The distillation curve for the recovered acid was a straight line with a distillation constant characteristic of acetic acid. The acid was therefore acetic, and the quantity recovered corresponded to one mole of acid from a mole of isotenulin.

Acetylation of Desacetylisotenulin.—A solution of 0.1 g. of the $C_{15}H_{20}O_4$ compound in 1 cc. of pyridine and 0.5 cc. of acetic anhydride was allowed to react overnight. Water was then added, causing the liquid to crystallize. Long colorless rods that melted at 160° were obtained. Recrystallization of these from methanol and water (1–3) raised their melting point to 161°. The product was identified as isotenulin by its melting point, mixed melting point with an authentic sample of isotenulin, and its optical crystallographic properties.

Hydrolysis of Dihydroisotenulin.—Dihydroisotenulin was hydrolyzed with concentrated sulfuric acid by the procedure used with isotenulin. Several days were required for complete crystallization from the reaction mixture. The product was purified by recrystallization from its methanol solution by adding water. It melted at 203°.

Anal. Calcd. for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 67.88; H, 8.61.

Sodium hydroxide was also used as a hydrolyzing agent. A mixture of 0.5 g. of dihydroisotenulin and 10 cc. of 10% sodium hydroxide was heated and stirred until a homogeneous solution resulted. This was then diluted with water to *ca.* 50 cc. and acidified to congo red with sulfuric acid. Colorless crystals (240 mg.) separated. They melted at 202°, and when they were mixed with the compound obtained above with sulfuric acid there was no depression of the melting point. The acid mother liquors were examined for acetic acid as reported under isotenulin. The results were identical.

Pyrotenulin.—A half gram of purified tenulin was heated until the first violent evolution of gas ceased. The resulting melt was then placed in a strong Bunsen flame and rapidly distilled. The distillate was caught in a thin-walled bulb blown close to the bottom of the test-tube. This was broken, and its contents dissolved in chloroform. The solution was filtered through Norit and diluted with several volumes of methanol. The liquid was distilled until the chloroform was removed, whereupon the methanol concentrate crystallized. The product consisted of colorless hexagonal plates, m. p. 235–236°.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 70.90; H, 7.22.

Summary

Evidence has been presented to show that tenulin contains a double bond, an acetoxyl group, and a hydroxyl and a carbonyl group, both of which are sterically hindered.

A summary of the reactions of tenulin which have been used in this discussion and which have hitherto been unrecorded is shown diagrammatically in a chart.

Two hitherto unexamined species of *Helenium*, *i. e.*, *H. quadridentatum* and *H. montanum*, have been investigated for bitter and sternutative substances. *H. quadridentatum* contains helenalin, while *H. montanum* contains tenulin.

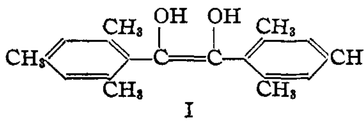
WASHINGTON, D. C. RECEIVED JANUARY 4, 1940

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

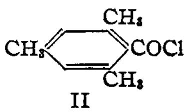
Enediols. III. 1,2-Dimesitylacetylene Glycol

BY REYNOLD C. FUSON, C. H. MCKEEVER[1] AND JOSEPH CORSE

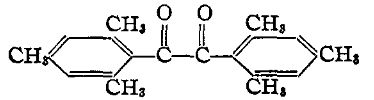
The isolation of a stable enediol, 1,2-dimesitylacetylene glycol (I), was reported recently.[2] The present paper presents the experimental details upon which the earlier communication was based. The enediol was obtained by the action of the binary mixture, Mg + MgI_2,[3] on mesitoyl chloride (II) or mesitil (III). The products from the two sources were identical. Both reverted to the benzil when exposed to the air or other oxidizing agents, and both rearranged to mesitoin (IV) under the influence of hydrochloric acid.



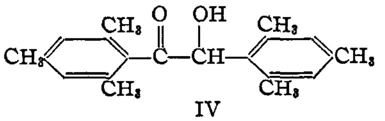
I



II



III



IV

Treatment of this enediol with acetic anhydride gave a diacetate (m. p. 164–165°) accompanied by a very small amount of a second diacetate (m. p. 218°). Mesitil and the acetate of mesitoin were also isolated.

Benzoylation with benzoyl chloride in the presence of pyridine converted the enediol into a dibenzoate melting at 188.5–189.5°.

By hydrogenation of mesitil in methanol,

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[1] Röhm and Haas Research Assistant.

[2] Fuson and Corse, THIS JOURNAL, **61**, 975 (1939).

[3] Gomberg and Bachmann, *ibid.*, **49**, 236 (1927).

Thompson[4] obtained an enediol which gave a dibenzoate melting at 235°, and concluded that he had a stereoisomer of the enediol of Fuson and Corse. We have shown that the enediol made by Thompson's method yields chiefly the high-melting diacetate when treated with acetic anhydride. However, a small amount of the low-melting diacetate is formed also along with a large amount of the acetate of mesitoin.

In view of this result, the benzoylation was repeated and the mother liquors from the crystallization of the high-melting dibenzoate were examined with great care. A small amount of the low-melting dibenzoate was found. The very remarkable discovery was then made that this dibenzoate was the sole product when the catalytic hydrogenation was carried out in low-boiling petroleum ether instead of methanol. It is, therefore, not entirely clear what relationship obtains between the source of the enediol and its behavior toward acylating agents. However, it can be said that any given sample of enediol, regardless of its history, yields predominantly one form or the other of the expected diester. The second diester if produced at all is always in small amount. This observation supports Thompson's conclusion that the enediol exists in two stereoisomeric forms. However, it implies that the samples which have been described may be mixtures. The alternative is to assume partial isomerization during esterification. This question is being studied.

Experimental

Action of the Binary Mixture on Mesitoyl Chloride.—The binary mixture was prepared according to the directions of Gomberg and Bachmann.[3] To 3 g. of magnesium turnings, 60 cc. of dry ether and 120 cc. of dry benzene was added 15.3 g. of iodine in several small portions. When the reaction mixture had become colorless and cooled to room temperature, the air in the flask was swept out by a stream of dry, oxygen-free nitrogen. A solution of 11 g. of the chloride in 10 cc. of dry ether was then added over a period of fifteen minutes by means of a dropping funnel. Stirring was continued for sixteen to eighteen hours, in a nitrogen atmosphere. At the end of this time the magnesium had nearly disappeared and the solution was dark red.

The reaction mixture was filtered through folded cheesecloth into a separatory funnel containing 8 cc. of acetic acid and 100 cc. of ice water. The ether–benzene layer was separated and washed *rapidly* with water, with 5% sodium thiosulfate solution, again with water, then with 10% potassium bicarbonate solution and finally once more with water. The solution was then dried for a few minutes over calcium chloride, filtered and evaporated to a thin sirup as rapidly as possible with the aid of the water pump. Dilution of the brown sirup with 50 cc. of petroleum ether and cooling, precipitated the enediol as a white crystalline material which was separated and washed with petroleum ether. The yield amounted to 3.1 g. or 35% of the theoretical.

The enediol was unstable in the presence of oxygen, being rapidly autoxidized to the benzil. It was soluble in ether, benzene and alcohol but insoluble in petroleum ether and aqueous alkali. It immediately decolorized solutions of 2,6-dichlorobenzeneoneindophenol; Tollens' reagent and cold cupric acetate solutions were also immediately reduced.

The mother liquors from the enediol yielded 3 g. of mesitil or 34% of the theoretical. A little tarry material also was isolated.

When only 1.5 g. of iodine was used instead of the usual 15.3 g., and the procedure carried out as before, no reaction was apparent; only mesitoic acid was isolated.

In one run out of thirteen mesitoin was isolated (28% yield) instead of the enediol.

Action of the Binary Mixture on Mesitil.—To the binary mixture, made from 1.5 g. of magnesium and 7.6 g. of iodine in 60 cc. of benzene and 30 cc. of ether, was added 4.4 g. of mesitil. Stirring was continued for twenty-four hours, the mixture being kept under a nitrogen atmosphere. When the mesitil was added the solution turned dark red-brown, probably because of the liberation of iodine.[3] After a few hours, a dark red-brown precipitate formed which later disappeared. At the end of the reaction the mixture had the same appearance as that obtained from mesitoyl chloride and the binary mixture; it was decomposed and treated in the same manner as in the preceding experiment. Two and seven-tenths grams of the enediol was obtained, a yield of 60% of the theoretical. In addition, mesitil was recovered.

Hydrogenation of Mesitil.—The enediol also was made by the hydrogenation of mesitil in low-boiling petroleum ether.

One and one-half grams of mesitil was almost completely dissolved in 50 cc. of low-boiling petroleum ether. Approximately 0.02 g. of platinum oxide catalyst was added and the mixture reduced at room temperature under a pressure of one and one-half atmospheres. The enediol precipitated as it was formed and the reduction was complete when the solution became colorless. The reaction mixture was filtered, the enediol dissolved in ether, this solution filtered to remove the catalyst, the ether evaporated to a small volume and the enediol precipitated by addition of low-boiling petroleum ether. The yields varied from 85 to 95% of the theoretical amount.

Ketonization of the Enediol.—A solution of 1.3 g. of the enediol and 6 cc. of methanol which previously had been saturated with dry hydrogen chloride was refluxed for forty-five minutes, allowed to cool and poured into 70 cc. of water. A white crystalline compound separated. It was collected on a filter and recrystallized from 70% aqueous methanol; yield 1.2 g. The compound melted at 130–131°, and a mixed melting point with an authentic sample of mesitoin[5] showed no depression.

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[4] Thompson, THIS JOURNAL, **61**, 1281 (1939).

[5] Fuson, Emerson and Weinstock, *ibid.*, **61**, 412 (1939).

The Acetate of Mesitoin.—A solution of 1.2 g. of mesitoin in 5 cc. of acetyl chloride was refluxed for two hours. It was poured into water, extracted with ether and the ether extracts were washed with water, 10% potassium bicarbonate and again with water. The ether solution was dried over calcium chloride and after filtration the ether was removed by an air blast. The solid which remained crystallized as long white needles from ether-petroleum ether and melted 106–107°; the yield was 1.2 g.

Anal. Calcd. for $C_{22}H_{26}O_3$: C, 78.07; H, 7.75; acetyl no., 12.7. Found: C, 78.11; H, 7.28; acetyl no., 10.6, 11.5.

Refluxing a solution of 0.085 g. of the acetate in 2.1 cc. of methanol and 0.2 cc. of concentrated hydrochloric acid for two hours gave mesitoin in good yield.

The Diacetates of the Enediol.—A solution of 1 g. of the enediol, prepared by the bimolecular reduction of mesitoyl chloride, and 5 cc. of acetic anhydride was refluxed for three hours and poured into water; the mixture was warmed to decompose the excess acetic anhydride and extracted with ether. The ether extracts were washed twice with a 10% solution of potassium bicarbonate, then with water and dried over calcium chloride; the ether was allowed to evaporate at room temperature. There was obtained a mixture of four compounds, which were separated as follows. The mixture was taken up in methyl alcohol; the very small amount of a diacetate which was insoluble was removed by filtration. After recrystallization from a benzene–low-boiling petroleum ether mixture it melted at 218°. It could be hydrolyzed to mesitil with dilute alcoholic potassium hydroxide.

Anal. Calcd. for $C_{24}H_{38}O_4$: C, 75.76; H, 7.43. Found: C, 75.69; H, 7.48.

When the methyl alcohol solution cooled to room temperature there precipitated a second diacetate, m. p. 156–160°, which after several recrystallizations from methyl alcohol melted at 164–165°.

Anal. Calcd. for $C_{24}H_{28}O_4$: C, 75.76; H, 7.43; acetyl no., 22.6. Found: C, 75.41; H, 7.61; acetyl no., 20.7.

When the methyl alcohol solution was evaporated to dryness, there was obtained the acetate of mesitoin contaminated with a small amount of mesitil. The structure of these compounds was proven by mixed melting point determinations with known samples.

All four compounds were obtained no matter how the enediol had been prepared. The enediol prepared by bimolecular reduction of the acid chloride and the one prepared by reduction of mesitil in low-boiling petroleum ether behaved exactly alike. They gave only a trace of the high-melting diacetate, a 30–40% yield of the diacetate melting at 164–165° and a mixture of mesitil and acetate of mesitoin.

In the case of the enediol prepared by catalytic reduction in methyl alcohol,[4] the amounts of the products were very different; the product consisted of a 20–30% yield of the high-melting diacetate, a trace (and sometimes none) of the diacetate which melted at 164–165° and a good yield of the acetate of mesitoin contaminated with small amounts of mesitil.

If mesitil is reduced in acetic anhydride according to the method of Thompson[4] a 90% yield of the diacetate, m. p. 164–165°, is obtained. This compound was also obtained when mesitil was treated with sodium according to the method of Kohler and Baltzly[6] with subsequent treatment with acetyl chloride rather than benzoyl chloride.

When acetyl chloride was used instead of acetic anhydride, the enediol yielded the acetate of mesitoin in 70–80% yield, together with only small amounts of the diacetates.

The Benzoates of the Enediol.—To 2 cc. of benzoyl chloride and 10 cc. of pyridine was added 0.3 g. of the enediol prepared by the bimolecular reduction of mesitoyl chloride. The mixture was refluxed gently for two hours, poured into water, acidified with dilute hydrochloric acid and extracted with ether. The ether extract was washed thoroughly with a 10% solution of potassium bicarbonate, water, dilute hydrochloric acid and water; it was then dried over calcium chloride and the ether was evaporated. The dibenzoate crystallized from ether–petroleum ether mixture, m. p. 188.5–189.5°. A second dibenzoate could not be found. The enediol prepared by catalytic reduction of mesitil in low-boiling petroleum ether, when treated as above, yielded the same compound, m. p. 188–189°. The enediol prepared from catalytic reduction in *methyl alcohol* yielded a dibenzoate, m. p. 235°.[2] Upon evaporation of the solvent, there was precipitated a second compound which after two recrystallizations from absolute alcohol melted at 188–189°. A mixed melting point determination proved it to be identical with the dibenzoate prepared above.

Summary

1,2-Dimesitylacetylene glycol has been prepared in three different ways. It has been caused to rearrange to the benzoin. The enediol gives two diacetates and two dibenzoates, presumably pairs of *cis-trans* isomers.

URBANA, ILLINOIS

RECEIVED DECEMBER 29, 1939

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(6) Kohler and Baltzly, THIS JOURNAL, **54**, 4015 (1932).