15. *The Synthesis of* 1-*Methyl*-6-iso*propylphenanthrene.*

By S. N. SLATER.

The synthesis of 1-*methyl*-6-iso*propylphenanthrene* by the Cook–Bogert method is described. It is shown to be different from the hydrocarbon obtained by dehydrogenating the diterpene rimuene.

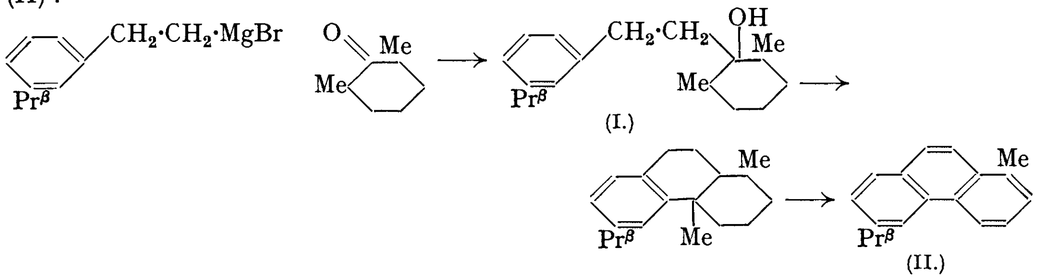
IN 1904 Easterfield and Bagley (J., 1904, **85**, 1238) isolated a hydrocarbon $C_{18}H_{18}$, m. p. 86°, from the dehydrogenation product of abietene, and Beath (*J. Soc. Chem. Ind.*, 1933, **52**, 338T) later isolated from the dehydrogenation products of the diterpene rimuene a hydrocarbon $C_{18}H_{18}$, m. p. 86—87° (picrate, m. p. 127°, giving a definite depression with authentic retene picrate, m. p. 127°). The similarity in m. p. and analytical figures between this hydrocarbon and that obtained by Easterfield and Bagley (to which the name *iso*retene had been given) suggested that the two might in fact be identical and Beath reported that a mixed m. p. determination (85—86°) confirmed this view. The structure 1-methyl-6-*iso*propylphenanthrene was proposed for *iso*retene, although there was little or no positive evidence to support this formula.

Hosking and McFadyen (*J. Soc. Chem. Ind.*, 1934, **53**, 195T) showed, however, that Easterfield and Bagley's hydrocarbon was almost certainly pimanthrene (1 : 7-dimethylphenanthrene, m. p. 86° ; picrate, m. p. 131°) derived from the dehydrogenation of varying amounts of pimarene normally present in abietene. On this view Beath's dehydrogenation product from rimuene would also be identified with pimanthrene.

In confirmation of this Brandt (*N. Z. J. Sci. Tech.*, 1938, **20**, No. **1**, 8*B*) subjected a sample of Beath's rimuene to selenium dehydrogenation and isolated a hydrocarbon, m. p. 86°, (50—60% yield) identified as pimanthrene by means of the picrate, styphnate, and quinone.

That Beath's original suggestion was erroneous is further proved by the synthesis of 1-*methyl*-6-iso*propylphenanthrene* described below. The hydrocarbon melted at 45—46°, the *picrate* at 143°, and the *quinone* at 144—146°.

Under conditions similar to those described by Sterling and Bogert (*J. Org. Chem.*, 1939, **4**, 26) the Grignard reagent from homocuminyl bromide (Simonsen and co-workers, J., 1936, 674) was condensed with 2 : 6-dimethyl*cyclo*hexanone (Ruzicka and co-workers, *Helv. Chim. Acta*, 1931, **14**, 1163), and the resulting *carbinol* (I) cyclodehydrated with sulphuric acid and dehydrogenated with selenium to 1-methyl-6-*iso*propylphenanthrene (II) :



(I.)
(II.)

A related problem is the dehydrogenation of phyllocladene, a diterpene which was shown by Briggs (J., 1937, 79) to be identical with the diterpenes dacrene and sciadopitene. Both rimuene and phyllocladene may be isomerised to the same substance, *iso*phyllocladene.

Uota (*J. Dept. Agr. Kyushu Imp. University*, 1937, **5**, 117) has studied the selenium dehydrogenation of phyllocladene (sciadopitene) and obtained a hydrocarbon (scianthrene), m. p. 86°. The m. p.'s of its derivatives are fairly close to those of retene, but Uota states that the hydrocarbon is distinct from retene and assigns it the structure 7-methyl-1-*iso*propylphenanthrene. Brandt, however (*loc. cit.*), has disputed this interpretation and states that the dehydrogenation of phyllocladene yields a mixture of substances, separated with difficulty into pimanthrene, retene, and two other hydrocarbons, one liquid and one crystalline, the last two being obtained in amounts too small for purification. It is suggested that scianthrene may be a mixture of retene and pimanthrene.

The liquid hydrocarbon obtained by Brandt in small amount gives a picrate, m. p. approx. 144°, and it would be of interest to compare this with the picrate of 1-methyl-6-*iso*propylphenanthrene. The latter hydrocarbon is difficult to crystallise unless pure.

EXPERIMENTAL.

Ethyl p-iso*Propylphenylacetate.*—*p-iso*Propylphenylacetonitrile (43 g.) (Baker, Dippy, and Page, J., 1937, 1777), ethyl alcohol (60 g.), and sulphuric acid (24 g.) were refluxed at 130° for 8 hours. The excess of alcohol was then distilled off, water added, and the ester taken up in ether, filtered from the amide formed, dried over anhydrous sodium sulphate, and distilled; b. p. mainly 135°/12 mm. Yield, 30 g.

β-p-iso*Propylphenylethyl Alcohol* (*Homocuminyl Alcohol*).—A solution of the preceding ester (38 g.) in well-dried ethyl alcohol (200 g.) was added to sodium (18 g.) at 180°. When the vigour of the reaction abated, heating was continued at 160°. From time to time additions of absolute alcohol and of alcohol containing increasingly large quantities of water were made while the temperature was allowed to fall to 100°. Most of the alcohol was then steam-distilled and the residual oil was taken up in ether, washed with dilute acid and with potassium bicarbonate solution, dried over anhydrous sodium sulphate, and distilled; b. p. 127—129°/11 mm. Yield, 17 g.

The carbinol was converted as described by Simonsen and co-workers (J., 1936, 674) into the bromide, b. p. 134—135°/17 mm.

2 : 6-*Dimethyl*-1-β-p-*cuminylethyl*cyclo*hexanol* (I).—The Grignard reagent prepared from homocuminyl bromide (18 g.), ether (2 vols.), and magnesium (1·9 g.) activated with iodine was cooled in a freezing-mixture, and 2 : 6-dimethyl*cyclo*hexanone (8 g.) in ether (1 vol.) dropped in with stirring. After standing in the freezing mixture for 2 hours and then at room temperature overnight, the product was decomposed with ice-cold dilute sulphuric acid, and the ethereal solution washed with sodium bicarbonate solution, dried over anhydrous sodium sulphate, and distilled. The yield of the *carbinol*, b. p. 164—172°/0·5 mm., was 8 g. (Found for a portion, b. p. 165°/0·5 mm. : C, 84·1; H, 10·9. $C_{19}H_{30}O$ requires C, 83·2; H, 10·9%).

1 : 12-*Dimethyl*-6-iso*propyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene.*—The carbinol (8 g.) was added slowly to a stirred well-cooled mixture of sulphuric acid (17 g.) and water (3 c.c.). The product was allowed to reach room temperature and then washed into a separating funnel

with light petroleum (b. p. 60—80°; 30 c.c.) and shaken with several portions of 85% sulphuric acid until the acid layer was almost colourless. The petroleum layer, possessing a slight fluorescence, was washed with potassium carbonate solution, then with water, dried over anhydrous sodium sulphate, and distilled, yielding a clear colourless oil (6·2 g.), b. p. 180—190°/12 mm.

1-*Methyl*-6-iso*propylphenanthrene*.—The above oil (6 g.) was heated with selenium (5 g.) at 300° for 6 hours and then at 340° for 1 hour. After cooling, the product was extracted with ether and distilled over sodium in a vacuum, yielding a viscous oil (4·2 g.) with a strong lilac fluorescence. This was converted by alcoholic picric acid (5 g.) into the *picrate*, which was obtained in orange microcrystalline needles, m. p. 143° (Found : C, 62·2; H, 4·5. $C_{18}H_{18},C_6H_3O_7N_3$ requires C, 62·2; H, 4·5%).*

The picrate, in ether, was decomposed by shaking with successive portions of concentrated aqueous ammonia until the yellow colour was completely removed. The ethereal solution was washed with dilute acid, with water, and with sodium bicarbonate solution, dried over anhydrous sodium sulphate, and distilled over sodium in a vacuum, yielding a fluorescent oil (2 g.). On cooling in a freezing mixture this solidified. 1-*Methyl*-6-iso*propylphenanthrene* crystallised from alcohol in masses of small plates, m. p. 45—46° (Found : C, 92·4; H, 7·6. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%).*

The *quinone* was prepared by slowly adding a solution of chromic acid (0·5 g.) in acetic acid (0·8 c.c.) and water (0·4 c.c.) to the hydrocarbon (0·2 g.) in acetic acid (1 c.c.) at 60—70°. After being heated on the water-bath for 1 hour, the product was cooled and diluted with water; the precipitated quinone crystallised from alcohol in fine needles, m. p. 144—146° (Found : C, 81·9; H, 6·1. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%).*

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