795. *The Synthesis of Polycyclic Aromatic Hydrocarbons. Part IV.* Convenient Syntheses of Chrysene and three Methylchrysenes.*

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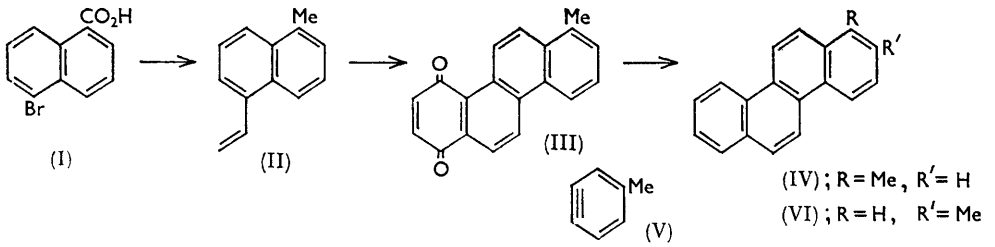
4-Methylbenzyne and 1-vinylnaphthalene give a separable mixture of 2- and 3-methylchrysene; benzyne with 1-vinylnaphthalene and 1-methyl-5-vinylnaphthalene gives chrysene and 1-methylchrysene, respectively, all in small yields. 1- and 2-Methylchrysene are formed when cholesterol is heated to 330°, and the former is also obtained by the lithium aluminium hydride reduction of 7-methylchrysene-1,4-quinone produced by the interaction of 1-methyl-5-vinylnaphthalene with benzoquinone. The unreliability of lithium aluminium hydride in this type of reduction is discussed.

It is known [1] that chrysene is formed when cholesterol is heated at a high temperature with palladium–charcoal, and also with selenium [2] at 240—310°. Cyclopentenophenanthrenes are also obtained from cholesterol by these or similar dehydrogenations, but it is now found that cholesterol, when heated alone in Pyrex to about 330°, undergoes thermal fission, rearrangement, and aromatisation. Various polycyclic aromatic hydrocarbons or their alkyl derivatives are produced under these conditions, which are attained in some domestic cooking processes, and this work is to be described elsewhere.

It has been claimed [3] that the product of heating cholesterol at 360° contained chrysene, as shown by an ultraviolet absorption spectrum, but this was very indefinite. Continuing our own investigations, we have isolated chrysene, 1-methylchrysene, and 2-methylchrysene from one of the fractions produced; there is also evidence of at least another chrysene derivative. It is of interest that chrysene [4] and 1-methylchrysene [5] may be carcinogenic.

These products were identified by direct comparisons with authentic specimens which, in the case of 1- and 2-methylchrysenes, have been synthesised by routes more convenient for our purpose than those already published.



The conversion in 70% yield of chrysene-1,4-quinone into chrysene by means of lithium aluminium hydride [6] suggests the similar production of 1-methylchrysene (IV) from the methylchrysenequinone (III). 1-Naphthoic acid was brominated to the 5-bromo-derivative (I) of which the carboxyl group was converted, with the bromine atom still intact, into methyl by the sequence: $\cdot CO_2H \longrightarrow \cdot CH_2 \cdot OH \longrightarrow \cdot CH_2Cl \longrightarrow \cdot CH_2I \longrightarrow \cdot CH_3$. (This synthesis of 1-bromo-5-methylnaphthalene is shorter and more convenient than that [7] from 1-amino-5-methylnaphthalene *via* the diazonium mercuric bromide complex, though the yield is much improved by adding the dry complex to refluxing xylene). The bromine atom in the bromomethylnaphthalene is replaced by hydroxyethyl

* Part III, Davies and Ennis, *J.*, 1960, 1488.

[1] Diels and Gädke, *Ber.*, 1927, **60**, 140.
[2] Diels, Gädke, and Körding, *Annalen*, 1927, **459**, 1.
[3] Falk, Goldstein, and Steiner, *Cancer Res.*, 1949, **9**, 438.
[4] Kennaway and Lindsey, *Brit. Med. Bull.*, 1958, **14**, 126.
[5] Shoppee and Gough, *Biochem. J.*, 1953, **54**, 630.
[6] Davies and Porter, *J.*, 1957, 4968.
[7] Bardhan, Nasipuri, and Jukherji, *J.*, 1957, 921.

by a Grignard reaction with ethylene oxide, and dehydration of this alcohol gives 1-methyl-5-vinylnaphthalene (II); this with *p*-benzoquinone forms 7-methylchrysene-1,4-quinone (III), which is reduced to the methylchrysene (IV). The yields are good except, surprisingly, in the reduction with lithium aluminium hydride, where the best yield (1·5%) was only obtained with selected samples of lithium aluminium hydride.

In a series of comparative reductions of chrysene-1,4-quinone the yields of chrysene vary from 2 to 34% with different commercial specimens of lithium aluminium hydride. The original yield of 70% was obtained from lump lithium aluminium hydride which was powdered immediately before use. It seems clear that lithium aluminium hydride cannot be relied on to give a good yield of the hydrocarbon in this type of reduction. It is curious that the highest yield of 1-methylchrysene is only 1·5% while the same lithium aluminium hydride gave a 34% yield of chrysene; the yield of chrysene was ten times greater than that of 1-methylchrysene when their quinones were reduced by distillation with zinc dust. An alternative and more rapid synthesis was sought by use of benzyne and its derivatives.

Benzyne, made [8] *in situ* from *o*-bromofluorobenzene, with 1-vinylnaphthalene gives chrysene and triphenylene. The latter and about 6% of 1-methylchrysene are formed when the methylvinylnaphthalene (II) is used. From 1-vinylnaphthalene and 4-methylbenzyne (V), prepared from 4-bromo-3-fluorotoluene, 2- (VI) and 3-methylchrysene are formed, both in very low yield; no triphenylene derivative was isolated though in all three reactions much yellow polymer was formed. The initial non-aromatic addition product was never isolated. This simultaneous formation of the 2- and 3-methylchrysenes—which are easily separated and identified—is the first instance, in our hands, of two structural isomers being produced simultaneously in Diels–Alder syntheses.

Experimental

The Synthesis of 1-Methylchrysene.—(i) *From 1-naphthoic acid.* 1-Naphthoic acid was brominated (75% yield) [9] and the 5-bromo-1-naphthoic acid (5·5 g.) slowly added to a suspension of lithium aluminium hydride (1·65 g.) in dry ether (30 ml.). The mixture was then worked up with moist ether, ethanol, or ethyl acetate to give the 5-bromo-1-naphthylmethanol (4·7 g., 90·5%), m. p. 123—124° (lit.[9] m. p. 123—124°). The carbinol (5·0 g.) in ether (50 ml.)–benzene (10 ml.) was kept at room temperature with thionyl chloride (2 ml.) for 4 hr., the solvents and excess of thionyl chloride were removed under reduced pressure, and the residual *1-bromo-5-chloromethylnaphthalene* crystallised, forming needles (from methanol) (4·8 g., 89%), m. p. 82—82·5° (Found: C, 51·9; H, 3·1. $C_{11}H_8BrCl$ requires C, 51·7; H, 3·15%).

1-Bromo-5-iodomethylnaphthalene. This *halide* (5·0 g.; 92%) is obtained in pale yellow needles, m. p. 110—111° (from ethanol) when the chloromethyl compound (4·0 g.) is refluxed in dry acetone (30 ml.) for 4 hr. with sodium iodide (4·0 g.), and the residue washed with water (Found: C, 38·3; H, 2·6. $C_{11}H_8BrI$ requires C, 38·1; H, 2·3%). For this preparation the crude chloromethyl compound is suitable. 1-Bromo-5-methylnaphthalene is formed (0·61 g., 79·8%; m. p. 62—63°) when the iodomethyl compound (1·2 g.) is added at room temperature to a suspension of lithium aluminium hydride (0·15 g.) in ether (10 ml.), and the crude product taken up in isohexane and passed through alumina. The solid obtained from the eluate crystallised from methanol in needles, m. p. 62—63° (picrate, m. p. 109—110°) (lit.,[10] m. p.s 63—64° and 110—111°, respectively).

2-(5-Methyl-1-naphthyl)ethanol was prepared by a similar method to that of Bardhan *et al.*[7] 1-Bromo-5-methylnaphthalene (10 g.) in ether (20 ml.) was added slowly to magnesium (1·3 g.) in ether (5 ml.), and the solution refluxed for ½ hr.; benzene (20 ml.) was added and then, slowly at 0°, ethylene oxide (3 g.) in ether (5 ml.). After 1 hr. at room temperature the mixture was refluxed for 1 hr. and worked up. The ethanol derivative had b. p. 150—156°/1·0 mm., m. p. 37—39° (6·3 g., 75%). Newman and Cline [11] give b. p. 154—157/1·0 mm., m. p. 40·2—41·2°. The use of a large excess of ethylene oxide should be avoided, since it leads

[8] Wittig and Ludwig, *Angew. Chem.*, 1956, **68**, 40.
[9] Shoesmith and Rubbli, *J.*, 1927, 3098.
[10] Vesely, Stursa, Olejnicek, and Rein, *Coll. Czech. Chem. Comm.*, 1930, **2**, 145.
[11] Newman and Cline, *J. Org. Chem.*, 1951, **16**, 934.

to troublesome polymer formation. The yield was not improved by use of a more active halide.

1-*Methyl*-5-*vinylnaphthalene*. This *hydrocarbon*, b. p. 154—157° (3·3 g., 73%), was obtained when the above alcohol (5 g.) in toluene (8 ml.) was added to molten potassium hydroxide in a distillation flask at 240°/20 mm. (Found: C, 92·9; H, 7·2. $C_{13}H_{12}$ requires C, 92·8; H, 7·2%).

7-*Methylchrysene*-1,4-*quinone*. This separated when the vinyl compound (0·5 g.) and benzoquinone (1·0 g.) were heated in acetic acid on the water bath for 6 hr. The product was washed with ether; it crystallised from glacial acetic acid in orange-red needles (0·51 g., 63%), m. p. 260—260·2° (Found: C, 83·5; H, 4·6. $C_{19}H_{12}O_2$ requires C, 83·8; H, 4·4%).

1,4-*Diacetoxy*-7-*methylchrysene*. The *diacetate* was formed when the quinone (25 mg.), sodium acetate (50 mg.), and zinc dust (50 mg.) were heated in acetic anhydride on the water bath for 1 hr., glacial acetic acid (2 ml.) added, and the hot solution filtered and diluted with water. It crystallised from ethanol in needles (29 mg., 88%), m. p. 233·5—234° (Found: C, 76·8; H, 5·1. $C_{23}H_{18}O_4$ requires C, 77·1; H, 5·1%).

1-*Methylchrysene*. An authentic specimen, m. p. 253—254°, was made by Shoppee and Gough's method; it gave a 2,4,7-*trinitrofluorenone* derivative as fine orange needles, m. p. 242—242·5°, from toluene (Found: N, 7·6. $C_{19}H_{14}$,$C_{13}H_5O_7N_3$ requires N, 7·5%).

Reduction of 7-*Methyl*-1,4-*chrysenequinone*.—Davies and Porter's method [6] for the reduction with lithium aluminium hydride of chrysene-1,4-quinone was used with the specimen of lithium aluminium hydride which gave a 34% yield of chrysene (see below). 7-Methylchrysene-1,4-quinone (0·5 g.) then gave 1-methylchrysene (7 mg., 1·5%), m. p. and mixed m. p. 253—254° (trinitrofluorenone derivative, m. p. 241·5—242·5°).

A mixture of zinc dust (5 g.) and the quinone (0·2 g.) was heated in a stream of nitrogen, and the sublimate chromatographed in toluene on alumina, giving 1-methylchrysene (2 mg.). This compares with 20 mg. of chrysene, m. p. 253—254°, from the same quantity of chrysene-1,4-quinone under the same conditions. This chrysene gave a trinitrofluorenone derivative, m. p. 248—249° (lit.,[12] m. p. 248·8—249°). Reduction by fusion with zinc dust of equal weights (0·2 g.) of chrysene-1,4-quinone, zinc dust, sodium chloride, together with zinc chloride (5 g.) at 290° gave only 2 mg. of chrysene.[13]

Use of Benzyne and Methylbenzyne in the Synthesis of Chrysenes.—Chrysene. *o*-Bromofluorobenzene (2 g.) in tetrahydrofuran (8 ml.) was slowly added to magnesium (300 mg.) in a solution of 1-vinylnaphthalene (1·0 g.) and *o*-bromofluorobenzene (0·1 g.) in tetrahydrofuran (2 ml.). After refluxing had ceased, the mixture was heated on the water bath for 10 min., chloroform (10 ml.) was added, the solution was poured into dilute hydrochloric acid, and the washed organic phase dried ($MgSO_4$) and the solvents were removed. The residual oil was chromatographed in isohexane on alumina; starting materials were first eluted, followed by triphenylene (10 mg.), and finally chrysene (40 mg.), m. p. and mixed m. p. 253—254° (identity also confirmed by ultraviolet absorption spectra). Triphenylene, m. p. and mixed m. p. 196—197°, was similarly identified. None of the initial dihydro-addition product was isolated.

1-*Methylchrysene*. *o*-Bromofluorobenzene (3·9 g.) in tetrahydrofuran (5 ml.) was added, sufficiently slowly to keep the reaction under control, to a mixture of 1-methyl-5-vinylnaphthalene (1 g.), magnesium (0·58 g.), and *o*-bromofluorobenzene (0·1 g.) in tetrahydrofuran (20 ml.), and the process was thereafter identical with the synthesis of chrysene. Triphenylene (90 mg.) was formed together with 1-methylchrysene (80 mg., 5·6%), m. p. 253—254°, identical (absorption spectra and mixed m. p.) with authentic material. The trinitrofluorenone derivative had m. p. 242—242·5°.

2- *and* 3-*Methylchrysenes*. An intermediate in the preparation of 4-methylbenzyne was 4-bromo-3-nitrotoluene [14] (90%). It was however, necessary to use 3 moles of hydrogen bromide per mole of the parent nitrotoluidine.

4-*Bromo*-3-*fluorotoluene*. 3-Amino-4-bromotoluene [15] (10 g.) was diazotised in hydrochloric acid, the mixture filtered, and the filtrate stirred vigorously as sodium borofluoride (0·075 mole) in water (25 ml.) was added. After ½ hr. at 5°, the precipitate was filtered off, washed with sodium borofluoride solution (5%; 8 ml.), cold methanol (10 ml.), and ether. The pale pink salt (7·6 g., 51%) was air-dried overnight; 5 g. were decomposed by heat, and the product was

[12] Orchin and Woolfolk, *J. Amer. Chem. Soc.*, 1946, **68**, 1727.
[13] Clar, *Ber.*, 1939, **72**, 1645.
[14] Gibson and Johnson, *J.*, 1929, 1246.
[15] Hodgson and Moore, *J.*, 1926, 2036.

steam-distilled. The methylene chloride extract of the steam distillate was washed with dilute sodium hydroxide solution and dried ($MgSO_4$), the solvent removed; the residual *4-bromo-3-fluorotoluene* (2·0 g., 60%) (Found: C, 44·6; H, 3·25. C_7H_6BrF requires C, 44·5; H, 3·2%) had b. p. 184—186°/760 mm. The specimen made by Varma *et al.*[16] by brominating 3-fluorotoluene had b. p. 169°/756 mm., was not analysed, and may have been impure.

4-Bromo-3-fluorotoluene (1·9 g.) in tetrahydrofuran (5 ml.) was slowly added to magnesium (0·270 g.) in a solution of 1-vinylnaphthalene (4·0 g.) and 4-bromo-3-fluorotoluene (0·1 g.) in tetrahydrofuran (15 ml.). When refluxing had ceased the mixture was heated on the water bath for 10 min. and worked up as in the chrysene synthesis; however, chromatography on alumina afforded only slight separation. The eluates were examined by means of their ultraviolet spectra and those containing the methylchrysenes were combined and passed through acetylated cellulose, prepared according to Spotswood.[17] The solvent system used was ethanol–toluene–water (17 : 4 : 1). Yellow polymer was first eluted followed by 2-methylchrysene (24 mg.), m. p. 228—229°, and 3-methylchrysene (14 mg.), m. p. 173—174° (both from ethanol). The total yield of the two methylchrysenes was of the order of 50 mg. No triphenylene derivative was isolated.

Reduction of Chrysene-1,4-quinone with Lithium Aluminium Hydride.—The method [6] was that of Davies and Porter, who however used lithium aluminium hydride supplied in large lumps, bought in 1950; these were powdered just before use. The present work was done with the modern product supplied already finely powdered (except in one instance of a private gift from Nicholas Pty. Ltd.). The hydride previously used [6] was not completely soluble in dilute hydrochloric acid, whereas the modern preparations are. Their interaction product with chrysenequinone remained coloured, varying with different batches of hydride from yellow to orange, unlike that of the above authors whose solutions became almost colourless. Additional refluxing had no effect on the final product which was sensitive to aerial oxidation, quickly becoming coloured and insoluble. The hydrocarbon present was isolated by chromatography on alumina.

Five batches of commercial lithium aluminium hydride were used, the percentage yields of chrysene being 2, 6, 8, 17, and 34. (A solution of lithium aluminium hydride freshly made from lithium hydride and anhydrous aluminium chloride gave a 25% yield of chrysene.) All batches gave good reductions (90% yield) of 1-naphthoic acid to the carbinol.

No chrysene or recognisable product was obtained when lithium aluminium hydride was replaced by mixtures of lithium aluminium hydride and aluminium chloride corresponding to the hydrides AlH_3,AlH_2Cl and $AlHCl_2$, the requisite proportion of available hydrogen to the quinone being maintained.

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[16] Varma, Venkataraman, and Nilkantiah, *J. Indian Chem. Soc.*, 1944, **21**, 112.
[17] Spotswood, *J. Chromat.*, 1960, **3**, 101.