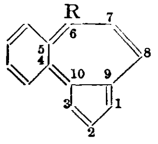
275. *Cyclic Conjugated Polyenes. Part IV. Attempted Synthesis of 6-Methyl-4 : 5-benzazulene.*

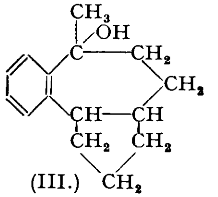
By J. R. Nunn.

An attempt to prepare 6-methyl-4 : 5-benzazulene by the dehydrogenation of 6-methyl-1 : 2 : 3 : 8 : 9 : 10-hexahydro-4 : 5-benzazulene is reported. This attempt failed but, instead, the latter hydrocarbon, on dehydrogenation, rearranged to 9-methylphenanthrene.

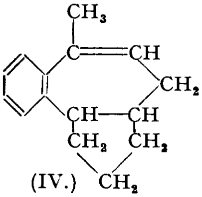
Recent attempts (Nunn and Rapson, *J.*, 1949, 1051) to isolate 4 : 5-benzazulene (I) in a pure state failed owing to instability. However, the molecular complexes of the hydrocarbon with 1 : 3 : 5-trinitrobenzene and 2 : 4 : 6-trinitrotoluene were isolated as reasonably stable compounds, presumably because of polarisation effects associated with complex formation. In an attempt to assess the factors which may control stability in the 4 : 5-benzazulene structure, an attempt has been made to prepare 6-methyl-4 : 5-benzazulene (II).



(I; R = H.)
(II; R = Me.)



(III.)



(IV.)

6-Hydroxy-6-methyloctahydro-4 : 5-benzazulene (III) was made by the action of methylmagnesium iodide on 6-keto-octahydro-4 : 5-benzazulene in the usual way, and was dehydrated to 6-*methyl*-1 : 2 : 3 : 8 : 9 : 10-*hexahydro*-4 : 5-*benzazulene* (IV) by heating it with potassium hydrogen sulphate. This was then dehydrogenated in the vapour phase in a vacuum. No conditions were found, however, under which the expected 6-methyl-4 : 5-benzazulene was produced and in all reactions the isomeric 9-methylphenanthrene was formed.

Substituted 4 : 5-benzazulenes are therefore not always accessible through dehydrogenation of hydro-derivatives, owing to the ease of rearrangement to yield derivatives of phenanthrene.

Experimental.

6-*Methyl*-1 : 2 : 3 : 8 : 9 : 10-*hexahydro*-4 : 5-*benzazulene* (IV).—Methylmagnesium iodide, from magnesium (0·97 g., 0·04 mol.) and methyl iodide (5·52 g., 0·039 mol.), in anhydrous ether was cooled in ice, and 6-keto-octahydro-4 : 5-benzazulene (4·0 g., 0·02 mol.) (Nunn and Rapson, *loc. cit.*) in a little anhydrous ether was added slowly with vigorous stirring. After 1 hour's refluxing the solution was set aside overnight. The complex was decomposed with ice-cold dilute sulphuric acid, and the ethereal layer was separated and washed with sodium hydrogen sulphite solution and water. Distillation of the dry neutral extract afforded 6-hydroxy-6-methyloctahydro-4 : 5-benzazulene as a colourless, very viscous oil (4·1 g., 95%), b. p. 123—125°/0·4 mm.

This carbinol (1·5 g.), mixed thoroughly with finely powdered potassium hydrogen sulphate (1·5 g.), was heated at 180—190° for 1·5 hours. The mixture was extracted with ether, and the ethereal solution washed with sodium carbonate solution (10%) and water. Distillation gave 6-*methyl*-1 : 2 : 3 : 8 : 9 : 10-*hexahydro*-4 : 5-*benzazulene* as a colourless mobile oil, b. p. 92—94°/0·3 mm., $n_D^{25\cdot0}$ 1·5769, $d_{25\cdot0}^{25\cdot0}$ 1·024, $[R]_D$ = 64·22 (Calc.: 63·00) (Found: C, 90·4; H, 9·1. $C_{15}H_{18}$ requires C, 90·9; H, 9·1%).

Dehydrogenation. The hexahydro-derivative was dehydrogenated in the vapour phase at 22 mm. over 30% palladium–charcoal, using an apparatus previously described (Nunn and Rapson, *J.*, 1949, 825). The hydrocarbon (0·80 g.) was passed through the catalyst, which was maintained at 340°, at the rate of 0·01 c.c./min. The dark distillate (0·395 g.) was dissolved in pentane (60 c.c.) and chromatographed on alumina (60 g.; Peter Spence Type H) in a column 25·5 × 1·87 cm. Fractions were collected as indicated in the table.

Fraction.	Eluent.	Eluate, c.c.	Residue, mg.	Remarks.
1—8	Pentane	420	275·9	Colourless mobile oil.
9	Pentane–benzene (9 : 1)	100	27·9	Colourless viscous oil.
10	,,	100	21·3	Colourless viscous oil.
11	Pentane–benzene (4 : 1)	100	30·9	Colourless crystals. Deep-blue fluorescence in ultra-violet light.
12	,,	100	9·6	Green oil.

Fraction 11 was again chromatographed on a column containing 5 g. of alumina with pentane only as the eluent. This afforded 24 mg. of crystalline material which, after 2 crystallisations from methanol, gave colourless prisms. These were sublimed at 85° (block temp.) at 0·01 mm. and then had m. p. 90—91° (Found: C, 93·7; H, 6·7. Calc. for $C_{15}H_{12}$: C, 93·7; H, 6·3%). The picrate formed orange-yellow needles, m. p. 151—153°, from methanol. Windaus, Jensen, and Schramme (*Ber.*, 1924, **57**, 1875) give m. p. 91—92° for 9-methylphenanthrene and m. p. 152—153° for the picrate.

Fractions 1—8 proved to be mainly unchanged starting material. Further dehydrogenations were carried out at 270°, 290°, 310°, and 360° without any of the desired product being obtained.

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