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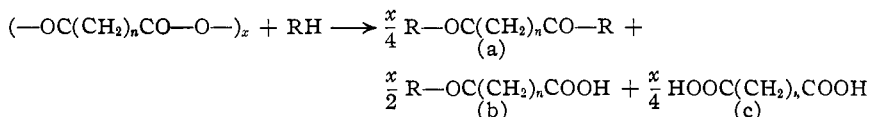
STUDIES ON POLYMERIZATION AND RING FORMATION.
 XVII. FRIEDEL-CRAFTS SYNTHESSES WITH THE
 POLYANHYDRIDES OF THE DIBASIC ACIDS

By JULIAN W. HILL

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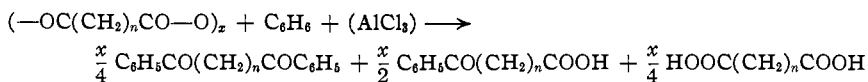
It has been shown that the polymeric anhydrides of aliphatic dibasic acids react smoothly and normally as acid anhydrides with aniline,¹ with phenol,^{1a} with ammonia,² and with diethylamine.^{2b} In each reaction three products are formed. The course of the reactions is shown by the following scheme, which does not consider the end groups of the polyanhydride



where R is C₆H₅NH—, C₆H₅O—, NH₂— or (C₂H₅)₂N—

It has been demonstrated on theoretical grounds that the products of types (a), (b) and (c) should be formed in the molecular ratio of 1:2:1. This has been verified quantitatively in the aniline reaction.¹

The dibasic acid polyanhydrides have now been found to react typically with benzene in the presence of anhydrous aluminum chloride to yield dibenzoyl alkane, ω -benzoyl fatty acid, and dibasic acid.



This reaction has been carried out with polymeric adipic and sebacic anhydrides and benzene. There is no reason to doubt that it is perfectly general and applicable to any polymeric dibasic anhydride and any suitable aromatic hydrocarbon.

This reaction is particularly interesting in providing a convenient method of synthesis for the ω -benzoyl fatty acids which have heretofore been prepared by more elaborate syntheses or in very low and uncertain yields as by-products in the Friedel-Crafts reaction of dibasic acid chlorides with aromatic hydrocarbons.³

Experimental Part

Friedel-Crafts Reaction between Adipic Polyanhydride and Benzene.—One hundred and forty-six grams (one mole) of adipic acid was refluxed with 400 cc. of acetic

¹ (a) Hill, *THIS JOURNAL*, **52**, 4110 (1930); (b) Hill and Carothers, *ibid.*, **54**, 1569 (1932).

² (a) Étaix, *Ann. chim.*, [7] **9**, 356 (1896); (b) Einhorn and Diesbach, *Ber.*, **39**, 1222 (1906).

³ Auger, *Ann. chim.*, [6] **22**, 360 (1891); Étaix, *ibid.*, [7] **9**, 391 (1896).

anhydride for six hours. The excess acetic anhydride and the acetic acid formed in the reaction were removed by distillation *in vacuo* up to 120° bath temperature. The resulting polyanhydride^{1a} was dissolved in 400 cc. of warm, dry benzene. Three hundred grams of anhydrous aluminum chloride was suspended in 1500 cc. of dry benzene contained in a 3-necked 3-liter flask fitted with a reflux condenser and a mechanical stirrer.

The anhydride solution was added with stirring over a period of one hour and the mixture allowed to stand overnight. The product was decomposed in ice and 250 cc. of concentrated hydrochloric acid added. The benzene layer was separated and extracted with dilute aqueous sodium hydroxide. The water phase deposited a small amount of crystals on standing which were identified after recrystallization from water as adipic acid by a mixed melting point determination.

The alkaline solution was acidified and the crystalline precipitate of ω -benzoyl-valeric acid filtered off: weight dry, 78 g.; yield, 75%. The product was recrystallized from a benzene-petroleum ether mixture, m. p. 70–71°.⁴

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.9; H, 6.8. Found: C, 70.1; H, 6.7.

The extracted benzene was distilled to a small volume and chilled; 56.5 g. of dibenzoylbutane was obtained, yield 85%. Recrystallized from alcohol, it was slightly pink and melted at 105–106°.⁵ It was identified by means of a mixed melting point determination with an authentic specimen.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.2; H, 6.8. Found: C, 80.6; H, 7.0.

Friedel-Crafts Reaction between Sebacic Polyanhydride and Benzene.—One hundred and one grams (0.5 mole) of sebacic acid was refluxed with 300 cc. of acetic anhydride for five hours. The excess anhydride and the acetic acid formed were distilled off *in vacuo* up to 120°. The residual polyanhydride was dissolved in 250 cc. of warm dry benzene and added to 150 g. of anhydrous aluminum chloride suspended in 750 cc. of dry benzene as in the previous preparation. The products were worked up in the same way. The crude precipitated ω -benzoylnonanoic acid was extracted with hot water to remove sebacic acid. Fifteen grams of sebacic acid separated from the washings and was identified by a mixed melting point determination with a known sample. The ω -benzoylnonanoic acid weighed 50 g., a yield of 78%. Recrystallized from dilute alcohol, it melted at 77–78°.⁶

Anal. Calcd. for $C_{16}H_{22}O_3$: C, 73.3; H, 8.4. Found: C, 73.3; H, 8.4.

The dibenzoyloctane was recovered from the benzene solution and weighed 35 g., a yield of 86%. Recrystallized from alcohol, it melted at 92–93°.⁷

Anal. Calcd. for $C_{22}H_{26}O_2$: C, 82.0; H, 8.1. Found: C, 81.7; H, 8.1.

Summary

The polymeric anhydrides of adipic and sebacic acids react with benzene in the presence of anhydrous aluminum chloride to yield mixtures of the appropriate dibenzoyl alkane, ω -benzoyl fatty acid, and dibasic acid. The reaction is doubtless general.

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⁴ Grateau, *Compt. rend.*, **191**, 947 (1930), gives 71°.

⁵ Étaix, *Ann. chim.*, [7] **9**, 372 (1896), gives 102–103°.

⁶ Auger, *ibid.*, [6] **22**, 364 (1891), gives 78–79°.

⁷ Auger, *ibid.*, [6] **22**, 363 (1891), gives 88–89°.