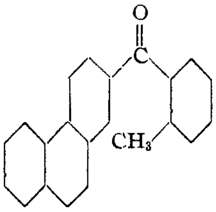
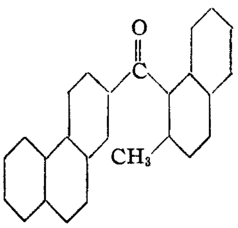
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Synthesis of Phenanthrene Derivatives. III. *o*-Toluoyl- and *β*-Methylnaphthoylphenanthrenes[1]

BY W. E. BACHMANN AND L. H. PENCE

From the reaction between *o*-toluoyl chloride, phenanthrene and aluminum chloride in carbon disulfide Clar[2] obtained an uncrystallizable oil; from the nature of the compounds which resulted on pyrolysis of the oil, he concluded that his product contained 2-, 3- and 9-*o*-toluoylphenanthrene, the 9-isomer being present in the largest proportion. Cook[3] likewise failed to obtain a crystalline product in his attempt to synthesize 3-*o*-toluoylphenanthrene by interaction of 3-phenanthroyl chloride and *o*-tolylmagnesium bromide. We have now found that if nitrobenzene is used as the solvent in the Friedel and Crafts reaction a mixture of 2-*o*-toluoylphenanthrene (I) and 3-*o*-toluoylphenanthrene is obtained which can be separated readily into its two crystalline components. These results are similar to those obtained recently in the benzoylation of phenanthrene.[4]


I


II

The structures of these new ketones were established by synthesis; reaction of 2- and 3-cyanophenanthrene with *o*-tolylmagnesium bromide gave the ketone-imines, which were easily hydrolyzed to the ketones. We have also prepared 9-*o*-toluoylphenanthrene by this reaction; this isomer had been prepared previously from 9-phenanthrylmagnesium bromide and *o*-tolunitrile.[5] These two methods now make 9-*o*-toluoylphenanthrene readily available for the preparation of 1,2,3,4-dibenzanthracene, the pyrolysis product of the ketone. Cook, Hieger, Kennaway and Mayneord[6] reported that they were uncertain whether 1,2,3,4-dibenzanthracene possessed cancer-producing properties, for most of their tests were made on impure specimens.

Since the 2-, 3- and 9-cyanophenanthrenes can be readily prepared,[7] the Grignard reaction offers one of the best methods for obtaining these pure ketones. We have used the reaction also to synthesize 2-(2′-methyl-1′-naphthoyl)-phenanthrene (II) and its 3- and 9-isomers; of these, the 3-isomer has been prepared previously by Cook[3] and the 9-isomer by Fieser and Dietz[8] by other methods. The ketone-imines which are obtained from the cyanophenanthrenes and the Grignard reagent from 2-methyl-1-bromonaphthalene are hardly affected when they are refluxed with dilute hydrochloric acid, presumably because of steric hindrance; complete hydrolysis to the ketones was effected at 200° in a sealed tube.

From the pure *o*-toluoylphenanthrenes and *β*-methylnaphthoylphenanthrenes we are preparing the polycyclic hydrocarbons that can be derived from them by pyrolysis. We are employing the Grignard reaction for making a large number of ketones for the purpose of obtaining polycyclic hydrocarbons and derivatives with carcinogenic properties.

Experimental

Reaction of *o*-Toluoyl Chloride with Phenanthrene.—To an ice-cold solution of 32 g. of aluminum chloride in 125 cc. of nitrobenzene was added a solution of 20 g. of phenanthrene in 50 cc. of nitrobenzene followed by 17 g. of *o*-toluoyl chloride. After being kept cold for two hours, the mixture was allowed to stand at room temperature for twelve hours and then hydrolyzed. The product which remained after the nitrobenzene had been removed by steam distillation was distilled under reduced pressure (200–265° at 3 mm.). The distillate was dissolved in a mixture of acetone and alcohol; on cooling, 5 g. of phenanthrene crystallized out. After the removal of the phenanthrene the chilled solution was "seeded" with crystals of synthetic 3-*o*-toluoylphenanthrene (prepared from 3-cyanophenanthrene). After several crops of the 3-isomer had been obtained, the mother liquor was "seeded" with synthetic 2-*o*-toluoylphenanthrene. After several recrystallizations of the various fractions there was obtained 6.08 g. (24%) of 3-*o*-toluoylphenanthrene and 0.85 g. (3.4%) of the 2-isomer.

2-*o*-Toluoylphenanthrene crystallizes in thin colorless plates from a mixture of acetone and alcohol; m. p.

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(1) From part of the Ph.D. dissertation of L. H. Pence.

(2) Clar, *Ber.*, **62**, 350, 1574 (1929).

(3) Cook, *J. Chem. Soc.*, 499 (1931).

(4) Bachmann, THIS JOURNAL, **57**, 555 (1935).

(5) Bachmann, *ibid.*, **56**, 1363 (1934).

(6) Cook, Hieger, Kennaway and Mayneord, *Proc. Roy. Soc.* (London), **B111**, 455 (1932).

(7) Mosettig and van de Kamp, THIS JOURNAL, **54**, 3328 (1932); Bachmann, References 4 and 5.

(8) Fieser and Dietz, *Ber.*, **62**, 1827 (1929).

115–116°. The ketone gives a deep-red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{22}H_{16}O$: C, 89.2; H, 5.4. Found: C, 88.8; H, 5.4.

3-*o*-Toluoylphenanthrene was obtained in clusters of thin colorless plates by recrystallization from 80% acetic acid; m. p. 89–90°. A deep-red color forms when the ketone is added to concentrated sulfuric acid.

Anal. Calcd. for $C_{22}H_{16}O$: C, 89.2; H, 5.4. Found: C, 88.8; H, 5.4.

Synthesis of *o*-Toluoylphenanthrenes.—To the Grignard reagent which had been prepared from 10 g. of *o*-bromotoluene in 20 cc. of ether was added 25 cc. of benzene and 4.3 g. of cyanophenanthrene (2-, 3- or 9-isomer). After the mixture had been refluxed for four hours, it was cooled and shaken with dilute acetic acid. Addition of concentrated hydrochloric acid to the ether–benzene layer precipitated the imine-hydrochloride as an oil which soon crystallized. The compound was hydrolyzed to the ketone when it was refluxed with water for several hours; the ketones were recrystallized twice from acetone–alcohol. The yields were: 2-*o*-toluoylphenanthrene, 48%; 3-*o*-toluoylphenanthrene, 79%; 9-*o*-toluoylphenanthrene, 83%.

Synthesis of β-Methylnaphthoylphenanthrenes.—To the Grignard reagent which had been prepared from 12.5 g. of 1-bromo-2-methylnaphthalene in 40 cc. of ether and 40 cc. of benzene was added 5 g. of cyanophenanthrene (2-, 3- or 9-isomer). After being refluxed for four hours, the mixture was shaken with dilute hydrochloric acid; the imine-hydrochloride, which precipitated and was filtered off, was hydrolyzed by 1 cc. of concentrated hydrochloric acid and 50 cc. of water in a sealed tube at 200° for six hours.

2-(2′-Methyl-1′-naphthoyl)-phenanthrene (II) was purified by recrystallization from acetone–alcohol and then from acetic acid; it crystallizes in fine colorless needles; yield, 73%. When heated slowly from room temperature the compound melts at 184–185°; however, the compound melts completely when the melting point tube is placed in a bath at 168–170°, the melt solidifies and remelts at 184–185°. The ketone gives a deep-red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{26}H_{18}O$: C, 90.2; H, 5.2. Found: C, 89.7; H, 5.2.

3-(2′-Methyl-1′-naphthoyl)-phenanthrene was obtained as colorless prisms after recrystallization from acetone–alcohol, distillation under reduced pressure and finally recrystallization from acetic acid; yield, 51%; m. p. 148.5–149.5° (Cook reported 145–146° for the ketone obtained from 3-phenanthroyl chloride and 2-methyl-1-naphthylmagnesium bromide). A crimson color is formed when the ketone is added to concentrated sulfuric acid.

A 65% yield of 9-(2′-methyl-1′-naphthoyl)-phenanthrene was obtained after the ketone had been recrystallized from toluene and twice from acetone; m. p. 176–177° (Fieser and Dietz gave 170° for the ketone made from 9-phenanthroyl chloride and 2-methyl-1-naphthylmagnesium bromide). The ketone crystallizes in clusters of thin sheets and gives a red color with concentrated sulfuric acid.

Summary

2- and 3-*o*-toluoylphenanthrenes have been isolated from the reaction between *o*-toluoyl chloride, phenanthrene and aluminum chloride in nitrobenzene.

2-, 3- and 9-*o*-toluoylphenanthrenes and 2-, 3- and 9-(2′-methyl-1′-naphthoyl)-phenanthrenes have been synthesized from the corresponding cyanophenanthrenes through the Grignard reaction.

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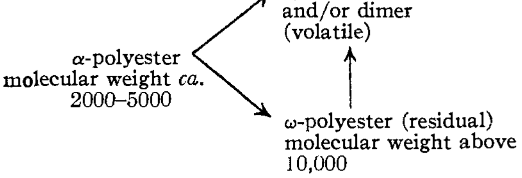
Polydecamethylene Oxide[1]

By Julian W. Hill

In a previous paper of this series[2] it was shown that polyesters, when heated under appropriate catalytic conditions in an evacuated vessel designed for the quick and irreversible removal of volatile material, undergo the series of transformations represented in the scheme



In the case of the polymethylene carbonates, the end-products under favorable circumstances were almost all obtained as volatile depolymerizate and very little residue remained. However, in certain instances in which it is now believed that the pressure rose too high on account of inadequate pumping, the residue became rubbery early in the experiments and distillation soon practically ceased. During the course of a large number of experiments on the depolymerization of polymeric decamethylene carbonate, a considerable amount of these residues accumulated, and it was thought worth while to attempt the recovery of decamethylene glycol from them by hydrolysis. Comparatively little

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(1) Paper XXVII on Polymerization and Ring Formation; Paper XXVI, This Journal, **57**, 935 (1935).

(2) *ibid.*, **55**, 5031 (1933).