SYNTHESIS OF PARA-BRIDGED BENZENE COMPOUNDS. III[1]

By M. F. Bartlett, S. K. Figdor, and K. Wiesner

ABSTRACT

2-5-Octamethylene tetrahydrophthalic anhydride does not form even a trace of the corresponding phthalic anhydride on dehydrogenation, but partly dissociates back into cyclododecadiene and maleic anhydride. 2-5-Nonamethylene tetrahydrophthalic anhydride dehydrogenates with considerable difficulty.

In a previous communication (2) we have shown that 2-5-decamethylene and 2-5-tetradecamethylene tetrahydrophthalic acids can be converted smoothly to the corresponding phthalic acids by dehydrogenation with Pd-charcoal in boiling naphthalene. We have now synthesized in exactly the same manner the 2-5-nonamethylene (II) and 2-5-octamethylene (I) tetrahydrophthalic acids and investigated their dehydrogenation. Under the conditions where the 10-membered bridge compound was formed smoothly neither of the two new compounds (I and II) gave a trace of dehydrogenated product. In both cases only starting material was recovered, with complete absence of the typical ultraviolet absorption spectrum of phthalic acid. If the dehydrogenation of Compound I was carried out without solvent with Pd-charcoal at 340° a small amount of a neutral volatile compound was obtained which gave an infrared spectrum identical with cyclododecadiene, showing that dissociation of the Diels-Alder adduct has taken place. The acidic fraction was starting material as checked by the complete absence of the typical ultraviolet absorption.

In the solvent free dehydrogenation of Compound II, no diene was found but the recovered acidic substance which was essentially starting material showed an absorption spectrum which corresponded to approximately 10% of the phthalic acid.

It was therefore concluded that although the dehydrogenation is hindered very strongly in this case, it nevertheless could be achieved under conditions that are sufficiently drastic. We have therefore subjected a larger amount of Compound II to a selenium dehydrogenation and analyzed carefully the products. The acidic material obtained by saponification of the dehydrogenation mixture was converted into an oily anhydride by sublimation.

The ultraviolet absorption spectrum of this product was perfectly in agreement with those of our previous 2-5-polymethylene phthalic anhydrides and is shown in Fig. 1, Curve I. (Curve II is the ultraviolet spectrum of 2-5-diethyl phthalic anhydride.)

The oily anhydride failed to crystallize and therefore it was not possible to make it analytically pure.

It was necessary to resort to oxidation studies to prove the structure. Oxidation with permanganate gave a good yield of 1,2,3,4-benzene tetra-

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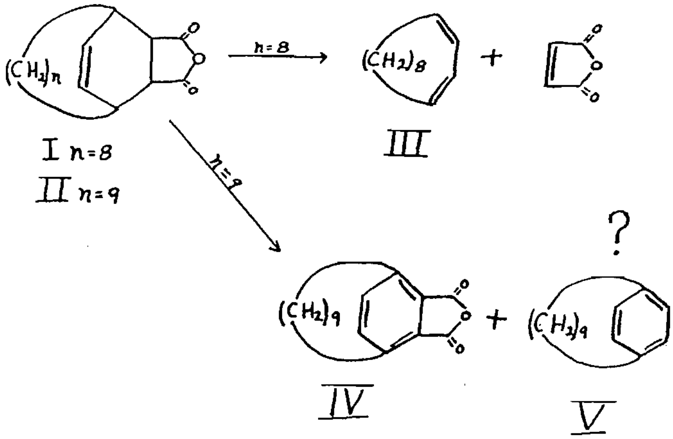

carboxylic acid, identified as methylester by mixed melting point and infrared spectrum. If we therefore combine this result with the agreement of the ultraviolet absorption there is hardly any doubt that we really had 2-5-nonamethylene phthalic anhydride IV.

The only other explanation, which is not considered likely, is that the nonamethylene bridge was ruptured in the middle during the dehydrogenation. The neutral fraction of the dehydrogenation mixture was chromatographed and a hydrocarbon was isolated which analyzed perfectly for 1-4-nonamethylene benzene. The quantity was not sufficient to allow structure proof by oxidation. The infrared spectrum showed bands at 1510 and 1600 cm.$^{-1}$, which are quite characteristic of an aromatic ring. Para substitution also causes characteristic bands at 800 and 875 cm.$^{-1}$ Bands at 796, 808, 858 cm.$^{-1}$, and 876 cm.$^{-1}$ are really present in the spectrum but they are weak. In view of the extremely small amount of the compound a definite decision as to whether or not the compound is 1-4-nonamethylene benzene was not possible.

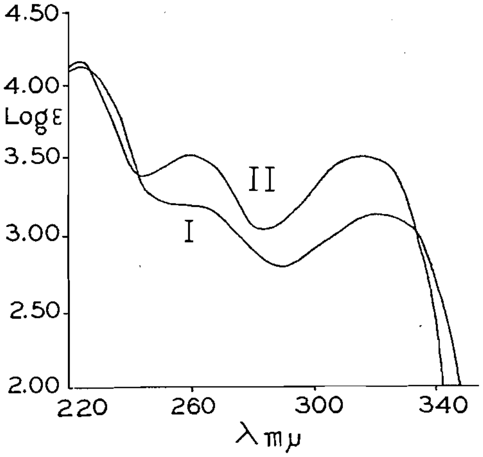

FIG. 1

EXPERIMENTAL

Synthesis of the tetrahydrophthalic acids I and II was performed exactly as previously (1). Therefore we give here only the analyses constants and yields of all new compounds.

Cyclododecene-one-3.—Yield 34%; b.p. 142°-153°C. at 16-18 mm.

Cyclododecene-ol-3.—Yield 90%; b.p. 105°-110°C. at 2-4 mm. Calculated for $C_{12}H_{22}O$: C, 79.06; H, 12.17; act. H, 0.54%. Found C, 79.09; H, 12.11; act. H, 0.54%.

Phenylurethane m.p. 95-96°C. Calculated for $C_{19}H_{27}O_2N$: C, 75.71; H, 9.03; N, 4.65%. Found: C, 75.54; H, 9.08; N, 4.78%.

Cyclododecadiene.—Yield 68%; b.p. 84°C. at 4 mm. Ultraviolet max. 230 mμ. Calculated for $C_{12}H_{20}$: C, 87.73; H, 12.27%. Found: C, 87.54; H, 12.27%.

2-5-Octamethylene tetrahydrophthalic anhydride I.—Yield of the oily anhydride 7.4%; b.p. in a collar flask 170-175°C. (outside temperature) at 0.6 mm. Calculated for $C_{16}H_{22}O_3$: C, 73.24; H, 8.45%. Found: C, 73.00, 73.03; H, 8.35, 8.25%.

Cyclotridecene-one-3.—Yield 46%; b.p. 119-125°C. at 0.5 mm.

Cyclotridecene-ol-3.—Yield 88%; b.p. 129-134°C. at 1 mm. Calculated for $C_{13}H_{24}O$: C, 79.54; H, 12.32; act. H, 0.51%. Found: C, 79.64; H, 12.30; act. H, 0.52%.

Cyclotridecadiene.—Yield 45%; b.p. 82°C. at 1 mm. Ultraviolet max. 232 mμ. Calculated for $C_{13}H_{22}$: C, 87.54; H, 12.44%. Found: C, 86.79; H, 12.48%.

2-5-Nonamethylene tetrahydrophthalic anhydride II.—Yield of oily anhydride 17.2%. Recrystallized from ether - petroleum ether to a constant melting point, it melted at 148-150°C. Calculated for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75%. Found: C, 73.69; H, 8.88%.

DEHYDROGENATION OF ANHYDRIDE I

Compound I (200 mgm.) was mixed with 200 mgm. of Pd-charcoal and heated for 30 min. to 340°C. After this the product was saponified by stirring 24 hr. with 10 ml. of 10% potassium hydroxide and separated into acidic and neutral material. The neutral product was a colorless oil (35 mgm.) which boiled in a collar flask at 65-67° at 4 mm. and gave an infrared spectrum identical with cyclododecadiene. The acidic material was reconverted into the anhydride by sublimation. It had no ultraviolet absorption.

SELENIUM DEHYDROGENATION OF ANHYDRIDE II

Compound II (2.18 gm.) and 8.7 gm. of selenium were heated in a sealed tube for 19 hr. at 370°C. The content of the tube was then extracted with ether and the residue, after the evaporation of the ether, saponified by stirring 24 hr. with 130 ml. of 10% potassium hydroxide. The products were then separated into neutral (453 mgm.) and acidic (720 mgm.) material. The neutral material was chromatographed on 18.1 gm. of alumina. Petroleum ether eluted from this column 106 mgm. of an oil which distilled in a collar flask at 85-95°C. at 0.05 mm. The middle fraction was analyzed. Calculated for $C_{15}H_{22}$: C, 89.02; H, 10.97%. Found: C, 88.92; H, 10.97%.

The acidic material was converted by sublimation in high vacuum into the oily anhydride.

The ultraviolet spectrum is given in Fig. 1, Curve 1.

OXIDATION WITH PERMANGANATE

This oxidation was done on 686 mgm. of 2-5-nonamethylene phthalic anhydride in exactly the same way as before (2). The yield after several recrystallizations was 14 mgm. of pure benzene 1,2,3,4-tetracarboxylic methylester, which melted at 129-131°C. alone and in admixture with an authentic specimen. Also the infrared spectra of both compounds were identical.

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REFERENCES

1. Ingraham, R. B., MacDonald, D. M., and Wiesner, K. Can. J. Research, B, 28: 453. 1950.
2. Wiesner, K., MacDonald, D. M., Ingraham, R. B., and Kelly, R. B. Can. J. Research, B, 28: 561. 1950.