456. *Polycyclic Systems. Part V.* A New Route to Azulenes.*

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A new, general route to hydroazulenes and azulenes is described (cf. *Nature*, 1951, **168**, 874). The synthesis of the parent compound starts with *cyclo*heptanone which is converted *via* *cyclo*heptenyl-lithium into 1-*cyclo*hept-1′-enylallyl alcohol (I; R = H). This is oxidised with manganese dioxide to the corresponding ketone (II; R = H) which is cyclised with formic and phosphoric acids to the octahydroketoazulene (III; R = H). Reduction of the keto-group with lithium aluminium hydride to the alcohol (IV; R = H), followed by dehydration, gives the hexahydroazulene (V; R = H), which is dehydrogenated to azulene (VI; R = H). 1-Methylazulene (VI; R = Me) and 1 : 2-benzazulene (XVI) have been synthesised in analogous ways. Each of the six steps leading to the azulene precursors (V) and (XV) afford yields of 60% or better, but the yields in the last step are poor, as in other methods.

Attempts to prepare precursors of the unknown non-benzenoid hydrocarbons pentalene and heptalene by similar procedures were unsuccessful.

SINCE the first total synthesis of azulene was achieved by Plattner and Pfau over fifteen years ago (*Helv. Chim. Acta*, 1937, **20**, 224), a considerable variety of synthetic routes to azulene and azulene derivatives have been devised (for reviews, see Pommer, *Angew. Chem.*, 1950, **62**, 281; Gordon, *Chem. Reviews*, 1952, **50**, 127). These methods, however, do not readily lend themselves to the preparation of azulenes on more than a small scale and this is no doubt the main reason why the reactions of this interesting non-benzenoid aromatic system have so far been comparatively little investigated.

The new route described here was suggested by the work reported in Part III (*loc. cit.*; cf. Baddeley, Taylor, and Pickles, *J.*, 1953, 124) on the formation of hydroindanones and hydrofluorenones by the cyclisation of alkenyl *cyclo*hexenyl ketones, now readily accessible by the use of lithium alkenyls. The extension of this approach to the *cyclo*heptenyl analogues provides a convenient method of preparing azulene precursors and is illustrated below by the synthesis of azulene, 1-methylazulene, and 1 : 2-benzazulene. In each case, the immediate azulene precursor, a hexahydroazulene, is obtained from *cyclo*heptanone in six steps, all affording yields of 60% or better and, up to this point, the new route appears to offer advantages over others. In common with earlier methods, however, the last step consists of a catalytic dehydrogenation in which the yield is low. The most promising way of overcoming this difficulty would appear to be the preparation of more highly unsaturated precursors, *i.e.*, tetrahydro- or dihydro-azulenes which may be expected to be dehydrogenated more readily. Work on these lines is in progress in these laboratories.

Some unsuccessful attempts to apply procedures similar to those developed for the synthesis of hexahydroazulenes to the preparation of pentalene and heptalene precursors are also recorded.

Synthesis of Azulene and 1-*Methylazulene*.—The conversion of *cyclo*heptanone into *cyclo*heptenyl-lithium, and the reactions of the latter with acraldehyde and crotonaldehyde to give the alcohols (I; R = H and Me) have already been described (Braude and Forbes, preceding paper). Oxidation with manganese dioxide in light petroleum suspension then gave excellent yields of the ketones (II; R = H and Me), characterised by their 2 : 4-dinitrophenylhydrazones. It has recently been found (Braude and E. A. Evans, to be published) that an alternative and, in some respects, more convenient method of oxidation consists in the use of the chromic oxide–pyridine reagent recently described by Sarett and his co-workers (*J. Amer. Chem. Soc.*, 1952, **74**, 4974; 1953, **75**, 422). The ketone (II; R = Me) was also prepared more directly, though in lower yield, by reaction of *cyclo*heptenyl-lithium with lithium crotonate (cf. Braude and Coles, *J.*, 1950, 2012).

Treatment of the dialkenyl ketones with a mixture of phosphoric and formic acids at 90° (Nazarov and Pinkina, *Bull. Acad. Sci. U.R.S.S., Cl. Sci. chim.*, 1946, **633**; 1947, **205**;

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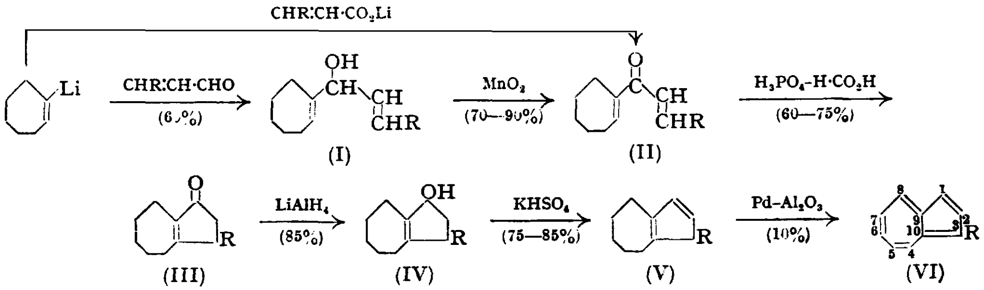
* Part III, *J.*, 1952, 1430. A paper by Braude and Fawcett, *J.*, 1952, 1528, is regarded as Part IV.

Nazarov, *Uspekhi Khim.*, **1948**, **18**, 377; Part III, *loc. cit.*) gave the octahydro-1-keto-azulenes (III; R = H and Me), the structures of which follow from their ultra-violet light absorptions (see Table) and by analogy with their tetrahydroindanone analogues (Part III, *loc. cit.*). The cyclic ketones were characterised by their 2 : 4-dinitrophenylhydrazones, and the lower homologue (III; R = H) also furnished a semicarbazone of m. p. 238°, in good agreement with the values recorded by Plattner and Büchi (*Helv. Chim. Acta*, **1946**, **29**, 1608) and Cook, Philip, and Somerville (*J.*, **1948**, 164) who prepared the ketone by different routes.



Reduction of the ketones (III) with lithium aluminium hydride afforded the octahydro-hydroxyazulenes (IV), characterised by their 3 : 5-dinitrobenzoates; direct cyclisation of the alcohols (I) is not possible because under acid conditions they preferentially undergo anionotropic rearrangement to the conjugated isomers (Braude and Forbes, *loc. cit.*). Dehydration of (IV) with potassium hydrogen sulphate or phthalic anhydride gave the dienes (V), the constitutions of which are confirmed by their ultra-violet light absorptions (see Table), typical of *cyclo*pentadienes. The physical properties of the higher homologue (V; R = Me) were in good agreement with those recorded by Plattner and Büchi (*loc. cit.*).

The final dehydrogenation of the dienes (V) to azulene and 1-methylazulene (VI; R = H and Me) was effected catalytically; the best results were obtained with palladium supported on alumina (cf. Anderson and Nelson, *J. Amer. Chem. Soc.*, 1951, **73**, 232), but the yields did not exceed 10%. This accords with the experience of other investigators, who reported yields of the same order even when highly elaborate techniques were employed (Gordon, *loc. cit.*; Günthard, Süess, Marti, Fürst, and Plattner, *Helv. Chim. Acta*, 1951, **34**, 959). Azulene was purified through the *s*-trinitrobenzene adduct and identified by its melting point and light absorption. 1-Methylazulene (which is a liquid at room temperature) was similarly purified, and was identified by its light absorption and by the mixed melting point of the *s*-trinitrobenzene adduct with a sample kindly provided by Professor Pl. A. Plattner.

Synthesis of 1 : 2-*Benzazulene.*—The extension of the route just described to the synthesis of 4 : 5- or 5 : 6-benzazulenes by starting with the appropriate benzosuberone involves no new principles, but the simplest analogous synthesis of 1 : 2-benzazulene requires the cyclisation of *cyclo*heptenyl phenyl ketone (XI). Since the cyclisation of substituted phenyl vinyl ketones, as distinct from that of substituted divinyl ketones, has previously been accomplished only under rather drastic conditions (cf. Mayer and Müller, *Ber.*, 1927, **60**, 2278), some experiments in corresponding six-membered ring series were carried out first. *cyclo*Hexenyl phenyl ketone (VII) was readily obtained from the alcohol (Braude and Coles, *J.*, **1950**, 2014) by oxidation with manganese dioxide and on treatment with phosphoric and formic acids under the conditions used previously, it was smoothly converted into the hexahydrofluorenone (VIII) which was a liquid at room temperature and was characterised by a 2 : 4-dinitrophenylhydrazone, m. p. 158°. This hexahydrofluorenone is different from that of m. p. 42°, obtained by Cook and Hewett (*J.*, **1936**, 62) by the Friedel–Crafts cyclisation of 2-phenylhexahydrobenzoic acid and now characterised by a 2 : 4-dinitrophenylhydrazone, m. p. 190°, prepared directly from the semicarbazone.*

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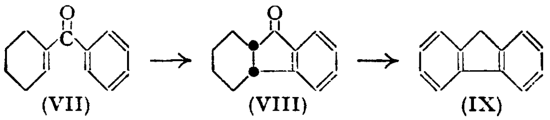
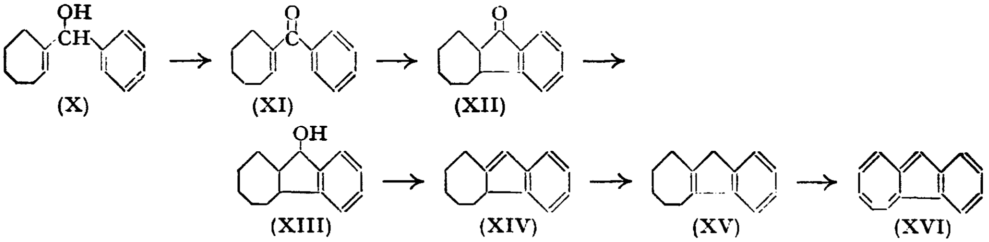
* We are indebted to Professor J. W. Cook, F.R.S., for drawing our attention to this point and for providing a generous sample of the semicarbazone.

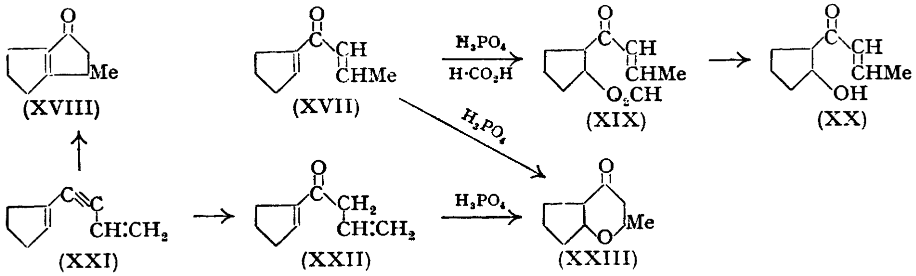
The two ketones are, in all probability, stereoisomers; the ketone obtained here would be expected, by analogy with earlier work (Braude and Coles, *loc. cit.*), to have a *cis*-fusion of the two alicyclic rings, whereas Cook and Hewett's ketone would be expected to have a *trans*-fusion, since the 1-phenyl*cyclo*hexanecarboxylic acid from which it was prepared was made by the reduction of *o*-phenylbenzoic acid with sodium and amyl alcohol. Catalytic dehydrogenation of (VIII) with palladium–charcoal at 330° gave fluorene, dehydrogenation being accompanied by reduction of the keto-group as observed in the case of decahydrofluorenone (Part III, *loc. cit.*).



No difficulty was experienced in carrying out analogous reactions with the *cyclo*heptene derivatives to give the octahydroketoazulene (XII). Reduction of the latter, followed by dehydration as before, afforded a hexahydro-1 : 2-benzazulene; this may have the structure (XV) (in which the double bond has moved away from the bridgehead position) rather than (XIV) since the location of the ultra-violet absorption maximum corresponds more closely to that expected for a 2 : 3- than a 1 : 2-dialkylated indene (see Table). Dehydrogenation with palladium–alumina gave 1 : 2-benzazulene (XVI) which was identified by its melting point and that of its *s*-trinitrobenzene adduct, and by its light absorption, all in good agreement with the values previously recorded (Plattner, Fürst, Chopin, and Winteler, *Helv. Chim. Acta*, 1948, **31**, 501; Nunn and Rapson, *J.*, 1949, 825).

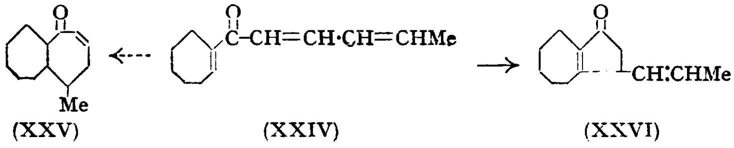


Attempted Syntheses of Pentalene and Heptalene Precursors.—Much interest has been shown in recent years in the possible " aromatic " properties of the unknown pentalene and heptalene, which resemble azulene in containing two fused odd-membered rings, and we attempted to apply procedures similar to those described above to the synthesis of suitable precursors. It was hoped to obtain the hexahydroketopentalene (XVIII) by the cyclisation of the ketone (XVII) prepared by oxidation of the corresponding alcohol (Braude and Forbes, *J.*, 1951, 1755). However, treatment of the ketone (XVII) with a mixture of phosphoric and formic acids gave instead a formate, probably (XIX), together with some of the corresponding alcohol (XX). The formate is evidently produced by the addition of formic acid to the *cyclo*pentenyl group, and the alcohol by subsequent hydrolysis. The addition of formic, as well as other, acids to *cyclo*alkenes has been observed in other cases (cf. Tilichenko, *J. Gen. Chem. Russia*, 1950, **20**, 2152; Morin and Bearse, *Ind. Eng. Chem.*, 1951, **43**, 1596); it appears to occur particularly readily in the *cyclo*pentenyl series (cf. Bergmann and Japhe, *J. Amer. Chem. Soc.*, 1947, **69**, 1826). The formate was characterised by a semicarbazone, and the alcohol by a 2 : 4-dinitrophenylhydrazone; the ester is easily hydrolysed under acid conditions and also gives the derivative of the alcohol on treatment with Brady's reagent. Both the formate and the alcohol, as well as their derivatives, exhibit ultra-violet light absorption characteristic of the presence of an αβ-ethylenic ketone system. When the cyclisation of the ketone (XVII) was attempted with phosphoric acid alone at room temperature, the product was isomeric with the alcohol (XX) but showed no intense absorption in the 2400-Å region and evolved little methane with methylmagnesium iodide in ether. This appears to be the tetrahydropyrone (XXIII), previously obtained by Nazarov and Burmistrova (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1947, 51) by the treatment of allyl *cyclo*pentenyl ketone (XXII) with phosphoric acid; it gives a semicarbazone which shows ultra-violet absorption ($\lambda_{max.}$ 2250 Å) corresponding to the derivative of a saturated ketone. It is surprising that the Russian authors were apparently able to obtain the desired bicyclic ketone (XVIII) by the direct treatment of 4-*cyclo*pent-1′-enylbut-3-yn-1-ene (XXI) with phosphoric acid, since the cyclisation of the acetylenic hydrocarbon would be expected to proceed by way of the allyl ketone (XXII).



In the meantime, other routes to unsaturated pentalene precursors have been developed and it has been shown that their conversion into pentalene cannot be effected by present methods (Blood and Linstead, *J.*, 1952, 2255; Roberts and Gorham, *J. Amer. Chem. Soc.*, 1952, **74**, 2278; Vogel, *Ber.*, 1952, **85**, 25); for this reason, the present approach was not pursued.

The envisaged approach to the heptalene ring system involved cyclisation of *cyclo*heptenyl pentadienyl ketone (XXIV), a vinylogue of (II), to (XXV), although it was realised that the alternate mode of cyclisation with the formation of a five-membered ring to give (XXVI) was more likely. Treatment of (XXIV) with phosphoric acid in the cold gave mainly unchanged material, but treatment with phosphoric and formic acids at 90° gave a cyclised product which was characterised by a 2 : 4-dinitrophenylhydrazone and exhibited ultra-violet light absorption (see Table) compatible with the structure (XXV); the location of the main maximum (2510 Å) is that expected for a dienone system C:C·CO·C:C (as in II) rather than an enone system C:C·C:O (as in III). Nevertheless the cyclised product must be the hydroazulene derivative (XXVI) and not the hydroheptalene derivative (XXV), for ozonisation gave a quantitative yield of acetaldehyde, showing the presence of a propenyl group.



Light Absorption Properties.—Ultra-violet light absorption data for the various compounds described are collected in the Table. The spectral properties of the conjugated unsaturated ketones of the *cyclo*heptenyl and *cyclo*pentenyl series are very similar to those of the *cyclo*hexenyl series. On the other hand, the maxima of the di-alicyclic unsaturated ketones lie at markedly longer wave-lengths in the hydroazulene than in the hydroindanone series. A particularly marked bathochromic displacement occurs in the propenyl derivative (XXVI); this is presumably due to interaction between the unconjugated propenyl group and the enone system (cf. Braude, *J.*, 1949, 1902). The absorption of the dicyclic dienes (V) is similar to that of *cyclo*pentadiene, but displaced to longer wave-lengths by *ca.* 80 Å, as expected from the presence of two alkyl substituents.

Ultra-violet light absorption (ethanol solutions).

Acyclic ketones.

	$\lambda_{max.}$, Å	ε	$\lambda_{max.}$, Å	ε
(II; R = H)	2510 2580	9,000	*	*
(II; R = Me)	2510	12,500	3280	80
*cyclo*Hexenyl propenyl ketone [1] ...	2570	14,500	3280	80
(XVII)	2510 2570	10,000	3230	75
(VII)	2470	12,000	*	*
(XI)	2490	11,500	2800	1900
			3280	120
(XXIV)	2810 2910	9,500	—	—
	3020	8,500	—	—

Hydroindanones and hydroketoazulenes.

	$\lambda_{max.}$, Å	ε	$\lambda_{max.}$, Å	ε
(III; R = H)	2410	12,500	2910	85
(III; R = Me)	2440	9,500	3000	70
(XXVI)	2470	9,500	*	*
	2510	10,000	—	—
Tetrahydroindanone [1]	2370	12,500	3020	50
(VIII)	2480	12,300	2800	1300
(XII)	2480	9,600	2800	2400

Cyclic dienes and indenes.

	$\lambda_{max.}$, Å	ε	$\lambda_{max.}$, Å	ε
*cyclo*Pentadiene [2] ...	2390	3,400	—	—
(V; R = H)	2470	4,500	—	—
(V; R = Me)	2460	3,500	—	—
3-Methylindene [3] ...	2530	8,000	—	—
(XV)	2580	11,000	—	—
	2650	12,000	—	—

* Not determined.

[1] Part III, *J.*, 1952, 1430. [2] Plattner and Büchi, *Helv. Chim. Acta*, 1946, **29**, 1608. [3] Ramart-Lucas and Hoch, *Bull. Soc. chim.*, 1938, **5**, 848.

EXPERIMENTAL

Ultra-violet light absorptions were determined photographically on a Hilger-Spekker instrument and are only quoted when not included in the Table above. The light absorptions of azulenes in the visible region were determined photoelectrically on a Unicam SP 500 instrument. All 2 : 4-dinitrophenylhydrazones were chromatographed on alumina in benzene–chloroform before crystallisation.

Azulene

cyclo*Hept-*1*-enyl Vinyl Ketone* (II; R = H).—A solution of 1-*cyclo*hept-1′-enylallyl alcohol (13 g.; Braude and Forbes, preceding paper) in light petroleum (b. p. 40—60°; 1300 ml.; sodium-dried) was vigorously shaken with active manganese dioxide (130 g.; vacuum-dried) under nitrogen for 2 days. After filtration and washing of the manganese dioxide with more petroleum, the combined filtrates were concentrated under reduced pressure and fractionated, giving cyclo*hept-*1*-enyl vinyl ketone* (9 g., 70%), b. p. 61°/0·5 mm., n_D^{21} 1·5138 (Found : C, 80·4; H, 9·7. $C_{10}H_{14}O$ requires C, 80·0; H, 9·4%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in fine red needles, m. p. 198° (Found: C, 58·3; H, 5·7; N, 16·7. $C_{16}H_{18}O_4N_4$ requires C, 58·2; H, 5·5; N, 17·0%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3860 Å, ε 29,000.

Δ^9-*Octahydro-*1*-ketoazulene* (III; R = H).—The above ketone (12 g.) was added cautiously to an ice-cold mixture of phosphoric acid (90%; 5 g.) and formic acid (98%; 13·5 g.). The addition is exothermic and the mixture gradually darkens. After being allowed to attain room temperature overnight, the solution was kept at 90° for 6 hr., then cooled, diluted with ice-water (200 ml.), and extracted with ether. The ethereal extracts were washed with sodium carbonate solution and with water, dried (Na_2SO_4) and fractionated, giving Δ^9-octahydro-1-ketoazulene (7·2 g., 60%) as a colourless liquid, b. p. 80°/0·8 mm., n_D^{21} 1·5237 (Cook *et al.*, *J.*, 1948, 164, give b. p. 58—60°/0·1 mm., $n_D^{11\cdot5}$ 1·5275). The semicarbazone crystallised from methanol in plates, m. p. 238° (Cook *et al.*, *loc. cit.*, give m. p. 235—236°; Plattner and Büchi, *Helv. Chim. Acta*, 1946, **29**, 1608, give m. p. 238°). Light absorption in EtOH : $\lambda_{max.}$ 2640 Å, ε 23,200; $\lambda_{infl.}$ 2580 and 2700 Å., ε = 21,700. The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in dark-red prisms, m. p. 226° (Found: C, 58·2; H, 5·6; N, 16·7. $C_{16}H_{18}O_4N_4$ requires C, 58·2; H, 5·5; N, 17·0%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3960 Å, ε 29,500.

Attempted Cyclisation of 1-cyclo*Hept-*1′*-enylallyl Alcohol* [with E. A. EVANS].—The alcohol (6 g.) was dissolved in a mixture of phosphoric acid (3 g.) and formic acid (7 g.) at 0° and then kept first at room temperature and then at 80° for 1 hr. under nitrogen. Dilution with water and isolation of the products with ether as above gave a mixture (4 g.) which showed $\lambda_{max.}$ 2370 Å ($E_{1\,cm.}^{1\%}$ 900) and 2700 Å ($E_{1\,cm.}^{1\%}$ 450) and consisted mainly of 2-allylidene*cyclo*heptanol (Braude and Forbes, *loc. cit.*) and, probably, 2-allylidene*cyclo*heptene. Oxidation of the products with manganese dioxide as above afforded 2-allylidene*cyclo*heptanone which gave no colour with Schiff's reagent and formed a 2 : 4-*dinitrophenylhydrazone* (dark red needles from ethyl acetate), m. p. 196°, $\lambda_{max.}$ 3000 Å (ε 13,000) and 3980 Å (ε 30,000) in $CHCl_3$ (Found : N, 17·0. $C_{16}H_{18}O_4N_4$ requires N, 17·0%). This derivative appears to be a stereoisomer of the 2 : 4-dinitrophenylhydrazone, m. p. 158°, described previously; it gave a marked m. p. depression on admixture with the derivative, m. p. 198°, of *cyclo*heptenyl vinyl ketone.

Δ^9-*Octahydro*-1-*hydroxyazulene* (IV; R = H).—Lithium aluminium hydride (7 g.) in ether (300 ml.) was slowly added to a stirred solution of the above octahydroketoazulene (10 g.) in ether (40 ml.) at 0°. After 30 min., excess of 2N-sulphuric acid was added, and the ethereal layer was separated, washed with aqueous sodium carbonate and water, dried (Na_2SO_4), and fractionated, giving the *alcohol* (8·5 g., 85%), b. p. 64°/0·1 mm., n_D^{20} 1·5132 (Found : C, 79·1; H, 10·9. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). The 3 : 5-*dinitrobenzoate* crystallised from ethanol in needles, m. p. 164° (Found : C, 59·0; H, 5·2; N, 8·3. $C_{17}H_{18}O_6N_2$ requires C, 59·0; H, 5·2; N, 8·1%).

1 : 4 : 5 : 6 : 7 : 8-*Hexahydroazulene* (V; R = H).—A mixture of the above octahydrohydroxyazulene (6 g.) and finely powdered potassium hydrogen sulphate (0·6 g.) was rapidly distilled at *ca.* 100° (bath)/*ca.* 0·5 mm. Refractionation of the product gave 1 : 4 : 5 : 6 : 7 : 8-*hexahydroazulene* (4 g., 75%), b. p. 56°/0·5 mm., n_D^{21} 1·5129 (Found : C, 89·5; H, 10·8. $C_{10}H_{14}$ requires C, 89·5; H, 10·5%).

Azulene (VI; R = H).—The final dehydrogenation was carried out in an apparatus similar to that described by Nunn and Rapson (*J.*, 1949, 825) but simplified by omission of the gas-burette, and replacement of the three-way tap by a two-way capillary tap carrying a small cylindrical funnel. The rate of flow of liquid into the catalyst chamber could be controlled quite satisfactorily merely by adjustment of the tap. The catalyst chamber was packed with 1% palladium–alumina and asbestos wool, and the copper heating block was maintained at 320° by means of a Bunsen burner. The hexahydroazulene was passed through the apparatus, evacuated to *ca.* 20 mm., at a rate of *ca.* 1 g./hr. The deep blue products which collected in the receiver were treated with a boiling solution of *s*-trinitrobenzene in ethanol. On cooling, the azulene–trinitrobenzene adduct separated in 3—8% yield; it formed brown needles, m. p. 163°, on recrystallisation from ethanol (Plattner and Pfau, *Helv. Chim. Acta*, 1937, **20**, 224, give m. p. 167°). On passage of a solution of the adduct in hexane through alumina, azulene was regenerated and crystallised in blue needles, m. p. 93° (Plattner and Pfau, *loc. cit.*, give m. p. 99°). A solution of the hydrocarbon in *n*-hexane showed light absorption maxima at 5320, 5565, 5800, 6040, 6330, 6600, and 6980 Å (Plattner and Heilbronner, *Helv. Chim. Acta*, 1947, **30**, 910, give 5410, 5580, 5800, 6030, 6320, 6610, and 6970 Å).

The attempted liquid-phase dehydrogenation of hexahydroazulene, as described below for the 1-methyl homologue, gave only negligible yields of azulene.

1-*Methylazulene*

cyclo*Hept*-1-*enyl Propenyl Ketone* (II; R = Me).—(*a*) A solution of 1-*cyclo*hept-1′-enylbut-2-en-1-ol (5·6 g.; Braude and Forbes, *loc. cit.*) in light petroleum (b. p. 40—60°; 500 ml.) was shaken with active manganese dioxide (60 g.) under nitrogen for 3 days. The product was worked up as above, giving cyclo*hept*-1-*enyl propenyl ketone* (5 g., 90%), b. p. 84°/0·4 mm., n_D^{25} 1·5166 (Found : C, 80·6; H, 10·1. $C_{11}H_{16}O$ requires C, 80·4; H, 9·8%). The 2 : 4-*dinitrophenylhydrazone* crystallised from methanol in red needles, m. p. 118° (Found : C, 59·5; H, 6·1; N, 16·0. $C_{17}H_{20}O_4N_4$ requires C, 59·3; H, 5·9; N, 16·3%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3900 Å, ε 26,500. A small quantity of a second form of the hydrazone, m. p. 129°, was also obtained; it showed identical ultra-violet light absorption.

(*b*) A solution of *cyclo*heptenyl-lithium (from Li, 6·9 g.; Braude and Forbes, *loc. cit.*) in ether (1 l.) was slowly added to a stirred suspension of anhydrous lithium crotonate (45 g.) in ether (100 ml.). After 24 hr. at room temperature, the mixture was cooled in methanol–carbon dioxide, and saturated aqueous ammonium chloride (500 ml.) was added. The ethereal layer was separated, dried (Na_2SO_4), and fractionated, giving *cyclo*heptenyl propenyl ketone (10 g., 14%), b. p. 87°/0·5 mm., identified by the 2 : 4-dinitrophenylhydrazone, m. p. 117°, undepressed on admixture with the specimen described above. The yield could probably be raised considerably by adjusting the conditions.

In another experiment, the formation of *cyclo*heptenyl-lithium from 1-chloro*cyclo*heptene and lithium was allowed to proceed in the presence of lithium crotonate. The consumption of the metal was incomplete, however, and working up as above gave only a 10% yield of ketone, together with much unchanged 1-chloro*cyclo*heptene.

Δ^9-*Octahydro*-1-*keto*-3-*methylazulene* (III; R = Me).—*cyclo*Heptenyl propenyl ketone (6 g.) was treated with a mixture of phosphoric (2·5 g.) and formic (6·5 g.) acids as described above for the lower homologue. Isolation of the product as before gave Δ^9-*octahydro*-1-*keto*-3-*methylazulene* (4·5 g., 75%) as a colourless liquid, b. p. 77°/0·4 mm., n_D^{23} 1·5118 (Found: C, 80·4; H, 9·8. $C_{11}H_{16}O$ requires C, 80·4; H, 9·8%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in red needles, m. p. 236° (Found: C, 59·5; H, 6·1; N, 16·0. $C_{17}H_{20}O_4N_4$ requires C, 59·3; H, 5·9; N, 16·3%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3940 Å, ε 26,000.

Δ^9-*Octahydro*-1-*hydroxy*-3-*methylazulene* (IV; R = Me).—The above ketone (3 g.) was reduced with lithium aluminium hydride (1·5 g.) in ether (80 ml.) at 0°. Isolation of the product as before afforded Δ^9-*octahydro*-1-*hydroxy*-3-*methylazulene* (2·5 g., 83%), b. p. 80°/0·4 mm., $n_D^{21·5}$ 1·5058 (Found: C, 79·5; H, 10·9. $C_{11}H_{18}O$ requires C, 79·5; H, 10·8%). Light absorption in EtOH: ε < 200 in the region 2200—4000 Å. The 3 : 5-*dinitrobenzoate* crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 87° (Found: C, 60·0; H, 5·7; N, 7·9. $C_{18}H_{20}O_6N_2$ requires C, 60·0; H, 5·6; N, 7·8%).

1 : 4 : 5 : 6 : 7 : 8-*Hexahydro*-1-*methylazulene* (V; R = Me).—A mixture of Δ^9-octahydro-1-hydroxy-3-methylazulene (8 g.) and potassium hydrogen sulphate (1 g.) was rapidly distilled at *ca.* 0·5 mm. Fractionation of the product gave the hydrocarbon (6 g., 84%), b. p. 66°/0·5 mm., $n_D^{19·5}$ 1·5124 (Plattner and Büchi, *Helv. Chim. Acta*, 1946, **29**, 1608, give b. p. 91—94°/13 mm.).

1-*Methylazulene* (VI; R = Me).—Hexahydro-1-methylazulene (1 g.) and 10% palladium–charcoal (1 g.; Linstead and Thomas, *J.*, 1940, 1130) were placed in a small glass bulb attached to the bottom end of a 30-cm. upright "Pyrex" glass tube, and the bulb was immersed in Wood's metal at 320—340°. A stream of nitrogen was passed through the bulb by means of a capillary tube. The mixture rapidly became dark blue and no further deepening was noticeable after 2 hr. After cooling, the products were extracted with boiling ethanol, and *s*-trinitrobenzene was added. On cooling, the 1-methylazulene–trinitrobenzene adduct (100—150 mg.) crystallised in nearly black prisms, m. p. 155°, undepressed on admixture with Plattner and Büchi's sample (m. p. 154°) (*Helv. Chim. Acta*, 1946, **29**, 1608). Chromatography of the adduct on alumina in hexane regenerated 1-methylazulene as a deep blue liquid. A solution in hexane exhibited light absorption maxima at 5860, 6070, 6330, and 6650 Å (Plattner and Heilbronner, *loc. cit.*, give 5860, 6080, 6350, and 6640 Å).

1 : 2-*Benzazulene*

cyclo*Heptenyl Phenyl Ketone* (XI).—A solution of α-*cyclo*hept-1′-enylbenzyl alcohol (40 g.; Braude and Forbes, *loc. cit.*) in light petroleum (b. p. 40—60°; 2 l.) was shaken with active manganese dioxide (180 g.) for 4 days under nitrogen. Isolation of the products as previously gave cyclo*hept*-1-*enyl phenyl ketone* (25 g., 60%), b. p. 95°/5 × 10^{-4} mm., n_D^{22} 1·5591 (Found: C, 83·7; H, 8·4. $C_{14}H_{16}O$ requires C, 84·0; H, 8·1%). The 2 : 4-*dinitrophenylhydrazone*, which was precipitated only on prolonged warming with Brady's reagent, crystallised from ethyl acetate–methanol in red prisms, m. p. 133—134° (Found: C, 63·1; H, 5·5; N, 15·0. $C_{20}H_{20}O_4N_4$ requires C, 63·1; H, 5·3; N, 14·7%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3900 Å, ε 31,000.

Octahydro-3-*keto*-1 : 2-*benzazulene* (XII).—*cyclo*Heptenyl phenyl ketone (18 g.) was treated with phosphoric (5 g.) and formic (20 g.) acids, under the conditions previously described. Fractionation of the products afforded *octahydro*-3-*keto*-1 : 2-*benzazulene* (14 g., 75%), b. p. 102°/3 × 10^{-3} mm., n_D^{25} 1·5668 (Found: C, 84·1; H, 8·3. $C_{14}H_{16}O$ requires C, 84·0; H, 8·1%). The 2 : 4-*dinitrophenylhydrazone* was precipitated slowly on treatment with Brady's reagent and crystallised from ethyl acetate in fine red needles, m. p. 206° (Found: C, 63·0; H, 5·4; N, 14·2. $C_{20}H_{20}O_4N_4$ requires C, 63·1; H, 5·3; N, 14·7%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3900 Å, ε 26,000.

Octahydro-3-*hydroxy*-1 : 2-*benzazulene* (XIII).—Octahydro-3-keto-1 : 2-benzazulene (14 g.) in dry ether (80 ml.) was cooled to 0° and lithium aluminium hydride (3 g.) in ether was slowly added. Stirring was continued for a further 30 min. and excess of dilute sulphuric acid was then added. The ethereal layer was separated, washed with aqueous sodium carbonate and water, and dried (Na_2SO_4). Removal of the solvent under reduced pressure gave solid *octahydro*-3-*hydroxy*-1 : 2-*benzazulene* (12 g., 85%), which crystallised from light petroleum (b. p. 40—60°) in colourless, monoclinic prisms, m. p. 121° (Found: C, 82·9; H, 9·0. $C_{14}H_{18}O$ requires C, 83·1; H, 9·0%). Light absorption in EtOH: $\lambda_{max.}$ 2650 (ε 750) and 2710 Å (ε 900).

1 : 4 : 5 : 6 : 7 : 8-*Hexahydro*-1 : 2-*benzazulene* (XV).—Octahydro-3-hydroxy-1 : 2-benzazulene (3 g.) and finely powdered potassium hydrogen sulphate (0·3 g.) were thoroughly mixed and rapidly distilled at 100—150° (bath)/10^{-3} mm. Fractionation of the product afforded the

hexahydro-1 : 2-*benzazulene* (2·5 g., 90%) as a colourless liquid, b. p. 86°/10^{-3} mm., n_{D}^{21} 1·5801 (Found : C, 91·1; H, 8·9. $C_{14}H_{16}$ requires C, 91·25; H, 8·75%).

1 : 2-*Benzazulene* (XVI).—Hexahydro-1 : 2-benzazulene was passed over palladium–alumina at 320—340°/20 mm. at a rate of *ca.* 1 g./hr. in the apparatus described above. The deep blue products were taken up in light petroleum (A) (b. p. 40—60°) and extracted with 90% phosphoric acid at 0°. The deep yellow acid solution was washed with light petroleum and diluted with ice-water. The aqueous solution was extracted with ether, and the ethereal layer was washed with aqueous sodium carbonate and water, dried (Na_2SO_4), and evaporated, giving green plates of 1 : 2-benzazulene, m. p. 170°, in 3—6% yield (Plattner, Fürst, Chopin, and Winteler, *Helv. Chim. Acta*, 1948, **31**, 501, give m. p. 176°). A solution in *n*-hexane exhibited absorption maxima at 5160, 5650, 6150, 6600, 6820, and 7900 Å. The *s*-trinitrobenzene adduct crystallised from ethanol in brown-black needles, m. p. 153° (Plattner *et al.*, *loc. cit.*, give m. p. 155°). Evaporation of the petroleum solution (A) gave largely unchanged hexahydro-1 : 2-benzazulene which could be re-cycled.

1 : 2-Benzazulene was also obtained in similar yield on passing octahydro-3-hydroxyazulene over palladium–alumina under identical conditions. On the other hand, attempts to effect the dehydration and dehydrogenation in one step by heating with iodine (cf. Treibs, *Annalen*, 1952, **576**, 110) were unsuccessful.

Fluorene

cyclo*Hexenyl Phenyl Ketone* (VII).—A solution of α-*cyclo*hex-1′-enylbenzyl alcohol (2 g.; Braude and Coles, *J.*, 1950, 2014) in light petroleum (b. p. 40—60°; 200 ml.) was shaken with active manganese dioxide (20 g.) for 3 days under nitrogen. Isolation of the product as previously described gave cyclo*hexenyl phenyl ketone* (1·5 g., 75%) as a colourless liquid, b. p. 86°/5 × 10^{-4} mm., n_{D}^{23} 1·5660, which solidified and crystallised from *n*-pentane in prisms, m. p. 38° (Found: C, 84·1; H, 7·6. $C_{13}H_{14}O$ requires C, 83·8; H, 7·6%). The 2 : 4-*dinitrophenylhydrazone*, which was precipitated only on prolonged warming with Brady's reagent, crystallised from ethyl acetate in orange plates, m. p. 168° (Found : C, 62·4; H, 5·1; N, 15·5. $C_{19}H_{18}O_4N_4$ requires C, 62·3; H, 5·0; N, 15·3%). Light absorption in $CHCl_3$: $\lambda_{\max.}$ 3870 Å, ε 28,000.

1 : 2 : 3 : 4 : 10 : 11-*Hexahydrofluorenone* (VIII).—*cyclo*Hexenyl phenyl ketone (1 g.) was treated with phosphoric (2 g.) and formic (7 g.) acids under the conditions described previously. Isolation and fractionation of the products gave 1 : 2 : 3 : 4 : (cis ?)10 : 11-*hexahydrofluorenone* (0·8 g., 80%) as a colourless liquid, b. p. 86°/2 × 10^{-3} mm., n_{D}^{25} 1·5631 (Found : C, 83·5; H, 7·8. $C_{13}H_{14}O$ requires C, 83·8; H, 7·6%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate–methanol in orange-red plates, m. p. 158° (Found: C, 62·0; H, 5·0; N, 15·3. $C_{19}H_{18}O_4N_4$ requires C, 62·3; H, 5·0; N, 15·3%). Light absorption in $CHCl_3$: $\lambda_{\max.}$ 3900 Å, ε 30,000.

Treatment of the hexahydrofluorenone semicarbazone, m. p. 212°, described by Cook and Hewett (*J.*, 1936, 71), with 2 : 4-dinitrophenylhydrazine in ethanol–sulphuric acid gave 1 : 2 : 3 : 4 : (trans ?)10 : 11-*hexahydrofluorenone* 2 : 4-*dinitrophenylhydrazone* which crystallised from ethyl acetate in needles, m. p. 190—191° (Found : C, 61·9; H, 4·8; N, 15·6%). Light absorption in $CHCl_3$: $\lambda_{\max.}$ 3910 Å, ε 28,000.

Fluorene (IX).—A mixture of hexahydrofluorenone (1 g.) and 25% palladium–charcoal (0·1 g.) was heated at 300° in a stream of nitrogen for 20 hr. The crude product did not give a precipitate with Brady's reagent. Extraction with boiling light petroleum (b. p. 60—80°) gave fluorene (0·4 g.) which after one recrystallisation had m. p. 110°, undepressed on admixture with an authentic specimen.

Attempted Syntheses of Pentalene and Heptalene Precursors

cyclo*Pent*-1-*enyl Propenyl Ketone* (XVII).—A solution of 1-*cyclo*pent-1′-enylbut-2-en-1-ol (30 g.; Braude and Forbes, *J.*, 1951, 1755) in light petroleum (b. p. 40—60°; 2 l.) was shaken with active manganese dioxide (230 g.) for 3 days under nitrogen. Isolation of the product in the usual manner gave cyclo*pent*-1-*enyl propenyl ketone* (18 g., 60%) as a colourless liquid, b. p. 66°/0·6 mm., n_{D}^{21} 1·5137, which solidified at 0° and crystallised from pentane in plates, m. p. 34° (Found : C, 78·9; H, 8·6. $C_9H_{12}O$ requires C, 79·35; H, 8·9%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in dark-red needles, m. p. 152° (Found : N, 17·6. $C_{15}H_{16}O_4N_4$ requires N, 17·7%). Light absorption in $CHCl_3$: $\lambda_{\max.}$ 3900 Å, ε 28,000.

Attempted Cyclisation of cyclo*Pentenyl Propenyl Ketone*.—(*a*) The foregoing ketone (16 g.) was treated with phosphoric (7·5 g.) and formic acid (20 g.) for 6 hr. at 90°. Isolation of the products as previously described and fractionation afforded (i) *2-hydroxy*cyclo*pentyl propenyl ketone* (XX) (7 g.), b. p. 40°/0·1 mm., n_D^{20} 1·4912, $\lambda_{max.}$ (in EtOH) 2310 and 3240 Å, ε 8000 and 50 (Found: C, 70·7; H, 8·8%; active H, 0·8 atom. $C_9H_{14}O_2$ requires C, 70·1; H, 9·15%), and (ii) the corresponding *formate* (XIX) (3 g.), b. p. 73°/0·1 mm., n_D^{20} 1·4840, which solidified and after crystallisation from pentane had m. p. 30°, $\lambda_{max.}$ (in EtOH) 2400 and 3100 Å, ε 10,000 and 40, $\lambda_{infl.}$ 3200 Å, ε 30 (Found: C, 65·9; H, 7·8. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·75%). The *semicarbazone* of the formate separated from methanol in fine colourless needles, m. p. 158° (Found: C, 55·1; H, 7·5; N, 18·1. $C_{11}H_{17}O_3N_3$ requires C, 55·2; H, 7·2; N, 17·6%). Light absorption in EtOH: Max. at 2570 Å (ε 23,500), inflections at 2510 and 2660 Å (ε 16,000 and 20,000). The hydroxy-ketone was also obtained when the formate was heated with 2N-hydrochloric acid in 60% ethanol at 80° for 30 min. On treatment of either the hydroxy-ketone or the formate with Brady's reagent, the 2 : *4-dinitrophenylhydrazone* of the hydroxy-ketone was obtained; it crystallised from methanol in fine red needles, m. p. 191° (Found: C, 54·0; H, 5·4; N, 16·6. $C_{15}H_{18}O_5N_4$ requires C, 53·8; H, 5·3; N, 16·7%). Light absorption in $CHCl_3$: Max. at 3880 Å, ε 26,000.

(*b*) Treatment of *cyclo*pentenyl propenyl ketone (3 g.) with phosphoric acid (15 g.) at room temperature for 15 hr. and isolation of the products as before gave the pyrone (XXIII) as a colourless liquid, b. p. 62°/0·1 mm., n_D^{24} 1·4861, ε < 1000 between 2200 and 3000 Å (Found: C, 70·5; H, 9·3. Calc. for $C_9H_{14}O_2$: C, 70·1; H, 9·15%) (Nazarov and Burmistrova, *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1947, 51, give b. p. 72—73°/4 mm., n_D^{20} 1·4802). With methylmagnesium iodide in ether, it evolved methane corresponding to 0·3 active hydrogen atom. The semicarbazone crystallised from ethanol in prisms, m. p. 182° (Found: N, 20·5. Calc. for $C_{10}H_{17}O_2N_3$: N, 19·9%) (Nazarov and Burmistrova give m. p. 181°). Light absorption in EtOH: Max. at 2280 Å, ε 11,000.

cyclo*Hept*-1-*enyl Pentadienyl Ketone* (XXIV).—A solution of 1-*cyclo*hept-1′-enylpenta-2 : 4-dien-1-ol (20 g.; Braude and Forbes, *loc. cit.*) in light petroleum (b. p. 40—60°; 2 l.) and active manganese dioxide (200 g.) were vigorously agitated for 36 hr. under nitrogen. Isolation of the product in the usual way and fractionation afforded the *ketone* (15 g., 75%) as a pale yellow liquid, b. p. 114°/4 × 10^{-4} mm., n_D^{17} 1·5413 (Found: C, 82·3; H, 10·0. $C_{13}H_{18}O$ requires C, 82·1; H, 9·55%). The 2 : *4-dinitrophenylhydrazone* crystallised from ethyl acetate in dark red prisms, m. p. 219—222° (decomp.) (Found: C, 61·1; H, 6·1; N, 15·0. $C_{19}H_{22}O_4N_4$ requires C, 61·6; H, 6·0; N, 15·1%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 4030 Å, ε 33,000.

Δ^9-*Octahydro*-1-*keto*-3-*propenylazulene* (XXVI).—The above ketone (9 g.) was treated with phosphoric acid (7·5 g.) and formic acid (20·1 g.) under the conditions previously described. Isolation of the product as before and fractionation gave mainly Δ^9-*octahydro*-1-*keto*-3-*propenylazulene* (2·2 g., 24%), b. p. 67°/5 × 10^{-4} mm., n_D^{20} 1·5290 (Found: C, 81·8; H, 9·85. $C_{13}H_{18}O$ requires C, 82·1; H, 9·55%). The 2 : *4-dinitrophenylhydrazone* crystallised from ethyl acetate in dark-red, rectangular prisms, m. p. 212° (decomp.) (Found: C, 61·8; H, 6·25; N, 15·1. $C_{19}H_{22}O_4N_4$ requires C, 61·6; H, 6·0; N, 15·1%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3930 Å, ε 31,500.

Ozone was passed through a solution of the ketone (0·8 g.) in acetic acid (10 g.) for 2 hr. (until the absorption had ceased). The resulting solution was steam-distilled and the distillate collected in a receiver containing Brady's reagent, giving acetaldehyde 2 : 4-dinitrophenylhydrazone (0·9 g., 90%) which on recrystallisation from ethyl acetate separated as red needles, m. p. 165°, undepressed on admixture with an authentic specimen.

Attempts to effect the cyclisation of (XXIV) by treatment with phosphoric acid alone at 0° only gave small yields of the octahydroazulene (XXVI), most of the starting material being recovered unchanged.

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