

An Improved Synthesis of *cis*- Δ^4 -Tetrahydrophthalic Anhydride and *cis*-Hexahydrophthalic Acid

BY EDWARD F. JENKINS AND EDWARD J. COSTELLO

In the course of a synthetic problem it became necessary to prepare some *cis*-hexahydrophthalic acid.

The syntheses of this acid described in the literature are those of Baeyer,¹ Willstätter and Jaquet,² and Diels and Alder.³ Because of slow reaction speeds and repeated recrystallizations these procedures are time-consuming and laborious.

By modifying the method of Diels and Alder it was found possible to prepare *cis*-hexahydrophthalic acid very easily and in excellent yield. All the repeated recrystallizations, as well as the vacuum concentration of the final product, were eliminated. In addition to this, the time required for the reaction of the maleic anhydride and butadiene was greatly reduced, as was also the time needed for the reduction of the *cis*- Δ^4 -tetrahydrophthalic anhydride.

Experimental

Preparation of *cis*- Δ^4 -Tetrahydrophthalic Anhydride.—Ninety-eight grams (1 mole) of finely ground maleic anhydride was partly dissolved and partly suspended in 150 ml. of benzene. After this suspension had been cooled to 5°, 54 g. (1 mole) of liquid butadiene was added. The mixture was then heated in an autoclave to 115°. At this temperature heating was discontinued, but within fifteen minutes the temperature had spontaneously risen to 145° and the pressure to 11 atmospheres. The reaction mixture was left to stand overnight in the autoclave.

The crude product was freed from benzene and was then extracted with ether by use of a Soxhlet extractor. A white crystalline mass of pure *cis*- Δ^4 -tetrahydrophthalic anhydride formed in the ether during the extraction, and more precipitated upon cooling to room temperature. The unreacted maleic anhydride remained in the ether solution but could be recovered by cooling the solution to 0°. The product melted at 103–104°. The yield was 137 g., or 90.3% of the theoretical amount.

Preparation of *cis*-Hexahydrophthalic Acid.—Instead of following the procedure of Diels and Alder and preparing the tetrahydrophthalic acid before hydrogenation, the anhydride itself was hydrogenated. The *cis*- Δ^4 -tetrahydrophthalic anhydride was ground up, suspended in glacial acetic acid, and hydrogenated at room temperature and a total pressure of 4.5 atmospheres of hydrogen. Adams platinum oxide catalyst was used, 100 mg. of the catalyst for every 15.2 g. (0.1 mole) of the anhydride.

30.4 g. (0.2 mole) of the anhydride was suspended in 150 ml. of glacial acetic acid; hydrogenation took place smoothly and quickly, and the theoretical amount of hydrogen was absorbed in one-half hour. In another experiment 60.8 g. (0.4 mole) of the anhydride was suspended in the same quantity of acetic acid and hydrogenation was complete in about the same time. In the resultant solution the reduction product was entirely dissolved in the solvent.

After separating the catalyst by filtration, the solution of *cis*-hexahydrophthalic anhydride was poured into 450 ml. of water. This solution was then cooled to 0° and allowed to stand at that temperature for about an hour. The crude anhydride, along with some *cis*-hexahydro-

phthalic acid, precipitated out as a white crystalline mass. In filtering this product in warm weather the filter should be cooled and the operation must be completed quickly, because the anhydride melts at 32°.

The acid was then prepared from the mixture by dissolving it in boiling water to which a little activated charcoal was added for purpose of purification. The mixture was boiled for fifteen minutes and filtered hot. On cooling, the *cis*-hexahydrophthalic acid crystallized out. This was purified by one recrystallization from water. The product melted at 190–191°. The yield was about 90% of the theoretical.

All the melting points obtained agreed with those recorded in the literature. Anschütz thermometers calibrated by the Bureau of Standards were used in taking the melting points.

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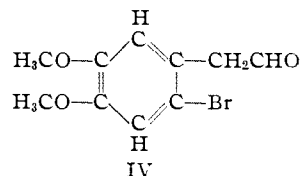
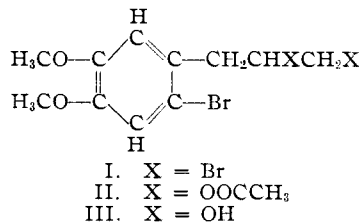
Halogenated Derivatives of Methyleugenol. II. 6-Bromomethyleugenol Glycol and 6-Bromomoveratraldehyde

BY ST. KAUFMANN, G. ROSENKRANZ¹ AND JOSEFINA LÓPEZ

Recently it was proved by G. Rosenkranz and Mercedes Pérez² in these Laboratories that the position of the nuclear bromine atom in bromomethyleugenol dibromide (I) is the position 6 of the benzene ring. On the basis of this knowledge we have synthesized, starting from 6-bromomethyleugenol dibromide, a number of new compounds which may serve as intermediates for further syntheses.

The reaction of 6-bromomethyleugenol dibromide with silver acetate in glacial acetic acid leads to the formation of the hitherto unknown diacetate of 6-bromomethyleugenol glycol (II). This diacetate constitutes a viscous yellow oil which is saponified by means of alcoholic potassium hydroxide to the corresponding glycol (III) without previous purification.

This glycol with an equimolecular quantity of lead tetraacetate in chloroform solution is cleaved



(1) Present address: Laboratorios "SYNTEX" S. A., Mexico City.

(2) Number I in this series: G. Rosenkranz and Mercedes Pérez, *Ciencia*, **6**, pp. 364–368 (1946).

(1) Bayer, *Ann.*, **258**, 219 (1890).

(2) Willstätter and Jaquet, *Ber.*, **51**, 776 (1918).

(3) Diels and Alder, *Ann.*, **460**, 98–122 (1928).