143. 9 : 10-*Dihydrophenanthrenes. Part I. The Formation of 9 : 10-Dihydrophenanthrene from 2 : 2′-Disubstituted Diphenyls.*

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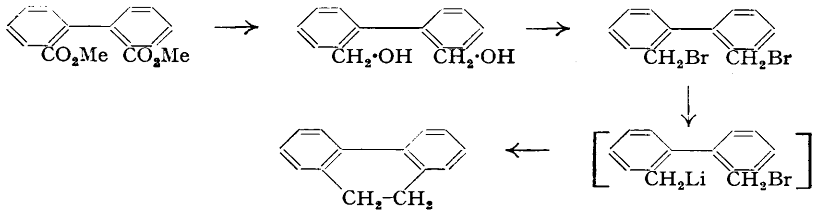
9 : 10-Dihydrophenanthrene is formed in high yield by the action of phenyl-lithium on 2 : 2′-di(bromomethyl)diphenyl, which is smoothly formed from the corresponding dihydroxy-compound. The latter is formed in almost quantitative yield by reducing alkyl diphenates with ethereal lithium aluminium hydride. Dihydrophenanthrene is formed in considerable quantities when the di(bromomethyl)diphenyl reacts with magnesium in the presence of ether.

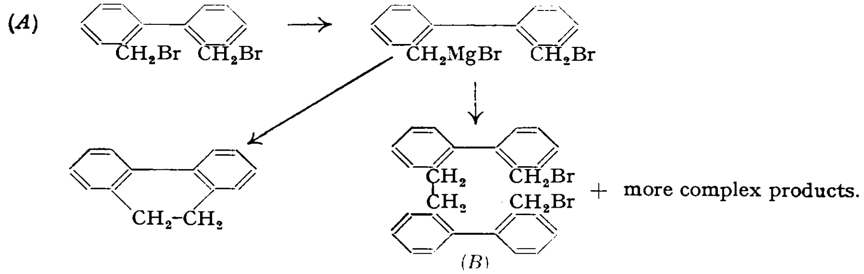
The most obvious routes to 9 : 10-dihydrophenanthrene are (*a*) the catalytic hydrogenation of phenanthrene and (*b*) the Wurtz–Fittig process from 2 : 2′-di(halogenomethyl)diphenyls. Burger and Mosettig (*J. Amer. Chem. Soc.*, 1935, **57**, 2731; 1936, **58**, 1857) obtained the hydrocarbon by the catalytic hydrogenation of phenanthrene, but the experimental conditions are beyond present resources. Dihydrophenanthrene must have been present in considerable quantities in the liquid product obtained by Kenner and Turner (*J.*, 1911, **99**, 2101) by the action of sodium on 2 : 2′-di(bromomethyl)diphenyl, since oxidation of the crude product gave a 26% yield of phenanthraquinone. Kenner and Turner were misled in their conclusions by the inaccurate work of Schmidt and Mezger (*Ber.*, 1907, **40**, 4240) who described 9 : 10-dihydrophenanthrene as a solid melting at 94—95°. Schroeter, Müller, and Huang (*Ber.*, 1929, **62**, 645) obtained 3 g. of dihydrophenanthrene, m. p. 34·5—35°, by the action of sodium on 25 g. of 2 : 2′-di(bromomethyl)diphenyl.

It is now found that although Kenner's conditions for the side-chain bromination of 2 : 2′-ditolyl cannot be materially improved, 2 : 2′-ditolyl can be obtained in 65% yield by heating *o*-iodotoluene with activated copper powder (Kleiderer and Adams, *J. Amer. Chem. Soc.*, 1933, **55**, 4219), a suitable alternative route being the Krizewsky–Turner reaction (*J.*, 1919, **115**, 559; *J. Proc. Roy. Soc. N.S.W.*, 1920, **54**, 37) with *o*-bromotoluene, when a yield of not less than 35% of ditolyl is obtained. Curiously enough, cupric chloride reacts indifferently with *o*-tolylmagnesium iodide, the main product of an attempted Krizewsky–Turner reaction with the latter being toluene, representing non-reaction.

As already indicated (*Nature*, 1949, **163**, 537), a more practicable route to 9 : 10-dihydrophenanthrene is the reduction of methyl diphenate by means of lithium aluminium hydride to 2 : 2′-di(hydroxymethyl)diphenyl, followed by conversion of the latter into 2 : 2′-di(bromomethyl)diphenyl and the interaction of this bromo-compound with phenyl-lithium. In this way, a 70% yield of dihydrophenanthrene from methyl diphenate is readily obtained.



When an attempt is made to prepare a Grignard reagent from 2 : 2′-di(bromomethyl)diphenyl (*A*) a mixture is obtained, the annexed scheme suggesting a probable sequence of reactions :



In the presence of either 2·2 or 1·0 atomic proportions of magnesium, 40% of the product is dihydrophenanthrene, the remainder containing high-melting products of which the main component appears to be 1 : 2-di-(2′-bromomethyl-2-diphenylyl)ethane (*B*), hydrolysable to 1 : 2-*di*-(2′-*hydroxymethyl*-2-*diphenylyl*)*ethane*.

EXPERIMENTAL.

2 : 2′-*Ditolyl*.—(*a*) Activated copper bronze was heated in a bath kept at about 260° and *o*-iodotoluene (50 g.) added at infrequent intervals. Heating was continued until refluxing ceased (about 20 hours). The somewhat cooled mixture was extracted with boiling chlorobenzene, and the filtered extract distilled. No unchanged iodotoluene was found. The main portion boiled at 254—256° and was almost pure ditolyl (13·5 g., 65% yield). Some commercial samples of copper bronze were found to be without perceptible action on boiling iodotoluene, even after attempted activation.

(*b*) A solution of *o*-tolylmagnesium bromide was prepared from 171 g. (1 g.-mol.) of *o*-bromotoluene and 24·5 g. of magnesium, in *ca.* 800 c.c. of ether. Finely-ground anhydrous cupric chloride (170 g.; 1·25 g.-mols.) was gradually added and the resulting mixture boiled for an hour. Ice and then concentrated hydrochloric acid were added and later (to oxidise the cuprous salts and render subsequent operations easier) about one g.-mol. of ferric chloride (about 400 g. of the dodecahydrate) in concentrated aqueous solution. The two layers were separated and the aqueous layer extracted several times with ether. The combined ethereal extracts were washed with water and alkali and fractionally distilled in steam. Fractions were cooled to about 10°. Oils which solidified were filtered and were pure ditolyl, m. p. 18°. Other fractions were separated or extracted with ether, and the dried ether extracts distilled. High-boiling materials (above 190°) were steam-distilled and the fractions treated as before. From a series of such operations, 836 g. of bromotoluene gave 156 g. (35% yield) of ditolyl, m. p. 18°, the highest individual yield being 42%.

Bromination of 2 : 2′-*Ditolyl*.—Ditolyl (9 g., 1 g.-mol.) was heated at 125—130° in a current of dry nitrogen which had bubbled slowly through 5·5 c.c. of bromine (just over 2 g.-mols.). Bromination took several hours, after which the product was cooled, stirred with dry light petroleum (b. p. 60—80°), and crystallised from this solvent. The process was not noticeably accelerated or improved if a trace of benzoyl peroxide was present. In all, 153·5 g. of ditolyl were brominated and gave 125·5 g. of 2 : 2′-di(bromomethyl)diphenyl, m. p. 89—92° (yield, 44%). One further crystallisation from light petroleum gave 119 g. of pure dibromide, m. p. 91—93°.

2 : 2′-*Di*(*hydroxymethyl*)*diphenyl*.—A solution of 76 g. of methyl diphenate in 700 c.c. of dry ether was added as fast as refluxing permitted to a solution of 17 g. of lithium aluminium hydride (1·6 g.-mols.) in 600 c.c. of ether. Water and then dilute sulphuric acid were added and the mixture freed from ether by heating on a water-bath. After the mixture had cooled, the solid was filtered off, washed, and dried. The *hydroxymethyl* compound crystallised from benzene in needles, m. p. 112—113° (yield, 55 g., 91%) (Found : C, 77·9; H, 6·8. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·6%).

Similar reduction of ethyl diphenate gave a 93% yield of diol.

2 : 2′-*Di*(*bromomethyl*)*diphenyl*.—The dihydroxyditolyl (15 g.) was added gradually to 750 c.c. of 46% hydrobromic acid at 90° and the mixture then boiled for 20 minutes. On cooling, a crystalline meal was formed and this was filtered off. The solid was dried *in vacuo* and crystallised from light

petroleum (b. p. 60—80°). From three such operations 67 g. (94% yield) of pure dibromo-compound were obtained.

9 : 10-*Dihydrophenanthrene.*—Freshly made lithium wire (3 g.) were cut into a nitrogen-filled flask containing 150 c.c. of dry ether, and 32 g. of bromobenzene were then gradually added. When interaction was complete, a solution of 54 g. of dibromoditolyl in 450 c.c. of ether was added as fast as refluxing allowed. Ice and water were then introduced and the two layers separated. Distillation of the dried ethereal solution gave 24·5 g. (86% yield) of dihydrophenanthrene, b. p. 174°/17 mm. After one crystallisation from methyl alcohol the hydrocarbon had m. p. 35·0—35·5°.

Action of Magnesium on 2 : 2′-*Di*(*bromomethyl*)*diphenyl.*—(*a*) The dibromo-compound (17 g.) reacted in ethereal solution with 0·5 atomic proportion of magnesium which had previously been activated with ethyl bromide. A further 0·5 atomic proportion of magnesium was added and the mixture boiled for 2 hours. A violet colour appeared at one stage and later disappeared. A white solid separated. Water and dilute hydrochloric acid were added without cooling and the solid separated and dried (4·4 g.). Crystallisation from a mixture of *cyclo*hexanone and light petroleum (b. p. 100—120°) gave 1 : 2-*di*-(2′-*hydroxymethyl*-2-*diphenylyl*)*ethane*, micro-crystalline, m. p. 242—244°, darkening at 235° [Found: C, 84·7; H, 6·8%; *M* (cryoscopic, in camphor), 422. $C_{28}H_{26}O_2$ requires C, 85·25; H, 6·65%; *M*, 394·5]. The ethereal layer, after being dried and distilled, gave 3·5 g. of dihydrophenanthrene (40%).

(*b*) Dibromoditolyl (34 g.) reacted in ethereal solution with 0·5 atomic proportion of activated magnesium and after further addition of 0·5 atomic proportion of magnesium the mixture was boiled for 6 hours. The white solid which separated was filtered off, washed with 47% hydrobromic acid, and dried (5·4 g.). The mixture of bromo-compounds obtained could not be separated, but crystallisation from a moist mixture of *cyclo*hexanone and light petroleum (b. p. 100—120°) gave the diol (m. p. 242—244°). From the ethereal mother-liquor 7·2 g. of dihydrophenanthrene were obtained.

(*c*) An ethereal solution of 17 g. of dibromoditolyl was boiled for several hours with 2·64 g. (2·2 atomic proportions) of activated magnesium. As in (*a*) and (*b*) a violet colour appeared intermediately and a solid separated. The yield of dihydrophenanthrene was 40%.

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