[Contribution from the Chemical Laboratory of Duke University]

Aromatic Cyclodehydration. VIII.[1] 6-Methyl- and 5-Methyl-6-ethylchrysene

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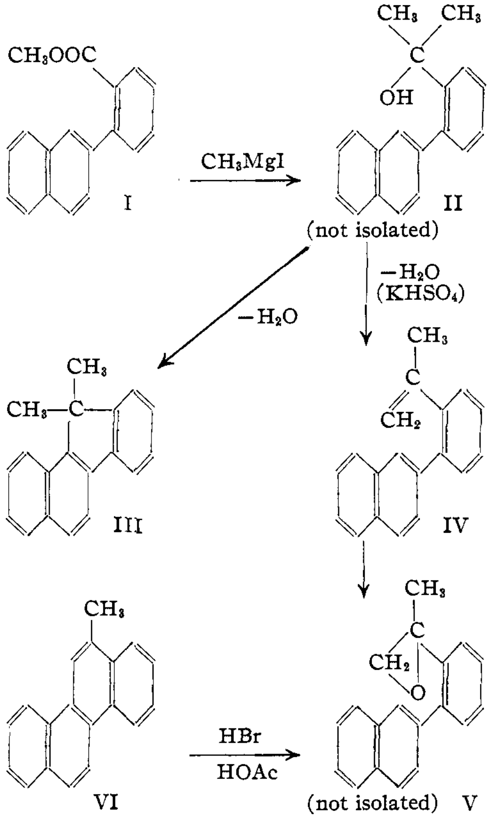
In preceding papers of this series we have described the synthesis of phenanthrene hydrocarbons by cyclization of biphenyl olefin oxides. The present communication deals with our efforts to extend this type of ring closure to the synthesis of alkyl chrysenes.

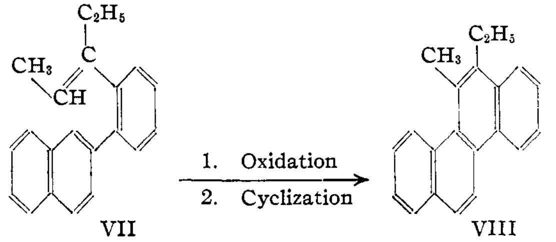
Chrysoquinone was fused with potassium hydroxide and lead dioxide according to the method of Graebe and Honigsberger[2] to give a mixture of α- and β-chrysenic acids as their potassium salts. The alpha acid, being the higher melting and more easily isolated of the two, was used as a starting material. The methyl ester (I) was treated with methylmagnesium iodide to give a product which probably consisted chiefly of the carbinol II.



Distillation under reduced pressure of this material yielded a hydrocarbon (m. p. 148°) having the composition of the desired olefin (IV), but giving no test for unsaturation. An attempt to convert this material to 6-methylchrysene by oxidation and cyclization was fruitless. We believe the hydrocarbon to be 11,11-dimethylchrysofluorene (III).

The desired olefin (IV) was obtained by heating the crude product of the Grignard reaction with potassium bisulfate. The dehydration product obtained under these conditions was a liquid at room temperature. This was oxidized with monoperphthalic acid and the crude oxide (V) cyclized by the action of hydrobromic and acetic acids. The hydrocarbon thus afforded was identical in every respect with the 6-methylchrysene (VI) of Newman[3] and showed no depression of melting point when mixed with an authentic specimen. The over-all yield was 13%, calculated from the α-chrysenic acid.

Next, this synthesis was repeated using ethylmagnesium bromide instead of methylmagnesium iodide. By analogy the olefin obtained by dehydration of the crude carbinol should have structure VII and the final cyclization product should be 5-methyl-6-ethylchrysene (VIII). Since our hydrocarbon has the expected composition, we have assigned to it the structure of the dialkylchrysene. This compound is of particular interest in the light of the observation of Hewett[4] that a homolog, 5,6-dimethylchrysene, has carcinogenic activity.



We are indebted to Dr. M. S. Newman for the gift of a sample of 6-methylchrysene.

Experimental

Synthesis of 6-Methylchrysene

2′-Carbomethoxy-2-phenylnaphthalene (I).—Ten grams of α-chrysenic acid (m. p. 188°) was dissolved in 125 cc.

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[1] For the preceding paper of this series see This Journal, 62, 2806 (1940).

[2] Graebe and Honigsberger, *Ann.*, 311, 257 (1900); Graebe, *ibid.*, 335, 122 (1904).

[3] Newman, This Journal, 60, 2947 (1938). Fieser, Joshel and Seligman, attempting the preparation of 5-methylchrysene, likewise obtained some of this hydrocarbon, *ibid.*, 61, 2134 (1939).

[4] Hewett, *J. Chem. Soc.*, 293 (1940).

of absolute methyl alcohol and the solution saturated with hydrogen chloride and allowed to stand overnight. After evaporation of most of the alcohol, water was added and the mixture extracted with ether. The ethereal extract was washed, dried and concentrated. Upon addition of petroleum ether, the ester precipitated as colorless cubes, m. p. 63°, yield 9 g. (86%).

2′-(2-Phenylnaphthalene)-dimethylcarbinol(?) (II).—A Grignard reagent was prepared from 1.3 g. of magnesium and 9.7 g. of methyl iodide. To this was added an ethereal solution containing 4.5 g. of the ester prepared above and the mixture refluxed overnight. The mixture was decomposed with a 20% ammonium chloride solution. Upon evaporation of the solvent, the carbinol was obtained as a yellow oil. This was not purified, but used directly in the following preparations.

11,11-Dimethylchrysofluorene (III).—One run such as described above was submitted to distillation at 18 mm. pressure. The product solidified in the receiver and upon recrystallization from acetic acid, gave colorless, irregular plates, m. p. 148–148.5°; yield 2.5 g. (56%, calcd. from the ester).

Anal. Calcd. for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.53; H, 6.60.

The hydrocarbon gave no evidence of unsaturation when tested with bromine in carbon tetrachloride solution. A concentrated alcoholic solution of the hydrocarbon deposited no picrate when treated with an alcoholic solution of picric acid.

A sample of the hydrocarbon (0.8 g.) in chloroform was treated with an excess of perbenzoic acid. After standing for twenty-four hours, the acids were extracted and the neutral fraction, after evaporation of the chloroform, was dissolved in 5 cc. of acetic acid and 5 cc. of 34% hydrobromic acid added. The mixture was refluxed for forty-eight hours and then diluted with water and extracted with ether. The ethereal extract was concentrated and the residue sublimed under reduced pressure. The sublimate, once recrystallized from alcohol, melted at 147–148° and was identical with the starting material; yield 0.29 g.

2′-Isopropenyl-2-phenylnaphthalene (IV).—The crude carbinol (II) prepared from 12.4 g. of the methyl ester (I) of α-chrysenic acid was dehydrated by heating it for one hour at 160° with 25 g. of potassium bisulfate. The olefin was extracted with benzene and vacuum distilled. The product was a yellow liquid, b. p. 180–185° (4 mm.); yield 5.8 g. (47% calculated from the ester).

6-Methylchrysene (VI).—The olefin (2.6 g.) was dissolved in ether and added to an ether solution containing three times its molecular equivalent of monoperphthalic acid.[5] After standing overnight the acids were extracted with sodium bicarbonate solution and the ether solution concentrated. The yellow viscous oil thus obtained was taken up in about 60 cc. of acetic acid and refluxed with 30 cc. of 40% hydrobromic acid for twenty hours. The mixture was then cooled and the crude hydrocarbon collected and dissolved in benzene. Once distilled under reduced pressure, and twice recrystallized from benzene–alcohol, the methylchrysene was obtained as colorless needles, m. p. 159.5°; yield 0.83 g. (31% calculated from the olefin or 13% calculated from α-chrysenic acid).

Anal. Calcd. for $C_{19}H_{14}$: C, 94.18; H, 5.82. Found: C, 94.16; H, 6.02.

A mixed melting point determination with an authentic specimen of 6-methylchrysene gave a melting point of 159.5°. The picrate crystallized from alcohol as orange-red needles, m. p. 170°.

5-Methyl-6-ethylchrysene (VIII).—A Grignard reagent was prepared from 1.5 g. of magnesium and 9.5 g. of ethyl bromide, and a solution of 4 g. of the methyl ester (I) of α-chrysenic acid added. The mixture was refluxed overnight, decomposed with ammonium chloride solution and worked up in the usual way. The crude carbinol thus obtained was dehydrated by heating at 160° with potassium bisulfate. The olefin was extracted with benzene and was obtained as a brown oil upon evaporation of the solvent. This material was dissolved in ether, treated with three molecular equivalents of monoperphthalic acid and allowed to stand for twelve hours. The product was worked up and cyclized exactly as in the case of the methylchrysene. The product crystallized from benzene–alcohol as colorless needles, m. p. 125.5–126.5°; yield 1.0 g. (24% calcd. from the ester).

Anal. Calcd. for $C_{21}H_{18}$: C, 93.30; H, 6.70. Found: C, 93.15; H, 6.64.

The picrate formed bright red needles from alcohol, m. p. 94.5–95.5°.

Summary

The olefin oxide type of aromatic cyclodehydration, previously used only for the synthesis of phenanthrene hydrocarbons, has now been applied to the synthesis of two chrysene derivatives. 6-methyl- and 5-methyl-6-ethylchrysene.

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[5] Böhme, "Organic Syntheses," Vol. 20. 1940, p. 70.