene adduct* had m. p. 109—110° (Found: C, 64·5; H, 4·2; N, 9·4. $C_{23}H_{17}O_6N_3$ requires C, 64·0; H, 4·0; N, 9·7%).

Synthesis of 5-*Benzylazulene.*—(a) *Attempted synthesis from* 3-*benzylpyridine.* Treatment of 3-benzylpyridine [18] with methylaniline and cyanogen bromide, as described above, gave 3-benzylpyridine hydrobromide, m. p. 143—145° (72%). By refluxing 3-benzylpyridine and 1-chloro-2,4-dinitrobenzene in benzene a 93% yield of 3-*benzyl*-1-(2,4-*dinitrophenyl*)*pyridinium chloride* was obtained, having m. p. 105—107° (from chloroform) (Found: C, 55·1; H, 4·2; N, 11·0; Cl, 9·4. $C_{18}H_{14}O_4N_3Cl,H_2O$ requires C, 55·5; H, 4·1; N, 10·8; Cl, 9·1%). This substance scarcely reacted with *N*-methylaniline in boiling ethanol, the pyridinium salt being recoverable as the perchlorate, in 50% yield after 6 hr. and 28% after 17 hr. The *perchlorate* had m. p. 209—210° (Found: C, 50·1; H, 3·5; N, 9·0; Cl, 7·6. $C_{18}H_{13}O_4N_3,HClO_4$ requires C, 49·6; H, 3·2; N, 9·6; Cl, 8·1%).

(b) *Synthesis from* β-*naphthol.* Δ^9-Octalin, prepared from 2-decalol,[19] was converted into cyclodecane-1,6-dione by treatment with hydrogen peroxide in formic acid, followed by

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[16] Morton and Massengale, *J. Amer. Chem. Soc.*, 1940, **62**, 121; Morton, Massengale and Gibbs, *ibid.*, 1941, **63**, 325.

[17] Benkesen and Holden, *ibid.*, 1951, **73**, 5861.

[18] Tschitschibabin, *Ber.*, 1903, **36**, 2711.

[19] Linstead, Wang, Williams, and Errington, *J.*, 1937, 1139.

TABLE 3. *Ultraviolet and visible spectra of the benzylazulenes in hexane solution (wavelengths in* mμ *and* log ε*).*

Azulene		1-Benzyl-		2-Benzyl-		4-Benzyl-		5-Benzyl-		6-Benzyl-		Pentabenzyl	
697·5	2·25	729	2·03	677	2·11	671·5	2·21	712	2·13	687	2·16	702	2·27
665*i*	2·15	—	—	—	—	—	—	—	—	—	—	—	—
659	2·18	692sh	2·09	650	2·07	—	—	674	2·16	649	2·16	675*i*	2·29
631·5	2·51	657·5	2·43	614	2·45	613	2·58	644	2·46	622·5	2·47	633·5	2·67
—	—	—	—	605sh	2·39	—	—	—	—	—	—	—	—
603·5	2·47	627	2·43	590	2·37	586sh	2·62	612	2·44	595	2·45	611·5	2·65
579	2·51	601·5	2·50	570	2·48	570	2·64	589	2·47	571·5	2·50	586	2·73
557	2·42	579*i*	2·42	564sh	2·47	547*i*	2·55	567*i*	2·39	551s	2·42	—	—
537	2·33	557*i*	2·34	523	2·33	—	—	547*i*	2·30	532s	2·33	545*i*	2·58
519	2·20	535*i*	2·22	—	—	—	—	526*i*	2·16	512*i*	2·20	—	—
352	3·05	361	3·58	358	3·12	355	3·09	356	3·40	—	—	366	3·32
340	3·67	345	3·72	345	3·79	342·5	3·65	344	3·60	346	3·83	350	4·19
336·5	3·61	—	—	—	—	339	3·57	340	3·64	—	—	—	—
332·5	3·43	—	—	—	—	—	—	331·5	3·44	338	3·60	—	—
326	3·51	336	3·52	330	3·70	330	3·48	328	3·43	330	3·65	334	3·87
322	3·43	331	3·48	—	—	328	3·48	324·5	3·39	324	3·47	326*i*	3·64
315	3·29	322	3·30	318*i*	3·30	318*i*	3·27	318	3·22	319	3·41	320*i*	3·57
296	3·63	298	3·81	302	3·80	299	3·63	298	3·69	299·5	3·83	303	4·17
279	4·76	289	4·65	286	5·03	289·5	4·74	283s	4·66	—	—	—	—
274	4·79	285	4·78	—	—	279	4·72	278·5	4·70	285	4·95	290	5·19
269·5	4·79	279	4·80	276	5·05	275*i*	4·69	275*i*	4·63	279·5	4·91	283	5·13
236	4·30	237	4·31	237	4·30	239	4·54	242	4·21	237	4·27	240	4·59

sh indicates a shoulder, not a peak. *i* indicates a point of inflexion.

TABLE 4. *Infrared absorption maxima (cm.$^{-1}$) of the benzylazulenes.*

Azulene	1-Benzyl	2-Benzyl	4-Benzyl	5-Benzyl	6-Benzyl	Pentabenzyl
1388	1393	1390	1360	1393	1387	1380
—	—	1319	—	—	1300	—
1288	1291	1290	(1253w)	—	—	1277
1195s	—	1195s	1215	1208	1195	1195w
—	—	—	1120w	1177w	—	—
—	1072m	1073m	1067	1079w	1075	1072
1051	—	—	—	1046w	1050	—
—	1028	1030	1029	1027	1028	1027
—	—	—	—	1010	—	—
960	—	—	960	987	961w	983
942	943	943	—	948	—	—
—	920w	928	915w	922	927	—
895m	885w	891s	—	890w	—	885w
819m	—	827m	815	825w	842	—
—	—	—	—	810w	807	—
—	—	793vs	—	775s	795	780
763s	765	764s	757s	755s	747	—
719m	728s	725s	727	742	717	726
—	694	697	695	696	693	695

Apart from 5-benzylazulene, which was examined in paraffin paste, the spectra were measured in carbon disulphide solution.

The intense band at 693—697 cm.$^{-1}$ is due to the phenyl group; another phenyl adsorption band in the 730—770 cm.$^{-1}$ region overlaps with a broadish band of the azulene system.

oxidation of the resulting 9,10-dihydroxydecalin with lead tetra-acetate by Dev's method.[20] The diketone with sodium carbonate yielded bicyclo[5,3,0]dec-1(7)-en-2-one,[21] which on hydrogenation at atmospheric pressure with 5% palladised charcoal furnished decahydroazulen-4-one.[22] This ketone (7·3 g.) and benzaldehyde (6 g.) were refluxed for ½ hr. with potassium hydroxide (2 g.) in ethanol (30 ml.) and, after cooling and dilution with water, 5-*benzylidenedecahydroazulen*-4-*one* was isolated and crystallised from ethanol (m. p. 73°) (Found: C, 84·4; H, 8·8. $C_{17}H_{20}O$ requires C, 84·9; H, 8·4%). This (5·8 g.) was hydrogenated in ethanol (50 ml.) at atmospheric pressure with Adams catalyst and, after removal of the catalyst and the ethanol, the product was reduced with lithium aluminium hydride in the normal way. Chromatography of the product gave a colourless oily hydrocarbon (1·5 g.), probably 5-benzyldecahydroazulene, and then an oil (2·9 g.) having the infrared spectrum of an alcohol.

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[20] Dev, *J. Indian Chem. Soc.*, 1954, **31**, 1.

[21] Anderson and Nelson, *J. Amer. Chem. Soc.*, 1951, **73**, 232.

[22] Hückel and Schnitzpahn, *Annalen*, 1933, **505**, 274.

Crystallisation of the latter from light petroleum yielded colourless needles (0·4 g.), m. p. 79—80° of one of the stereoisomers of *5-benzyldecahydroazulen-4-ol* (Found: C, 83·5; H, 9·8. $C_{17}H_{24}O$ requires C, 83·5; H, 9·9%).

The alcohol (2·5 g.) was heated at 180° for 10 min. with potassium hydrogen sulphate (2·4 g.), then cooled, treated with water, and extracted with light petroleum. The dried petroleum solution on evaporation gave a brown oil (2·2 g.) which was distilled slowly, in a stream of nitrogen under reduced pressure, through a tube containing 5% palladised charcoal (0·4 g.) and asbestos fibre (0·4 g.) at 320—325°. A blue oil (1·6 g.) was obtained and this by chromatography gave 1·56 g. of a colourless oil and 0·035 g. of a blue oil. Crystallisation of the latter from light petroleum (b. p. $<30°$) gave 5-benzylazulene, m.p. 54·5—55·5°. Its *trinitrobenzene adduct* crystallised from ethanol as brown needles, m. p. 103—105° [Found (for 0·824 mg.): C, 63·2; H, 4·7. $C_{23}H_{17}O_6N_3$ requires C, 64·0; H, 4·0%).

APPENDIX

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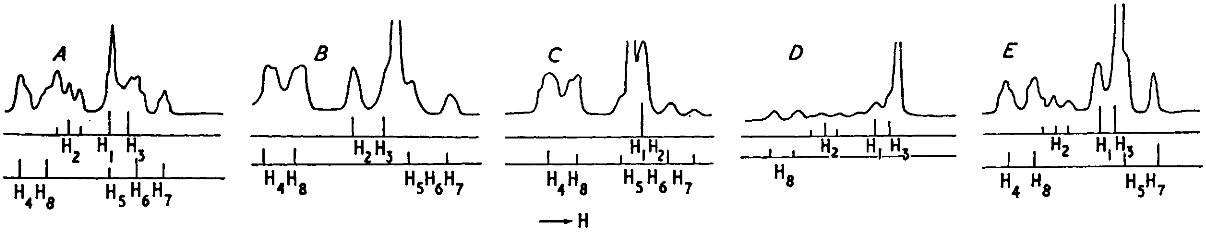
The following report relates to the radical-substitution product, m. p. 46—47°, of azulene, for which at that time only ultimate analysis was available.

The synthesis of authentic 2-benzylazulene was completed later, the identity of the two being then confirmed.

The proton magnetic resonance spectra of the radical product and of a number of benzylazulenes were investigated. The limited quantity of material made it necessary to use spherical samples. The solution of the material in chloroform or carbon disulphide was contained in a bubble in a gelatine matrix or in a 3 mm. glass sphere with capillary inlet.[23] The spectra were measured with a high-resolution apparatus, using a fixed frequency of 29·9200 Mc./sec. and a permanent magnet.[24] The work of Schneider, Bernstein, and Pople [25] on azulene was used in assigning the lines.

In addition to the azulene spectrum, the radical product gave lines for the CH_2 and C_6H_5 hydrogen atoms of the benzyl group. There was no evidence of a line for a CH_3 group which should give a resonance at higher applied fields. To check the sensitivity of the apparatus a sample containing 3 mg. of toluene was used for comparison. The only feature not present in the other benzylazulenes was a large peak on the high applied-field side of the phenyl peak. Its intensity was approximately equal to that of the peak due to the CH_2 group. The only situation in which a single peak of this intensity could be produced in an azulene is for two protons to have the same unsplit resonance frequency. This is the case with the hydrogens in the 1- and the 3-position of 2-benzylazulene. Further, the radical product gave the absorption spectrum expected for an unsubstituted 7-membered azulene ring. All these results are most consistent with the radical product's being 2-benzylazulene.

Proton magnetic resonance spectra of (*A*) *azulene and* (*B*) 1-, (*C*) 2- (*D*) 5-, *and* (*E*) 6-*benzylazulene.*



Spectra measured are reproduced herewith.

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[23] Higham and Richards, *Proc. Chem. Soc.*, 1959, 128.

[24] Leane, Richards, and Schaefer, *J. Sci. Instr.*, 1959, **36**, 230.

[25] Schneider, Bernstein, and Pople, *J. Amer. Chem. Soc.*, 1958, **80**, 3497.