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.

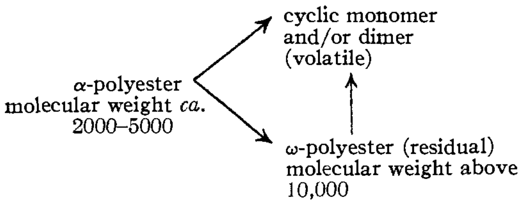
ANN ARBOR, MICHIGAN RECEIVED APRIL 26, 1935

[CONTRIBUTION NO. 156 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

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).

glycol was recovered in this way. The major product isolated from the hydrolysis mixture was a wax-like material which examination showed to be polydecamethylene oxide[3]

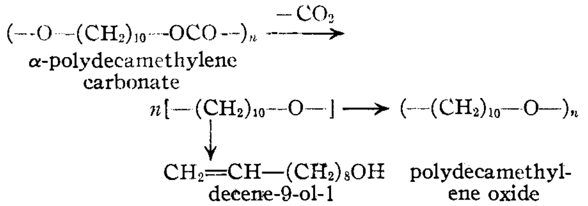
$$\cdots(CH_2)_{10}—O—(CH_2)_{10}—O—(CH_2)_{10}—O—(CH_2)_{10}—O\cdots$$

The hydrolysis of the rubbery residue was carried out by means of alcoholic potassium hydroxide. The resulting solution was filtered from a small amount of insoluble matter. Most of the alcohol was distilled and replaced by hot water. The insoluble upper layer was allowed to solidify and separated. It was then heated under vacuum in a Claisen flask until the distillation of decamethylene glycol ceased. The residue was repeatedly extracted with boiling water until no more glycol could be removed in this way. It was then recrystallized once from acetone, once from alcohol, dried and analyzed.

Anal. Calcd. for $(CH_2)_{10}O$: C, 76.92; H, 12.82; mol. wt., 156. Found: C, 76.18, 76.31; H, 12.44, 12.37; mol. wt. (cryoscopically in benzene), 1200, 1200.

It was soluble in benzene, carbon tetrachloride, chloroform and concentrated sulfuric acid, insoluble in cold alcohol, ethyl acetate and acetone, and insoluble, hot or cold, in petroleum fractions. From recrystallizing solvents, it separated as a microcrystalline powder of melting point 58–60°. From a melt it was obtained as a soft wax.

The probable course of the reaction leading to the polyether may be represented by the following scheme in which it is supposed that the polyester undergoes scission and gives carbon dioxide and decamethylene oxide radicals. These may rearrange to decene-9-ol-1 or combine to give the polymeric ether.



$$\begin{tikzcd}
(—O—(CH_2)_{10}—OCO—)_n \arrow[r, "-CO_2"] & {} \\
n[—(CH_2)_{10}—O—] \arrow[r] \arrow[d] & (—(CH_2)_{10}—O—)_n \\
CH_2{=\!=}CH—(CH_2)_8OH &
\end{tikzcd}$$

Support for this mechanism is the fact that in the depolymerization experiments yielding considerable polyether residues, the distillates were always contaminated with decene-9-ol-1.[4]

The constitution of the material was established by its analyses and molecular weight and by its transformation by the following reactions to decamethylene glycol.

$$(—(CH_2)_{10}—O—)_n \xrightarrow{HI} I(CH_2)_{10}I— \xrightarrow{KOAc}$$
$$AcO(CH_2)_{10}OAc \xrightarrow{H_2O} HO(CH_2)_{10}OH$$

The intermediate compounds were not purified.

Twenty grams of recrystallized polymer, 40 cc. of glacial acetic acid, and 75 cc. of constant boiling hydriodic acid were refluxed together for six hours. The resulting dark red lower layer was separated and refluxed briefly with a suspension of calcium carbonate which removed the color. The heavy oil was recovered by means of an ether extraction and then refluxed with 40 g. of powdered freshly fused potassium acetate, 15 cc. of glacial acetic acid and 3 cc. of acetic anhydride for four hours. This mixture was drowned in water and the product recovered by ether extraction. This was then hydrolyzed by refluxing for ten hours with a solution of 15 g. of sodium hydroxide in 150 cc. of 50% alcohol. The alcohol was removed by steam distillation which was continued for several hours to remove a very small amount of oil, which smelled like decene-9-ol-1. The oil on top of the residual liquid solidified and from it was isolated, by two crystallizations from benzene, 5 g. of pure decamethylene glycol, m. p. 71–72°. It showed no depression in melting point when mixed with a known sample of decamethylene glycol.

Summary

The depolymerization of polydecamethylene carbonate, under certain experimental conditions, pursues an abnormal course and yields a distillate contaminated with decene-9-ol-1 together with a large amount of residue. This residue has been examined and found to consist largely of a polymeric substance which has been characterized as polydecamethylene oxide. A mechanism for the side reaction has been suggested.

WILMINGTON, DEL. RECEIVED APRIL 26, 1935

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[3] It is of interest to mention that Franke [*Monatsh.*, **53–54**, 577 (1929), and earlier papers] obtained, by the dehydration of decamethylene glycol with sulfuric acid, not a decamethylene oxide, but α-amyl pentamethylene oxide.

[4] THIS JOURNAL, **55**, 5037 (1933).