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.

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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

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(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).

diazomethane as a reagent in the preparation of the rarely occurring isomeric pairs of N-methyl ethers of the aldoximes. To date, such isomeric N-methyl derivatives are known with certainty only in the case of the two N-ethers of 3-amino-2,6-dichlorobenzaldoxime, prepared from the aldehyde and N-methylhydroxylamine.[5]

Five nitrobenzaldoxime isomers were accordingly prepared and the action upon them of diazomethane in ethereal solution was studied. A reaction occurred in every case. The results have been summarized in Table I, along with the results of Forster and Dunn and previous data of the N-methyl ethers. Four of the five oximes reacted with diazomethane to yield the corresponding O-methyl ethers. The change in configuration of *β-m*-nitrobenzaldoxime on methylation, which was reported by the earlier workers, was not observed. However, as was previously reported, *β-p*-nitrobenzaldoxime failed to yield any O-methyl ether.

TABLE I

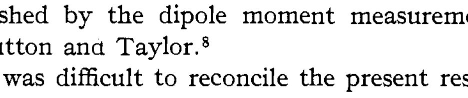
	Ether obtained			
Nitrobenzaldoxime	By Forster and Dunn with CH_2N_2	In this work with CH_2N_2	M. p., °C.	Prev. reported N-methyl ether, m. p., °C.
α-o-	α-O-	α-O-	59	
		N-(HCl)	128–132	125–128
α-m-	α-O-	α-O-	61	
		N-	117	117
β-m-	α-O-	β-O-	72	
		N-	86–88	117
α-p-	α-O-	α-O-	101.5	
		N-	201	205
β-p-		N-	147–149	205

Each of the five oximes studied reacted to furnish small but definite amounts of N-methyl ether. Such N-ethers had never before been isolated as products of the reaction of aldoximes with diazomethane. Moreover, each of the oximes furnished one definite individual N-methyl ether, although all previous methods of alkylation had furnished but one N-methyl ether from a pair of stereoisomeric aldoximes.[6]

The two N-methyl ethers resulting from the *β* forms of *m*- and *p*-nitrobenzaldoximes were, therefore, new substances. Their structures followed from their reactions. Thus, they were readily hydrolyzed by acids at room temperature (in contrast to the oximes) to yield the aldehydes and N-methylhydroxylamine. With concentrated hydrogen iodide they yielded methylamine. The N-methyl ether melting at 147–149° which resulted from *β-p*-nitrobenzaldoxime was readily converted, simply by heating, into the known isomer melting at 201°. This behavior exactly paralleled that of the labile N-methyl ether of 3-amino-2,6-dichlorobenzaldoxime, melting at 171°, which was reported by Meisenheimer to rearrange, on heating, to the stable isomer melting at 207°. That these two N-ethers were stereoisomers of the known N-ethers of *m*- and *p*-benzaldoximes was indicated by these facts and by the method of preparation. They resulted from the *β* oximes under conditions identical with those which produced the two known N-ethers from the *α* forms of *m*- and *p*-nitrobenzaldoxime.

The formation of these two new N-ethers necessitated a reëxamination of the configuration of the previously known N-methyl ethers. There has never before been an isomeric pair of aldoxime N-methyl ethers prepared from the corresponding oximes. Thus the N-methyl ethers of 3-amino-2,6-dichlorobenzaldoxime were prepared by Meisenheimer[5] by the reaction of the aldehyde with N-methylhydroxylamine, and could not be related to the parent oximes.

Brady and Dunn[7] have discussed the configuration of the N-methyl ethers of the nitrobenzaldoximes at some length. All acted alike and *p*-nitrobenzaldoxime may be taken as an example. Brady and Dunn assigned its N-methyl derivative the *β* configuration on the basis of a *trans* interpretation of the Beckmann rearrangement, which occurs readily in acetic anhydride to yield *p*-nitrobenzomethylamide.



$$O_2NC_6H_4-\underset{\underset{O \longleftarrow N-CH_3}{\|}}{C}-H \xrightarrow{Ac_2O} O_2NC_6H_4CONHCH_3$$

Also, they found it to be the main product formed on methylation of *β-p*-nitrobenzaldoxime, and formed in much smaller amount from the *α* oxime, which yielded mostly O-ether.

Further support for the *β* configuration was furnished by the dipole moment measurements of Sutton and Taylor.[8]

It was difficult to reconcile the present results with this interpretation. The known N-methyl ether of *p*-nitrobenzaldoxime melting at 201° which Brady assigned the *β* configuration was here obtained exclusively from the *α* oxime and

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[5] Meisenheimer, Theilacker and Beisswenger, *Ann.*, **495**, 253 (1932).

[6] Brady. Dunn and Goldstein, *J. Chem. Soc.*, 2386 (1926).

[7] Brady and Dunn, *ibid.*, 2413 (1926).

[8] Sutton and Taylor, *ibid.*, 2190 (1931).

the β oxime yielded exclusively the new stereoisomeric N-methyl ether melting at 147–149°. The same relationships obtained in the meta series. More work will have to be done to explain these results. Aldehydes are being sought which will give more favorable yields of the isomeric N-methyl ethers, so that the Beckmann rearrangement can be studied on both forms. In this way it is hoped to arrive at definite configurations for both N-methyl ethers of the aldoximes.

The authors wish to acknowledge the assistance of Mr. B. P. Gray, who aided with some of the experimental work in this paper.

Experimental

Diazomethane was prepared from nitrosomethylurea[9] in the usual manner. The ethereal solution so obtained was dried, filtered to free it of polymethylene, and standardized by titration of excess benzoic acid.

The five isomeric nitrobenzaldoximes used were prepared from the aldehydes and hydroxylamine in the usual way.[10]

Reaction of α-*o*-Nitrobenzaldoxime with Diazomethane.—One-half gram (3 milliequivalents) of the oxime was dissolved in 25 cc. of ether containing 3.5 milliequivalents of diazomethane and the solution was allowed to stand overnight, when the yellow color disappeared. The ether was evaporated and the residue was steam distilled. The distillate, on shaking with chloroform and evaporation, yielded the O-methyl ether. On recrystallization from dilute alcohol 8 mg. was obtained, m. p. 59°; recorded 58°.

The residue from the steam distillation was extracted with sodium hydroxide. The material insoluble in sodium hydroxide was taken up in ether and dry hydrogen chloride gas was passed in. A hydrochloride crystallized out, m. p. 128–132°. The m. p. of *o*-nitrobenzaldoxime N-methyl ether hydrochloride is given by Brady[11] as 125–134°.

Reaction of α-*m*-Nitrobenzaldoxime with Diazomethane.—0.250 gram (1.5 milliequivalents) of oxime was dissolved in 12 cc. of ether containing 2.1 milliequivalents of diazomethane. The reaction mixture was treated as described under α-*o*-nitrobenzaldoxime. Twenty-five mg. of O-methyl ether was obtained, m. p. 61°, recorded 63°, and 10 mg. of N-methyl ether, m. p. 117°, recorded 117°. The N-methyl ether with phenyl isocyanate yielded a derivative, m. p. 119–120°, recorded 119°.

Reaction of β-*m*-Nitrobenzaldoxime with Diazomethane.—0.400 gram of oxime was allowed to stand in a solution of 4 milliequivalents of diazomethane in 20 cc. of ether overnight. After filtration to remove polymethylenes, and extraction with sodium hydroxide to remove unchanged oxime, the ether was evaporated. Extraction with petroleum ether yielded 40 mg. of O-methyl ether, m. p. 72°; recorded 71–72°. The residue on recrystallization from ligroin yielded 10 mg. of a new compound, m. p. 86–88°. On standing with 50% hydrochloric acid *m*-nitrobenzaldehyde was obtained and the solution, freed from aldehyde with ether, reduced Fehling solution in the cold, indicating the presence of N-methylhydroxylamine. With concentrated hydrogen iodide the characteristic odor of methylamine was observed. The method of isolation and properties indicate that this substance is a new N-methyl ether corresponding to the β-form of *m*-nitrobenzaldoxime.

Reaction of α-*p*-Nitrobenzaldoxime with Diazomethane.—One-half gram (3 milliequivalents) of oxime was dissolved in 40 cc. of ether containing 8 milliequivalents of diazomethane. It was treated like the other oximes. Forty mg. of O-methyl ether was obtained, m. p. 101.5°, recorded 101°. Fifty mg. of N-methyl ether was obtained, m. p. 199–201°, recorded 205°.

Reaction of β-*p*-Nitrobenzaldoxime with Diazomethane.—0.940 gram (5.65 milliequivalents) of oxime was dissolved in 35 cc. of ether containing 6.15 milliequivalents of diazomethane and the solution was allowed to stand overnight. It was worked up in the usual manner. The oxime was extracted as usual but no O-methyl ether was obtained by extraction with petroleum ether. The residue on recrystallization from ligroin yielded 9 mg. of substance melting at 147–149°. On remelting the substance in the same tube, a melting point of 196–198° was obtained, undoubtedly the known N-methyl ether.

The substance on hydrolysis with sulfuric acid and extraction of the aldehyde formed gave a positive test for N-methylhydroxylamine with Fehling solution. On treatment with concentrated hydrogen iodide, methylamine was obtained, characterized as N-methylpicramide, m. p. 112°. This indicates the substance is a new N-methyl ether of *p*-nitrobenzaldoxime.

Reaction of α-*p*-Nitrobenzaldoxime O-Methyl Ether with Diazomethane.—To test the hypothesis that the N-ethers might possibly result from action of diazomethane upon the O-ethers, which were first formed, the O-ether of α-*p*-nitrobenzaldoxime was treated with diazomethane under the same conditions as were used with the oximes. The O-ether was prepared in good yield, free from N-ether, by warming the pure potassium salt of the oxime, prepared by shaking the oxime in ethereal solution with solid potassium hydroxide, with methyl iodide. It failed to interact with diazomethane in any manner but was recovered unchanged from the reaction mixture.

Summary

The interaction of diazomethane and five isomeric nitrobenzaldoximes has been investigated. The following oximes yielded the corresponding products: α-*o*-nitrobenzaldoxime, the O-methyl and N-methyl ethers; α-*m*-nitrobenzaldoxime, the O-methyl and N-methyl ethers; β-*m*-nitrobenzaldoxime, the O-methyl and N-methyl ethers; α-*p*-nitrobenzaldoxime, the O-methyl and N-methyl ethers; β-*p*-nitrobenzaldoxime, the N-methyl ether. The N-methyl ethers obtained from the β-*m*-nitrobenzaldoxime, and β-*p*-nitrobenzaldoxime were new substances, isomeric with the known N-methyl ethers derived from these oximes. The question of the configuration of these N-ethers has been discussed.

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(9) "Organic Syntheses," Vol. 15, 1935, p. 48.

(10) Forster and Dunn, *J. Chem. Soc.*, **95**, 430 (1909).

(11) Brady, Dunn and Goldstein, *ibid.*, 2394 (1926).