

[CONTRIBUTION NO. 40 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND COMPANY]

STUDIES ON POLYMERIZATION AND RING FORMATION. VI. ADIPIC ANHYDRIDE

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RECEIVED JULY 26, 1930

PUBLISHED OCTOBER 6, 1930

The anhydrides of succinic and glutaric acids are known and are monomeric rings of five and six atoms, respectively. The monomeric anhydride of the next member of the series, adipic acid, is a seven-atom ring, and therefore the direct preparation of this anhydride by the removal of water from the acid should give a polymolecular product, in accordance with the generalizations formulated in the previous papers in this series.¹ This has been found to be the case. We have also been successful in preparing monomeric adipic anhydride for the first time.

Adipic anhydride has been prepared by Voerman² and by Farmer and Kracovski,³ both of whom describe it as a solid. Voerman prepared the compound by treating adipic acid with acetyl chloride, removing volatile compounds *in vacuo*, and finally crystallizing from benzene. He gives a melting point of 98°. On the basis of a molecular weight determination in phenol, with which, however, we have found it to react, he seemed to regard the compound as a monomeric ring. The abnormally high molecular weight obtained in boiling acetone, the lack of definite crystallinity, and the relatively low solubility of the compound, however, led him to consider that it might be polymeric. He does not make his viewpoint altogether clear, but apparently he regarded the anomalous properties of the compound as due to some sort of association of simple rings and did not consider the probability of the existence of a long chain or large ring.

Farmer and Kracovski state that adipic anhydride is definitely unimolecular and ascribe to it a melting point of 97°. This is certainly not correct since we have found the monomer to melt at a very much lower temperature.

We have prepared adipic anhydride by both of these methods and have found that the product before subsection to distillation is polymeric, as we had anticipated and Voerman suspected. Polymeric adipic anhydride separates from hot benzene as a microcrystalline powder. Samples prepared in various experiments showed melting points ranging from 70 to 85°. This variation and the difference between the melting points of our products and those of previous investigators may be due to differences in molecu-

¹ Carothers, *THIS JOURNAL*, **51**, 2548 (1929); Carothers and Arvin, *ibid.*, **51**, 2560 (1929); Carothers and Van Natta, *ibid.*, **52**, 314 (1930); Carothers and Dorough, *ibid.*, **52**, 711 (1930).

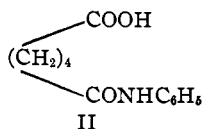
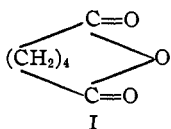
² Voerman, *Rec. trav. chim.*, **23**, 265 (1904).

³ Farmer and Kracovski, *J. Chem. Soc.*, 680 (1927).

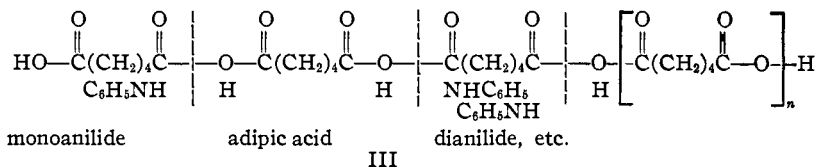
lar size. A molecular weight determination in boiling benzene gave a value about six times the normal value. This value is probably low as the substance is very sensitive to moisture, and only the ordinary precautions were taken to exclude it. The compound hydrolyzes in boiling water to yield the acid and reacts rapidly with aniline and phenol. It is hygroscopic and on standing unprotected gradually reverts to the acid. It is not distillable as such, but when heated *in vacuo* to somewhat above 200°, it breaks down and yields the true monomeric adipic anhydride, which distils out.

Monomeric adipic anhydride is a liquid freezing at about 20° and boiling at about 100° at 0.1 mm. It reacts with cold water quickly with the evolution of much heat to yield the acid. It reacts almost instantly with aniline to give a very high yield of pure monoanilide. On being heated at 100° for a few hours, it changes to a polymer melting at 80–85°. On standing at room temperature for ten days or more, it gradually solidifies. It is probable that traces of water bring about the polymerization. When a sample of liquid anhydride is transferred to a vessel which has not been very carefully dried, an amorphous skin soon coats the glass.

The reactions of the monomeric and polymeric adipic anhydrides with aniline establish the structures of these compounds, the former as a seven-membered ring and the latter as a long chain, which may be a large ring or an open chain with terminal carboxyl groups. Monomeric anhydride (I), which has a symmetrical structure, can react with aniline to give but one product, adipic acid monoanilide (II). This has been verified experi-



mentally. Polymeric adipic anhydride, to which we may assign formula III, on the other hand, is no longer symmetrical as soon as one anhydride



group reacts with aniline. The product formed, therefore, depends on which side of the oxygen atom the next anhydride group along the chain breaks. It will be seen from the scheme above that the reaction of polymeric adipic anhydride with aniline may lead to three products: adipic acid, adipic acid monoanilide and adipic acid dianilide. All of these compounds have been isolated from the reaction of the polymer with aniline.

On the assumption that a random reaction takes place and that the carboxyl groups which are probably at the ends of the chain may be neglected, these products should be formed in the proportion of one mole of acid to one mole of dianilide to two moles of monoanilide. In a quantitative experiment a 25% yield of dianilide was obtained. The adipic acid and monoanilide formed were not estimated quantitatively. Similarly the solid anhydride yields diphenyl adipate on warming with phenol.

The experiments with aniline show definitely that the solid adipic anhydride is a true condensation polymer in which the structural units are held together by primary valence forces. It is presumed that the polymers are open chains with carboxyl groups at the ends as has been demonstrated in the case of some of the polymeric ethylene succinates.⁴ This view is further supported by the presence of adipic acid in the distillate when the polymeric anhydride is cracked to form the monomer.

The writer wishes to thank Dr. W. H. Carothers for his interest and advice, and Mr. S. B. Kuykendall for determinations of carbon and hydrogen.

Experimental Part

Preparation of Polymeric Adipic Anhydride.—One hundred grams of recrystallized adipic acid and 300 cc. of redistilled acetic anhydride were refluxed together for four to six hours, and the volatile constituents were removed in a vacuum at 100°. The residue melted at about 70°. It was repeatedly recrystallized from dry benzene, from which it separated as a micro-crystalline powder. Various samples prepared in this same way melted at temperatures varying from 70 to 85°. At temperatures above the melting point, all these samples were viscous liquids, which solidified on cooling to waxy masses. In all experiments moisture was carefully excluded. In the most careful preparation carried out, moisture was excluded by phosphorus pentoxide tubes, the residue was heated overnight in an exhausted system which contained caustic potash in an adjacent vessel and then recrystallized four times with one filtration in a closed system. After each recrystallization the mother liquor was removed by careful decantation. The product melted at 73–75°. The polymeric anhydride melted under boiling water and gradually went into solution. On cooling adipic acid crystallized out.

Anal. Calcd. for $(C_6H_8O_5)_n$: saponification equiv., 64.0. Found: saponification equiv., 63.2, 63.4.

Reaction of Polymeric Adipic Anhydride with Aniline.—A sample of polymer prepared directly from adipic acid and acetic anhydride (m. p. 75°) was added to a slight excess of aniline and triturated in a mortar. Reaction took place spontaneously with the evolution of heat. The mixture was treated with dilute hydrochloric acid and the solid precipitate was filtered off. The filtrate was evaporated to dryness and the residue was then taken up in a volume of water not quite sufficient for complete solution, filtered and washed. The residue after crystallization from water was identified as adipic acid by a mixed melting point determination. The residue from the hydrochloric acid treatment was boiled with water and filtered. The filtrate deposited needles on cooling, which, after recrystallization from water, were identified as adipic acid monoanilide by a mixed

⁴ Carothers and Dorough, *THIS JOURNAL*, **52**, 711 (1930).

melting point with an authentic sample. The residue insoluble in boiling water, consisting of adipic acid dianilide, was recrystallized from alcohol; needles, m. p. 240–241°.⁵ This experiment was carried out with various samples of polymeric anhydride: crude polymer prepared directly from adipic acid and acetic anhydride, recrystallized polymer, polymer formed by heating the monomer, and still-residue from distillation of the monomer. In every case dianilide was isolated and identified. The experiment with the heat polymer was carried out quantitatively and gave a 25% yield of dianilide.

Anal. Calcd. for $C_{18}H_{20}O_2N_2$: C, 72.96; H, 6.81. Found: C, 73.31, 73.24; H, 6.95, 7.12.

Reaction of Polymeric Adipic Anhydride with Phenol.—Polymeric adipic anhydride was warmed with phenol to fusion and poured into cold water. On agitation a white solid separated out. This, after two recrystallizations from a mixture of alcohol and water (1:1), separated as lustrous plates of m. p. 105.5–106°. The method of preparation and the ultimate analysis showed this compound to be diphenyl adipate.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.45; H, 6.08. Found: C, 72.63, 72.19; H, 6.07, 6.29.

Preparation of Monomeric Adipic Anhydride.—One hundred grams of adipic acid and 300 cc. of acetic anhydride were refluxed together for four hours. The acetic acid formed in the reaction and the excess acetic anhydride were removed by distillation in a vacuum. The residue was transferred to a Claisen flask and heated under vacuum. After the removal of the residual acetic anhydride at 0.1 mm. no further distillation took place up to 210° bath temperature. At this temperature the pressure rose, and in different experiments from 50 to 60 g. distilled between 105 and 125° under pressure from 3 to 8 mm., the bath temperature ranging from 210 to 235°. The residue was viscous when hot and solidified to a dark colored mass on cooling. The distillate consisted of a light pink liquid containing a small amount of crystalline material. The liquid and solid phases were separated by centrifuging. The crystalline material was washed with benzene, recrystallized from ethyl acetate, and identified as adipic acid by a mixed melting point determination. The liquid was redistilled in an all-glass apparatus. The boiling point was 98 to 100° at 0.1 mm. at a bath temperature of 117 to 120°. Only about half of the material could be recovered by distillation since the residue gradually polymerized. Samples of the colorless distillate were sealed in small, carefully dried glass tubes for freezing point determinations. The compound froze at 19° to large translucent plates and remelted at 22°.

Anal. Calcd. for $C_8H_8O_3$: C, 56.25; H, 6.30; mol. wt., 128; saponification equiv., 64.0. Found: C, 55.89, 55.98; H, 6.51, 6.52; mol. wt. (in boiling benzene), 134, 131; saponification equiv., 63.7, 63.6.

Polymerization of Monomeric Adipic Anhydride.—When monomeric adipic anhydride was transferred to a vessel which had not been carefully dried, a translucent coating appeared on the surface of the glass. The coating was amorphous and in places skin-like. It melted at 60–65°. When the liquid was heated in a sealed tube at 100°, it polymerized completely and a maximum melting point of 80–84° was reached in about seven hours. On being heated at 138°, a maximum melting point of 81–85° was reached in about two hours. In neither experiment did further heating affect the melting point.

Anal. Calcd. for $(C_8H_8O_3)_n$: saponification equiv., 64.0. Found: saponification equiv., 63.5, 63.3; mol. wt. (in boiling benzene), 860, 710.

⁵ Böttker [*Ber.*, 39, 2765, 4003 (1906)] gives 240°; Balbiano [*Gazz. chim. ital.*, 32, I, 446 (1902)] gives 240–241°; Bouveault and Titry [*Bull. soc. chim.*, [3] 25, 444 (1901)] gives 235°.

Reaction of Monomeric Adipic Anhydride with Aniline.—One cubic centimeter of anhydride was added to about eight cubic centimeters of aniline with stirring. Reaction was immediate and much heat was evolved. The excess aniline was dissolved in dilute hydrochloric acid. The solution was diluted to 200 cc. and filtered. The crude product was dried and weighed; m. p. 152–153°; yield 80%. The monoanilide of adipic acid has previously been prepared by heating $C_6H_5NHCOCH(COOH)(CH_2)_3COOH$.⁶

Recrystallization from water did not raise the melting point. The crude compound was completely soluble in hot water (absence of dianilide). A similar experiment was carried out and worked up in smaller volume; m. p. (crude), 151–153°; yield, 87%.

Anal. Calcd. for $C_{12}H_{16}O_4N$: C, 65.12; H, 6.80; neutralization equiv., 221. Found: C, 64.76, 64.86; H, 6.81, 7.01; neutralization equiv., 222, 223.

Summary

The monomeric and polymeric forms of adipic anhydride have been prepared, the former for the first time, and they have been shown to be mutually interconvertible. The reactions of the compounds with aniline have shown the monomer to be a seven-atom ring and the polymer a long chain or large ring. Diphenyl adipate is described.

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[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

BRAZIL NUT OIL

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RECEIVED JULY 28, 1930

PUBLISHED OCTOBER 6, 1930

Data pertinent to the composition of the oil in the seeds of the Brazil nut tree, *Bertholletea excelsa*, are few. A statement by Andes¹ that this oil consists of stearin, palmitin and olein, and several reports by others² on a few of its more common chemical and physical constants appear to represent the published information on its chemical composition.

This oil finds a limited use in the arts in this zone but in the country of its origin it serves the inhabitants much the same as olive oil does elsewhere, that is, for alimentary purposes, for soapmaking and, to some extent, as a fuel for lamps. The nut meats contain approximately 70% of oil, more than one-half of which may be removed merely by expression in a hand press.

In view of the situation which obtains as above noted, and the ambiguity surrounding the methods of recovery of the oil used by others, it seemed worthwhile to re-investigate the chemical and physical characteristics of

⁶ Dieckmann, *Ann.*, 317, 62 (1901). The melting point given is 152–153°.

¹ Andes, "Vegetable Fats and Oils" (translated by Salter), Scott, Greenwood and Co., London, 1902, p. 187.

² De Negri and Fabris, *Z. anal. Chem.*, 33, 563 (1894); De Negri, *Chem.-Ztg.*, 22, 961 (1898); Merrill, *Maine Agr. Expt. Sta. Bull.*, 65, 111 (1900); Grimme, *Analyst*, 36, 21 (1911); Niederstadt, *Ber. deut. pharm. Ges.*, 35, 145 (1902).