15% sodium hydroxide until the ester completely dissolved. The solution was acidified with dilute hydrochloric acid and evaporated to dryness. It was ground to a fine powder and, after drying for twenty-four hours over phosphorus pentoxide, was treated with 30 cc. of thionyl chloride. The reaction mixture was allowed to stand overnight at room temperature, then warmed to 60° for three hours. The excess thionyl chloride was removed and the fluffy solid transferred to a 250-cc. three-necked flask. Fifty grams of mesitylene and 50 cc. of carbon disulfide were added and stirring was started; then 25 g. of aluminum chloride was introduced in small portions over a period of thirty minutes. The reaction mixture, a thick dark red paste, was diluted with an additional 50 cc. of carbon disulfide and stirred vigorously for two hours. It was decomposed by pouring upon a mixture of 500 g. of ice and 50 cc. of concentrated hydrochloric acid. The carbon disulfide was evaporated, the solution extracted with 250 cc. of benzene and the benzene extracts were washed thoroughly with water, 10% potassium bicarbonate and again with water. The benzene and mesitylene were removed at diminished pressure. There remained a tan solid which was washed with methyl alcohol then crystallized from absolute alcohol. The 1,3,5-trimesitoylcyclohexane crystallized in long white needles and melted at 210–212°; yield, 4.5 g. The melting point of a mixture of this compound and the trimer of vinyl mesityl ketone showed no lowering.

Summary

Vinyl mesityl ketone has been prepared from mesitylene and β-chloropropionyl chloride by the Friedel–Crafts method.

It is remarkably stable and fails to undergo polymerization in the presence of peroxides.

However, when heated in the presence of methanol and potassium carbonate it trimerizes to 1,3,5-trimesitoylcyclohexane. The structure of the triketone has been proved by synthesis.

Urbana, Illinois Received April 22, 1940

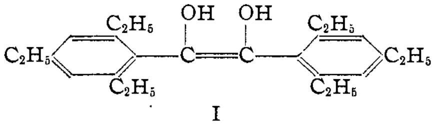
[Contribution from the Noyes Chemical Laboratory, University of Illinois]

Enediols. IV. *cis–trans* Isomerism

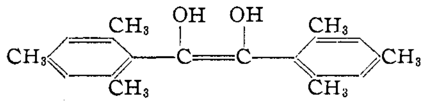
By Reynold C. Fuson, S. L. Scott, E. C. Horning[1] and C. H. McKeever[2]

Stilbenediols might be expected to exist in *cis* and *trans* modifications. Of those known up to now one (I), that from hexaethylbenzil, has been isolated in a single form[3] while the other (II), derived from mesitil, has been reported to exist in two forms.[4] Thompson[4b] recognized these two forms as geometrical isomers. The fact that these enediols are stable in the absence of oxygen, showing no tendency to rearrange spontaneously to the corresponding benzoins, is in keeping with Thompson's interpretation.

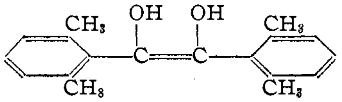
It has now been possible to confirm the correctness of this idea and to extend it to the hexaethyl (I) and tetramethyl (III) analogs.



I



II



III

Each of the three is now known in two modifications. By analogy with other *cis-trans* compounds, it seems highly probable that of a given pair the lower melting compound possesses the *cis* configuration and the higher melting form has the *trans* arrangement. Accordingly, these designations will be used in describing the enediols.

The method for making them is essentially that of Thompson.[4b] It has been found that catalytic hydrogenation can be used to prepare either form at will. Whether the product is the *cis* or the *trans* form of the enediol, depends only on the duration of the treatment with platinum and hydrogen. If the hydrogenation is interrupted as soon as the yellow color of the benzil has disappeared the product is the *cis* compound. If the process is sufficiently prolonged the *trans* compound is produced.

Apparently the *cis*-enediol, always produced initially, slowly isomerizes in the presence of the catalyst and hydrogen to yield the corresponding *trans*-enediol. In fact, the pure *cis* modification can be transformed to the corresponding *trans*

---

(1) Du Pont Fellow in Chemistry, 1939–1940.

(2) Röhm and Haas Research Assistant.

(3) Fuson, Corse and McKeever, This Journal, **61**, 2010 (1939).

(4) (a) Fuson and Corse, *ibid.*, **61**, 975 (1939); (b) Thompson, *ibid.*, **61**, 1281 (1939); (c) Fuson, McKeever and Corse, *ibid.*, **62**, 600 (1940).

form by this treatment. Whether this rearrangement is a direct process or involves dehydrogenation and subsequent hydrogenation of the benzil is not yet certain.

The *cis* and *trans* modifications of the enediols differ not only in melting point but also in solubility and in the rate at which they are oxidized by exposure to the air. The *cis*-enediol from 2,6-xylil (III) melts at 123–124° and is noticeably affected by two or three hours of contact with the air. The corresponding *trans* compound, melting at 151–152°, is only slightly oxidized by four days of exposure to the air.

Similarly, the *trans*-enediol from hexaethylbenzil, melting at 181.5–183.5°, is much less sensitive to the action of air than is its *cis* isomer (II), which melts at 154–155°.

The *trans*-enediol from mesitil melts at 166–168° in a sealed nitrogen-filled capillary. When the capillary is allowed to cool the compound crystallizes and gives the same melting point as before. This process can be repeated over and over with no noticeable lowering of the melting point. In other words, the compound is thermally stable. However, a slight trace of impurity seems to produce a considerable lowering of the melting point. This may be the explanation of the lower melting point reported by Thompson.[4b] The *trans*-enediol gives exclusively the high-melting diacetate when acetylated with acetic anhydride, whereas Thompson's material yields a little of the low-melting diacetate as well.[3]

The 2,6-xylil (IV) from which the tetramethyl stilbenediols were made is a new benzil. It was synthesized from 2,6-xylidine by the following series of transformations.

$$(CH_3)_2C_6H_3NH_2 \longrightarrow (CH_3)_2C_6H_3CN \longrightarrow (CH_3)_2C_6H_3CO_2H \longrightarrow (CH_3)_2C_6H_3COCl \longrightarrow \underset{\text{IV}}{(CH_3)_2C_6H_3COCOC_6H_3(CH_3)_2}$$

The coupling was effected by treatment of the acid chloride with the binary mixture, Mg + MgI_2.[5] In this process some 2,6-xyloin also was produced. An enediol was likewise present, for the original solution readily decolorized a solution of 2,6-dichlorobenzeneoneindophenol. The 2,6-xyloin was characterized by preparation of an acetate and by oxidation to 2,6-xylil. It was also obtained by heating of the *trans*-enediol with methanol and hydrogen chloride.

The *cis*- and *trans*-enediols from 2,6-xylil were converted into the corresponding diacetates by treatment with acetic anhydride. There was no evidence of change of configuration during the acetylation. Benzoylation, however, gave the same dibenzoate from either enediol. Rearrangement evidently takes place in the benzoylation of one of the forms.

The *cis*-diacetate was also obtained by the action of acetic anhydride on the mixture resulting from treatment of 2,6-xylil with the binary mixture. Catalytic hydrogenation of 2,6-xylil in acetic anhydride gave the same isomer.

Experimental

2-Bromo-1,3-dimethylbenzene.—2,6-Xylidine was diazotized and treated with cuprous bromide according to the procedure given for the preparation of *p*-bromotoluene in "Organic Syntheses."[6] The chief product (60%) was 2,6-xylenol, melting at 48–49°. A 10% yield was obtained of 2-bromo-1,3-dimethylbenzene, b. p. 97–98° (28–30 mm.).[7]

2,6-Xylonitrile.—The procedure was that described in "Organic Syntheses"[8] for the synthesis of *o*-tolunitrile. Sixty grams of the xylidine gave 37.5 g. of the nitrile, m. p. 89–89.5°.[9]

2,6-Xylic Acid.—The procedure of Berger and Olivier[10] was used to convert the nitrile to the acid. The latter melted at 115–116°.[9] A small amount of this acid was also made from 2-bromo-1,3-dimethylbenzene by carbonation of the corresponding Grignard reagent.

2,6-Xyloyl Chloride.—A mixture of 35 g. of thionyl chloride and 20 g. of 2,6-xylic acid was allowed to react until the spontaneous reaction subsided. The mixture was then heated for several minutes and allowed to stand overnight. The chloride boiled at 67–69° (7 mm.)[11]; yield 96% of theory.

Conversion of 2,6-Xyloyl Chloride to 2,6-Xylil and 2,6-Xyloin.—The procedure was that described for the preparation of 2,2′,4,4′,6,6′-hexaethylstilbenediol from 2,4,6-triethylbenzoyl chloride.[4c] The ether–benzene solution of the product instantly decolorized a solution of 2,6-dichlorobenzeneoneindophenol. However, the enediol could not be induced to crystallize. The solution was concentrated and allowed to stand. The product was a mixture of white and yellow crystals. These were separated mechanically and crystallized from high-boiling petroleum ether.

The yellow compound was 2,6-xylil, m. p. 153–154° (cor.). The yield was 8 g.

Anal.[12] Calcd. for $C_{18}H_{18}O_2$: C, 81.16; H, 6.81. Found: C, 80.99; H, 6.73.

The white crystals proved to be 2,6-xyloin, m. p. 127–128° (cor.); yield, 3 g.

---

(5) Gomberg and Bachmann, This Journal, **49**, 236 (1927).

(6) "Organic Syntheses," Coll. Vol. I, p. 131.

(7) Jacobsen and Deike, *Ber.*, **20**, 903 (1887).

(8) "Organic Syntheses," Coll. Vol. I, p. 500.

(9) Noyes, *Am. Chem. J.*, **20**, 789 (1898).

(10) Berger and Olivier, *Rec. trav. chim.*, **46**, 600 (1927).

(11) Lock and Schmidt, *J. prakt. Chem.*, **248**, 229 (1934).

(12) The analyses reported in this paper are microanalyses. They were carried out by Mr. L. G. Fauble and Mr. W. H. Taylor.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.55; H, 7.51. Found: C, 80.47; H, 7.62.

There remained 7 g. of a brown tar which could not be induced to crystallize.

Oxidation of 2,6-Xyloin to 2,6-Xylil.—A mixture of 0.3 g. of the xyloin, 0.7 g. of copper sulfate, 2 g. of pyridine and 5 cc. of water was heated under reflux for six hours. The product was crystallized from high-boiling petroleum ether. A 91% yield of 2,6-xylil was obtained. A mixed melting point determination with the sample from the coupling reaction confirmed the identity.

Acetate of 2,6-Xyloin.—A mixture of 0.3 g. of 2,6-xyloin was heated under reflux for three hours with 10 cc. of acetic anhydride. Water was added to decompose the anhydride and the acetate extracted with ether. It separated from methanol in small white crystals, m. p. 104–105° (cor.). The yield was 0.17 g.

Anal. Calcd. for $C_{20}H_{22}O_3$: C, 77.38; H, 7.15. Found: C, 77.19; H, 7.11.

***cis*-2,2′,6,6′-Tetramethylstilbenediol.**—A mixture of 0.5 g. of 2,6-xylil, 50 cc. of methanol, 1 drop of glacial acetic acid and 0.1 g. of platinum oxide was hydrogenated until the yellow color disappeared. This required about ten minutes. The reaction mixture was filtered rapidly to remove the catalyst, and the solvent was distilled rapidly under diminished pressure.[13] The white residue was dissolved in ether and the solution, after being filtered, was evaporated almost to dryness. Low-boiling petroleum ether was added and the solvent once more evaporated. This process was repeated until the enediol crystallized. The flask was stoppered tightly while the solvent was still boiling and was plunged into an ice-bath. When the mixture was cold the enediol was collected on a filter and washed several times with low-boiling petroleum ether. The enediol was obtained as glistening white prisms melting at 123–124° (cor.). The yield was nearly quantitative.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.55; H, 7.51. Found: C, 80.30; H, 7.43.

The **diacetate** was prepared by heating a mixture of 0.1 g. of the enediol with 5 cc. of acetic anhydride for three hours under reflux. It formed glistening white prisms melting at 166–167° (cor.). The yield was 60 mg.

Anal. Calcd. for $C_{22}H_{24}O_4$: C, 74.96; H, 6.87. Found: C, 74.69; H, 6.74.

The same diacetate was obtained by hydrogenation of a mixture of 0.5 g. of 2,6-xylil, 50 cc. of acetic anhydride, 0.1 g. of platinum oxide, 0.5 g. of fused zinc chloride, and four drops of concentrated hydrochloric acid. In this experiment a small amount of the *trans* diacetate was also isolated. The diacetates were separated mechanically and crystallized from high-boiling petroleum ether. The *cis* isomer melted at 166.5–167.5° (cor.) and was identified by the mixed melting point method.

Anal. Calcd. for $C_{22}H_{24}O_4$: C, 74.96; H, 6.87. Found: C, 75.12; H, 6.90.

The *trans* diacetate melted at 196–197° (cor.) and proved to be identical with the diacetate obtained from the *trans*-enediol described later in this paper.

To prepare the **dibenzoate** from the *cis*-enediol a mixture of 0.65 g. of the enediol, 5 cc. of benzoyl chloride and 20 cc. of pyridine was heated under reflux for four hours. The dibenzoate, after crystallization from a benzene–absolute alcohol mixture, melted at 261–263° (uncor.); yield, 0.83 g. Also obtained was 0.15 g. of 2,6-xylil.

Anal. Calcd. for $C_{32}H_{28}O_4$: C, 80.63; H, 5.93. Found: C, 80.66; H, 6.06.

The configuration of this dibenzoate is uncertain. When 0.3 g. of the *trans*-enediol was used in place of the *cis* form 0.35 g. of the same dibenzoate was obtained along with 0.02 g. of 2,6-xylil.

***trans*-2,2′,6,6′-Tetramethylstilbenediol.**—The procedure was the same as that for the *cis* isomer except that no acetic acid was used in the hydrogenation and the treatment with hydrogen was continued for about twelve hours. The *trans*-enediol crystallized in long white needles melting at 151–152° (cor.). The yield was nearly quantitative.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.55; H, 7.51. Found: C, 80.28; H, 7.65.

The *trans*-enediol was only slightly oxidized after exposure to air for four days. Under the same conditions the *cis* isomer was bright yellow after two days.

The **diacetate** from the *trans*-enediol was formed by heating 0.1 g. of the enediol with 10 cc. of acetic anhydride for four hours under reflux. The diacetate, after recrystallization from high-boiling petroleum ether, melted at 196–197° (cor.). The yield was 90 mg.

Anal. Calcd. for $C_{22}H_{24}O_4$: C, 74.96; H, 6.87. Found: C, 75.11; H, 6.89.

Rearrangement of the Tetramethylstilbenediol to 2,6-Xyloin.—A solution of 0.25 g. of the enediol in 20 cc. of methanol was saturated with hydrogen chloride and heated under reflux for one and one-half hours. The flask was stoppered tightly and allowed to stand overnight at room temperature. Removal of the solvent left a mixture of yellow and white crystals. These were separated mechanically and recrystallized from high-boiling petroleum ether. In this way were isolated 0.20 g. of 2,6-xyloin and 0.04 g. of 2,6-xylil. They were identified by the method of mixed melting points.

Reaction of 2,6-Xylil with Phenylmagnesium Bromide.—A solution of 0.675 g. of the xylil in 100 cc. of dry *n*-butyl ether was added to *n*-butyl ether solution containing about four moles of phenylmagnesium bromide to one of the diketone. The mixture, which immediately developed an orange color, was heated under reflux, with stirring, for nine hours. At the end of this time the mixture was cream colored. It was allowed to stand overnight and poured into a funnel containing 100 g. of cracked ice and 10 cc. of glacial acetic acid. The ether layer was separated, washed with water, twice with 10% potassium bicarbonate solution and twice again with water. The residue left after distillation of the ether was taken up in low-boiling petroleum ether and the solution allowed to stand. The yellow and white crystals which formed were separated by hand and recrystallized from low-boiling petroleum ether. In this way 0.13 g. of the xylil and 0.55 g. of the xyloin were isolated.

***trans*-2,2′,4,4′,6,6′-Hexaethylstilbenediol.**—One gram of hexaethylbenzil was dissolved in 20 cc. of methanol, a small

---

(13) In the distillation of solvents from enediols a nitrogen-filled capillary was used. Also the melting points of the enediols were determined in sealed nitrogen-filled tubes.

amount of platinum oxide added and the mixture hydrogenated at one and one-half atmospheres. The mixture was shaken for fifteen hours and filtered. The solvent was distilled at reduced pressure. The solid residue was dissolved in 10 cc. of ether, filtered and the solution concentrated to a small volume. The addition of 20 cc. of low-boiling petroleum ether caused the stilbenediol to separate as white needles melting at 181.5–183.5°.

Anal. Calcd. for $C_{26}H_{36}O_2$: C, 82.05; H, 9.53. Found: C, 82.19; H, 9.55.

The hexaethylstilbenediol reduced Tollens reagent and decolorized a solution of sodium 2,6-dichlorobenzeneoneindophenol. In contact with the air it was oxidized slowly to the benzil.

Conversion of the *cis*-Hexaethylstilbenediol to the *trans*-Modification.—A mixture of 0.45 g. of the *cis*-enediol,[3] 12 cc. of methanol and a small amount of platinum oxide was shaken overnight in a hydrogenation apparatus. No hydrogen was absorbed. From the reaction mixture 0.25 g. of the *trans*-enediol was isolated.

The **diacetate,** obtained by treatment with acetic anhydride, melted at 188–190° and was shown to be identical with the high-melting (*trans*) diacetate obtained previously.[3] No other product could be isolated.

The **dibenzoate** melted at 234–236° (cor.). A mixed melting point with the *trans* dibenzoate[3] showed no lowering. No *cis*-dibenzoate could be detected.

***trans*-2,2′,4,4′,6,6′-Hexamethylstilbenediol.**—A mixture of 1 g. of dimesityl diketone, 0.040 g. of platinum oxide catalyst and 40 cc. of methanol was reduced at a pressure of 1.5–2 atmospheres. The hydrogen absorption was very rapid, and was complete in fifteen minutes. However, the solution was allowed to shake for four and one-half hours. After about thirty minutes it became slightly cloudy and a very small amount of white solid separated. The reaction mixture was filtered and the solid dissolved in a little ether and added to the filtrate. The solvents were removed under diminished pressure. When about three-fourths of the methanol had been removed, the enediol started to precipitate. It was dissolved in ether and the ether solution evaporated to a small volume. Upon addition of low-boiling petroleum ether the enediol precipitated as white flakes. It was washed with small amounts of low-boiling petroleum ether. The melting point in an open capillary was 157–165°; in a sealed nitrogen-filled capillary 166–168°. In the latter case it was possible to remelt the compound several times with no change in the melting point.

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.75; H, 8.21.

The enediol reduced Tollens reagent immediately and gave a positive test with sodium 2,6-dichlorobenzeneoneindophenol. It was much less soluble in methanol, ether, or low-boiling petroleum ether than was the corresponding *cis*-enediol. Likewise it was much more stable to oxidation by the air. Even after twenty-four hours' standing in the air it was only partially oxidized to the diketone.

The **diacetate** melted at 215–216° and was shown to be identical with that reported earlier.[4c]

The **dibenzoate** melted at 235–236° (cor.). A mixture with an authentic specimen showed no depression.

Summary

Catalytic hydrogenation of mesitil by the method of Thompson has been made to yield either the *cis*- or *trans*-enediol. Similar pairs of isomers have been made by this method from 2,6-xylil and 2,2′,4,4′,6,6′-hexaethylbenzil. It has been shown in each instance that the *cis* form can be changed to the corresponding *trans* form by prolonged contact with hydrogen in the presence of platinum.

URBANA, ILLINOIS RECEIVED MAY 6, 1940

[CONTRIBUTION NO. 227 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Reactions of Certain Aldoximes with Diazomethane

BY A. F. THOMPSON, JR., AND MASSIMO BAER[1]

Not much systematic work has been done on the reactions of oximes with diazomethane. In 1909 Forster and Dunn[2] investigated the action of diazomethane upon both forms of the oximes of ortho-, meta- and para-nitrobenzaldehydes. They reported the formation of the corresponding O-methyl ether from the stable[3] (α) form of each oxime, but stated that the O-methyl ethers of the unstable (β) forms of the oximes were never obtained. The only β oxime which reacted, β-*m*-nitrobenzaldoxime, yielded the O-methyl ether corresponding to the α oxime. In this same paper Forster and Dunn reported evidence for the formation of an N-methyl ether by treatment of a benzilmonoxime with diazomethane. In 1908 Forster and Holmes[4] had reported the formation of N-methyl ether in the reaction of the stable form of isonitrosocamphor with diazomethane.

These results suggested the possibility of using

---

(1) From the thesis submitted by Massimo Baer in partial fulfillment of the requirements for the degree of Bachelor of Science.

(2) Forster and Dunn, *J. Chem. Soc.*, **95**, 425 (1909).

(3) See Brady and Bishop, *ibid.*, **127**, 1361 (1925). Their method of designating oximes is followed in this discussion. The N-methyl ethers in this paper will be identified simply by their melting points.

(4) Forster and Holmes, *ibid.*, **93**, 242 (1908).