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# POLYNUCLEAR AROMATIC HYDROCARBONS—X

## SYNTHESIS OF TETRAPHENE[1] BY THE ROBINSON-MANNICH REACTION

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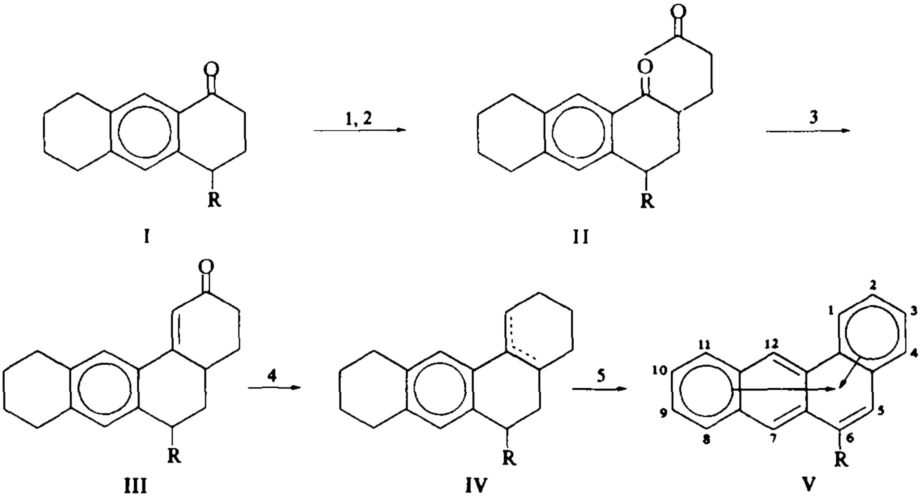
**Abstract**—A method of synthesis of tetraphene and 6-methyltetraphene by the Robinson–Mannich reaction on 1-oxo-1,2,3,4,5,6,7,8-octahydroanthracene and its 4-methyl derivative, respectively, is described.

A NUMBER of syntheses of tetraphene and its 6-methyl derivative have been recorded.[2–4] Another method of synthesis employing the Robinson-Mannich reaction[5] offers an approach for the construction of a fused 6-membered alicyclic ring on an appropriate hydroaromatic ketone. This reaction was adopted with considerable technical improvement by Wilds *et al.*[6–8] for the synthesis of chrysene and benzo(c)-phenanthrene. By a similar approach we have synthesized tetraphene and 6-methyltetraphene according to the following sequence of reactions:



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[1] The new nomenclature and numbering of benzo(a)anthracene as recommended by E. Clar. *Polycyclic Hydrocarbons*, Vol. I; p. 307 Academic Press, London (1964) was adopted.

[2] E. Clar, *Polycyclic Hydrocarbons* Vol. I, pp. 314–16. Academic Press, London (1964).

[3] O. P. Vig, S. V. Kessar, V. P. Kubba and S. M. Mukherji, *J. Ind. Chem. Soc.* **32**, 697 (1955).

[4] S. M. Mukherji, S. N. Sawhney and K. S. Sharma, *J. Ind. Chem. Soc.* **42**, 176 (1965).

[5] E. C. de Feu, F. J. McQuillin and R. Robinson, *J. Chem. Soc.* 53 (1937); 586 (1941).

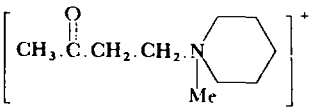
[6] A. L. Wilds and C. H. Shunk, *J. Am. Chem. Soc.* **65**, 469 (1943).

[7] A. L. Wilds and R. G. Werth, *J. Org. Chem.* **17**, 1149 (1952).

[8] A. L. Wilds and R. G. Werth, *J. Org. Chem.* **17**, 1154 (1952).

[a, R = H;
b, R = Me]

1, NaOEt/HCOOEt;

2 
$I^-$;

3, HCl – HOAc;

4, Zn – Hg/HCl; 5 Pd–C.

For the synthesis of the parent compound tetraphene (Va), 1-oxo-1,2,3,4,5,6,7,8-octahydroanthracene (Ia) was prepared from tetralin through succinoylation[9] and Clemmensen reduction of the keto-acid thus obtained, followed by intramolecular acylation of the resultant γ-(6-tetralyl) butyric acid through its acid chloride.[3] The ketone Ia was formylated[10] in 70% yield and the formyl derivative condensed with 1-N-piperidino-3-butanone methoiodide[7] to give the diketone IIa in 55·4% yield. Cyclization of IIa was effected with acetic acid–hydrochloric acid mixture[6] to furnish the unsaturated ketone IIIa in 83·2% yield, characterized through its 2,4-dinitrophenylhydrazone, m.p. 242–243°. Clemmensen reduction of IIIa gave the corresponding hydrocarbon in 70% yield, which was smoothly dehydrogenated with 30% Pd–C to afford tetraphene (Va), m.p. 157–158°. The hydrocarbon Va was characterized by UV and IR spectra, its picrate, m.p. 141–142° and by oxidation[11] to tetraphene-7,12-quinone, m.p. 168–169°. Its structure was further confirmed by the mixture m.p. with an authentic sample obtained by dehydrogenation of 1,2,3,4,4a,5,6,8,9,10,11,12b-do-decahydrotetraphene.[12]

The method as developed above was then extended to the synthesis of 6-methyltetraphene for which 1-oxo-4-methyl-1,2,3,4,5,6,7,8-octahydroanthracene (Ib) was obtained by following the procedure prescribed by Vig *et al.*[3] The aforementioned sequence of reactions on this ketone gave 6-methyl-2-oxo-2,3,4,4a,5,6,8,9,10,11-decahydrotetraphene (IIIb), which was characterized through its 2,4-dinitrophenylhydrazone, m.p. 221–222°, UV and IR spectra. The enone IIIb on Clemmensen reduction followed by aromatization gave 6-methyltetraphene (Vb), m.p. 122–123° undepressed when mixed with an authentic sample.[4] It was further characterized through its UV and IR spectra and its picrate, m.p. 146–147°, undepressed when mixed with an authentic sample.[4]

## EXPERIMENTAL*

*1-Oxo-1,2,3,4,5,6,7,8-octahydroanthracene* (Ia). This compound was prepared from tetralin by succinoylation followed by reduction of the keto-acid[9] and ring closure through the acid chloride of γ-(6-tetralyl) butyric acid.[3]

*1-Oxo-2-(γ-oxo-butyl)1,2,3,4,5,6,7,8-octahydroanthracene* (IIa). To an ice-cold suspension of EtONa (from 3 g Na) in dry benzene, ethyl formate (10 g) was added gradually with stirring and after 2 hr, Ia (20 g), dissolved in 40 ml dry benzene, was added with shaking and ice-cooling. A scarlet coloured solid separated. The reaction mixture was kept for 6 hr in iced water. Crushed ice was then added and the benzene layer separated, the aqueous layer washed with benzene and then acidified with ice-cold conc HCl to liberate the formyl derivative. The oil was taken up in ether, washed twice with water and dried over $MgSO_4$. After

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* B.ps and m.ps are uncorrected.

[9] M. S. Newman and H. V. Zahm, *J. Am. Chem. Soc.* **65**, 1097 (1943).

[10] S. M. Mukherji, V. S. Gaind and P. N. Rao, *J. Org. Chem.* **19**, 328 (1954).

[11] H. Bendas and C. Djerassi, *J. Am. Chem. Soc.* **78**, 2474 (1956).

[12] J. W. Cook and G. A. D. Haslewood, *J. Chem. Soc.* 767 (1935).

removal of the solvent and distillation under reduced press, 16 g (70 %) of the formyl derivative, b.p. 182–185°/4 mm, was obtained. It gives an intense violet coloration with alcoholic $FeCl_3$.

To MeONa (from 1·5 g Na and 100 ml dry MeOH) 16 g of the above formyl derivative was added followed by 1-piperidine-3-butanone methoiodide (36 g) in 50 ml MeOH. The reaction mixture was kept for 24 hr at room temp and thereafter it was diluted with water and extracted thoroughly with benzene, washed with 10 % NaOH aq and finally with water till alkali-free and dried over $MgSO_4$. After removal of the solvent, the residual liquid was distilled under reduced press, giving 10·5 g (55·4 %) of IIa, b.p. 215–217°/4 mm. (Found: C, 79·63; H, 7·87. Calc. for $C_{18}H_{22}O_2$: C, 80·0; H, 8·15 %.)

*2-Oxo-2,3,4,4a,5,6,8,9,10,11-decahydrotetraphene* (IIIa). To IIa (9 g) AcOH (250 ml) and conc HCl (50 ml) was added and the mixture refluxed for 23 hr. The reaction mixture was diluted with water and after working up with benzene, distillation under reduced press produced 7 g (83·2 %) of IIIa, b.p. 210–212°/4 mm. (Found: C, 85·24; H, 7·80. Calc. for $C_{18}H_{20}O$: C, 85·74; H, 7·94 %.)

The 2,4-dinitrophenylhydrazone was prepared and crystallized from AcOEt in bright red needles, m.p. 242–243°. (Found: N, 13·32. Calc. for $C_{24}H_{24}N_4O_4$: N, 12·96 %.)

*Tetraphene* (Va). The ketone IIIa (6·0 g) was reduced with ZnHg (30 g), conc HCl (60 ml), water (30 ml), toluene (30 ml) and AcOH (20 ml) by refluxing for 30 hr. After every 6 hr, conc HCl (5 ml) was added. The reaction mixture yielded 4 g (70·5 %) of the reduced product b.p. 204–206°/5 mm.

The above product (3 g) was dehydrogenated with 30 % Pd–C (0·3 g) for 5 hr at 320–340° in the atmosphere of $CO_2$. The product, after usual working up, was sublimed *in vacuo*, yield 1·7 g (70 %). The product was converted into its picrate and crystallized from EtOH. The purified picrate (1 g) was decomposed by passing through a column of alumina and the regenerated hydrocarbon was crystallized from benzene–pet ether (40–60°) to furnish 0·5 g pure Va, m.p 157–158°. (Found: C, 94·28; H, 5·52. Calc. for $C_{18}H_{12}$: C, 94·74; H, 5·26 %.)

UV Spectrum (cyclohexane): 220, 255, 266, 277, 286, 327, 340, 358 and 384 mμ (log ε 4·62, 4·56, 4·66, 4·80, 4·72, 3·80, 3·90, 3·65 and 2·90). IR (Nujol): 2950, 2600, 2300, 1450, 1330, 1250, 885, 810, 735 $cm^{-1}$. Superimposable on that of an authentic sample[13].)

The picrate was prepared and crystallized from EtOH, in reddish brown needles, m.p. 141–142°. (Found: N, 9·60. Calc. for $C_{24}H_{15}O_7N_3$: N, 9·19 %.)

*Tetraphene* (Va, *authentic sample*). 1,2,3,4,4a,5,6,8,9,10,11,12b-Do-decahydrotetraphene was prepared[12] and the do-decahydrotetraphene (2 g) aromatized with 30 % Pd–C (0·2 g) at 320–340° for 5 hr in the atmosphere of $CO_2$. The product was sublimed *in vacuo*, yield 1·3 g (70 %) and converted into its picrate and crystallized from EtOH. The purified picrate (0·8 g) was decomposed by passing through a column of alumina and the regenerated hydrocarbon (0·4 g) Va crystallized from benzene–pet ether (40–60°), m p 157–158°. (Mixture m.p with the earlier sample undepressed).

The picrate was prepared and crystallized from EtOH, m.p. 141–142°. (Mixture m.p. with the earlier sample undepressed.)

*Oxidation of tetraphene* (Va) *to tetraphene-7,12-quinone*. Tetraphene was oxidized[11] by treating 0·2 g of the hydrocarbon with boiling AcOH (15 ml) and $CrO_3$ (0·4 g) for 5 min. After cooling the reaction mixture was added to water, and the yellow solid (0·15 g) recrystallized twice from benzene–EtOH, m.p. of the quinone, 168–169° (lit.[14] m.p. 168°).

UV Spectrum (EtOH) 248, 270 and 324 mμ (log ε 4·97, 4·57 and 3·95). IR (Nujol): 2900, 2350, 1670, 1600, 1470, 1380, 1340, 1305, 1180, 1290, 1020, 945, 815, 775, 755, 700 $cm^{-1}$. (Characteristic stretching frequency[15] of carbonyl group is at 1670 $cm^{-1}$.)

1-*Methyl*-4-*oxo*-1,2,3,4,5,6,7,8-*octahydroanthracene* (Ib). This compound was prepared[3] by the cationoid alkylation of tetralin, followed by hydrolysis and intramolecular acylation of the corresponding acid chloride in the presence of stannic chloride.

6-*Methyl*-2-*oxo*-2,3,4,4a,5,6,8,9,10,11-*decahydrotetraphene* (IIIb). EtONa was prepared from Na dust (3 g) and anhyd EtOH (6 g) in thiophene-free benzene (300 ml) To this ice-cold suspension of EtONa in benzene, was added dropwise with shaking ethyl formate (10 g) and after 2 hr Ib (19 g), dissolved in 50 ml dry benzene was added with shaking and ice-cooling. A scarlet coloured solid separated immediately.

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[13] W. West, *Technique of Organic Chemistry* Vol IX; *Chemical Applications of Spectroscopy* p. 401. Interscience, London (1956).

[14] K. Dziewonski and E. Ritt, *Bull. intern. acad. Polonaise* 181 (1927A); *Chem. Abstr.* **22**, 2561 (1928).

[15] M. L. Josien and N. Fuson, J.-M. Lebas and T. M. Gregory, *J. Chem. Phys.* **21**, 331 (1953).

The reaction mixture was kept for 6 hr in iced water. Crushed ice was added and the benzene layer separated, the aqueous layer washed with benzene and then acidified with ice-cold conc HCl to liberate the formyl derivative. The oil was taken up in ether, washed twice with water and dried over $MgSO_4$. After removal of the solvent and distillation under reduced press, the formyl derivative (14 g; 70%), b.p. 192–195°/5 mm, was obtained giving a violet coloration with alcoholic $FeCl_3$.

To MeONa (from 1·5 g Na and 100 ml dry MeOH) the above formyl derivative (14 g) and 1-piperidine-3-butanone methoiodide (36 g) in MeOH (50 ml was added). The reaction mixture was kept for 24 hr at room temp, and thereafter it was diluted with water and extracted thoroughly with benzene, washed successively with 10% NaOH aq and water till alkali-free and dried over $MgSO_4$. After removal of the solvent, the residual liquid was distilled under reduced press giving the diketone (10 g; 54·8%), b.p. 200–205°/1 mm.

To the above diketone (9 g) AcOH (250 ml) and conc HCl (50 ml) was added and the mixture refluxed for 23 hr. It was then diluted with water and after working up with benzene, distillation under reduced press produced 7 g (78·6%) of IIIb, b.p. 175–177°/1 mm. (Found: C, 86·21; H, 7·88. Calc. for $C_{19}H_{22}O$: C, 85·70; H, 8·27%.)

UV Spectrum (EtOH): 230 and 272 mμ (log ε 4·1 and 4·56). IR (Nujol): 2900, 2840, 2820, 2650, 1720, 1680, 1590, 1560, 1550, 1490, 1475, 1450, 1440, 1430, 1410, 1395, 1380, 1310, 1285, 1270, 1255, 1200, 1185, 1145, 1115, 1090, 1020, 980, 940, 905, 880, 865, 845, 825, 810, 765, 730, 680 $cm^{-1}$

The 2,4-dinitrophenylhydrazone was prepared and crystallized from AcOEt in bright red needles, m.p. 221–222°. (Found: N, 12·24. Calc. for $C_{25}H_{26}N_4O_4$: N, 12·61%.)

6-*Methyl*-2,3,4,4a,5,6,8,9,10,11-*decahydrotetraphene* (IVb). The ketone IIIb (6 g) was reduced with Zn Hg (30 g), conc HCl (60 ml), water (30 ml), toluene (30 ml) and AcOH (20 ml) by refluxing for 30 hr. After every 6 hr, conc HCl (5 ml) was added. The reaction mixture yielded 4 g (70%) of IVb, b.p. 190–192°/3 mm. (Found: C, 90·98; H, 9·32. Calc. for $C_{19}H_{24}$: C, 90·46; H, 9·54%.)

6-*Methyltetraphene* (Vb). The product IVb (3 g) was dehydrogenated with 30% Pd–C (0·3 g) for 5 hr at 320–340° in the atmosphere of $CO_2$. The product was sublimed *in vacuo*, yield 1·7 g (70%) and converted into its picrate and crystallized from EtOH. The purified picrate (1 g) was decomposed by passing through a column of alumina and the regenerated hydrocarbon was crystallized from benzene–pet ether (40–60°) to furnish 0·5 g of pure Vb, m.p. 122–123°. (Found: C, 94·62; H, 6·04. Calc. for $C_{19}H_{14}$: C, 94·20; H, 5·80%.) The mixture m.p. with the authentic sample[4] was undepressed.

UV Spectrum (cyclohexane): 226, 256, 266, 276, 295 and 324 mμ (log ε 4·54, 4·59, 4·66, 4·82 and 3·6). IR (Nujol): 2900, 1450, 1360, 950, 885, 780, 755, 745 $cm^{-1}$. (Superimposable on that of an authentic sample[16].)

The picrate was prepared and crystallized from EtOH in reddish brown needles, m.p. 146–147°. (Found: N, 9·36. Calc. for $C_{25}H_{17}N_3O_7$: N, 8·92%.) The mixture m.p. with the authentic sample[4] was undepressed.

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[16] W. West, *Technique of Organic Chemistry* Vol. IX, *Chemical Applications of Spectroscopy* p 404. Interscience, London (1956).