

*The Structural Assignments for the Geometrical  
Isomers of  $\alpha, \alpha'$ -Dimethylstilbene*

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Wessely and Welleba<sup>1)</sup> assigned to  $\alpha, \alpha'$ -dimethylstilbene of m. p. 107°C the trans- and to the isomer of m. p. 67°C the cis-configuration on the basis of their dipole moment measurement, although without giving any experimental details. Some ambiguity, however, yet exists in the application of this method to the present case, because the substances examined are hydrocarbons probably with a small dipole

moment value at most, even for the cis-compound. Suzuki<sup>2)</sup> reached the same assignments by a theoretical consideration of their ultraviolet absorption spectra in relation to the shift of the absorption maximum due to the change in conjugation caused by the steric requirement of the substituent groups. It seemed desirable to confirm these conclusions by an unambiguous method. We now report the synthesis of *cis*- and *trans*-4, 4'-dinitro- $\alpha, \alpha'$ -

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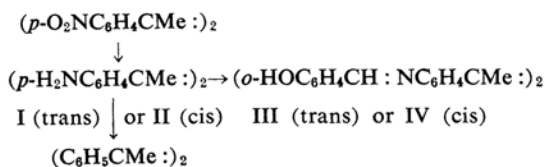
1) F. v. Wessely and H. Welleba, *Ber.*, **74**, 777 (1941).

2) H. Suzuki, *This Bulletin*, **25**, 145 (1952).

dimethylstilbene, whose geometrical configurations have been determined unequivocally by dipole moment measurement, and their conversion into *cis*- and *trans*- $\alpha, \alpha'$ -dimethylstilbene. This constitutes chemical evidence in favor of the already assumed configuration of isomeric  $\alpha, \alpha'$ -dimethylstilbenes.

4, 4'-Dinitro- $\alpha, \alpha'$ -dimethylstilbene was prepared from *p*-nitroacetophenone hydrazone with a method similar to that of Vargha and Kovacs's synthesis<sup>3)</sup> of some substituted diethylstilbenes. The product was fractionated by recrystallization into the *trans*-, m. p. 222.4°C, and the *cis*-isomer, m. p. 151.8°C. The geometrical configurations were derived from dipole moment measurement in benzene<sup>4)</sup>, the former having a dipole moment of 0.68D and the latter a dipole moment of 6.88D. For the oxidation of the hydrazone to *p*-nitrophenyldiazoethane, one of the intermediates, we found that lead dioxide was much more efficient than mercuric oxide originally<sup>3)</sup> used.

Catalytic reduction of *trans*-4, 4'-dinitro- $\alpha, \alpha'$ -dimethylstilbene in the presence of a Raney nickel catalyst yielded 58% of 4, 4'-diamino- $\alpha, \alpha'$ -dimethylstilbene (I), m. p. 157.5°C, and an oily mixture, which gave, on treatment with salicylaldehyde, two isomeric *N, N'*-disalicylidene derivatives (III and IV) in 6 and 13% yield, respectively, based on the dinitro compound used. In a separate experiment, pure diamine I gave disalicylidene derivative III in a nearly quantitative yield, but never gave the isomeric derivative IV; therefore, the latter was presumed to be formed only from the geometrically isomeric diamine II, which could not be isolated as such in this study.



Although the assignment of configuration to the salicylidene derivatives is irrelevant to the main theme of the present report, it is obvious that the geometrical configurations of these compounds (III and IV) correspond with those of diamines I and II, respectively, since it is impossible for the complete inversion to the other configuration to take place in both *cis*- and *trans*-isomer.

Similarly reduced, *cis*-4, 4'-dinitro- $\alpha, \alpha'$ -dimethylstilbene gave an oily mixture, which afforded *N, N'*-disalicylidene derivatives III and IV in yields of 12 and 61%, respectively,

indicating the formation of diamine II in a yield of over 61%.

Although the catalytic reduction of 4, 4'-dinitro- $\alpha, \alpha'$ -dimethylstilbene was thus accompanied by *cis*-*trans* isomerization, it follows from the above results that diamine I corresponds to the *trans*- and diamine II to the *cis*-configuration. If diamine I which was isolated from the reduction product of the *trans*-dinitro compound in a yield of at least 58% had had the *cis*-configuration, the equilibrium mixture of the isomeric diamines after stereomutation under the obtaining experimental conditions would have contained 58% or more of the *cis*-form, and, consequently, this compound (diamine I) should have been formed from the *cis*-dinitro compound in a yield of at least 58%, which is impossible because the other isomer (diamine II) was formed in 61% yield.

*trans*-Diamine I was diazotized and reduced with hypophosphorous acid, giving (67.4% of)  $\alpha, \alpha'$ -dimethylstilbene, m. p. 107°C, as the sole isolable product. This result shows that little, if any, stereomutation took place in the course of the deamination; extensive stereomutation would have given a mixture which melted much lower and, finally, an equilibrium mixture containing about 45%<sup>5)</sup> of the lower melting isomer. Similarly, the diamine mixture (containing at least 61% of the *cis* form) from the catalytic reduction of *cis*-dinitrodimethylstilbene gave (58% of) a mixture of isomeric  $\alpha, \alpha'$ -dimethylstilbenes consisting of 78% (or 70%) of the form, m. p. 67°C, and 22% (or 30%) of the form, m. p. 107°C. These results establish that dimethylstilbene, m. p. 107°C, has the *trans*- and the isomer, m. p. 67°C, the *cis*-configuration.

### Experimental

Melting points are corrected.

***cis*- and *trans*-4, 4'-Dinitro- $\alpha, \alpha'$ -dimethylstilbene.**—*p*-Nitroacetophenone hydrazone (10 g.) and lead dioxide (100 g.) were stirred in benzene (500 ml.) for 5 hr. at room temperature, the mixture was filtered, and sulphur dioxide was passed into the red filtrate until the solution turned light yellow. Removal of the benzene on a water-bath gave a solid product, which, recrystallized from acetic acid, afforded *trans*-4, 4'-dinitro- $\alpha, \alpha'$ -dimethylstilbene (5.0 g., 60.1%) in colorless crystals, m. p. 221.6~222.4°C (Found: N, 9.71.  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4$  requires N, 9.40%). On slow evaporation at room temperature, the mother liquor deposited a mixture of the *trans*- and the *cis*-dinitro compound in large crystalline forms; the *cis*-isomer was picked out and recrystallized from acetone, giving *cis*-4, 4'-dinitro- $\alpha, \alpha'$ -dimethylstilbene in pale yellow prisms (1.9 g., 22.8%), m. p. 150.8~151.8°C (Found: N, 9.56.  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4$  requires N, 9.40%). When light

3) L. v. Vargha and E. Kovács, *Ber.*, **75**, 794 (1942).

4) T. Simozawa and Y. Nagai, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **81**, 22 (1960).

5) O. Simamura and H. Suzuki, *This Bulletin*, **28**, 231 (1954).

petroleum was used instead of benzene in the above preparation and the solvent was allowed to evaporate at room temperature from the filtered reaction mixture, 1-*p*-nitrophenyldiazoethane was obtained in red needles, m. p. 84.5~87.5°C (decomp.) (Found: N, 23.69.  $C_8H_7O_2N_3$  requires N, 23.73%). Passage of sulphur dioxide into a solution of 1-*p*-nitrophenyldiazoethane in light petroleum gave a white precipitate of 1, 2-bis-(*p*-nitrophenyl)-1,2-dimethylethylene sulphone which was difficult to purify, decomposition at 130~200°C (Found: N, 8.31.  $C_{16}H_{14}N_2O_6S$  requires N, 7.73%).

**Reduction of *trans*-4, 4'-Dinitro- $\alpha$ ,  $\alpha'$ -dimethylstilbene.**—With Stannous Chloride.—Powdered *trans*-4, 4'-dinitro- $\alpha$ ,  $\alpha'$ -dimethylstilbene (1.43 g.) was allowed to stand overnight with anhydrous stannous chloride (18 g.) in acetic acid (80 ml.) saturated with hydrogen chloride. The mixture was heated for 1 hr. on a water-bath and cooled. The precipitate was filtered off and dissolved in hot water, and the solution made alkaline with sodium hydroxide. The white precipitate was filtered off and recrystallized from benzene, affording *trans*-4, 4'-diamino- $\alpha$ ,  $\alpha'$ -dimethylstilbene (I) (1.149 g., 98%) in needles, m. p. 156.6~157.6°C (recrystallized from ethanol) (lit<sup>6</sup>, m. p. 146°C) (Found: N, 12.1. Calcd. for  $C_{16}H_{18}N_2$ : N, 11.8%).

This diamine and excess of salicylaldehyde in ethanol gave a nearly quantitative yield of *N*, *N'*-disalicylidene-4, 4'-diamino- $\alpha$ ,  $\alpha'$ -dimethylstilbene (III) (0.74 g.), m. p. 222.5~226.1°C (from benzene) (Found: N, 6.52.  $C_{30}H_{26}N_2O_2$  requires N, 6.28%).

**Catalytic Reduction.**—The catalyst was a Raney nickel prepared according to the directions for W6 catalyst<sup>7</sup>, washed with acetone and stored in it. The nitro compound (1.373 g.) was reduced with hydrogen in the presence of the nickel catalyst (from 4 g. of Raney alloy) in ethanol (20 ml.) under cooling with water. After the catalyst was filtered off, concentration of the filtrate gave *trans*-4, 4'-diamino- $\alpha$ ,  $\alpha'$ -dimethylstilbene (I) (0.635 g., 57.8%), m. p. 157.6°C. Removal of the ethanol from the mother liquor gave an oil which, on treatment with salicylaldehyde and fractional crystallization of the product from ethanol-benzene, yielded *trans*-*N*, *N'*-disalicylidene-4, 4'-diamino- $\alpha$ ,  $\alpha'$ -dimethylstilbene (III) (0.130 g., 6.3%) and the *cis*-isomer (IV) (0.282 g., 13.2%), m. p. 150.0~153.5°C (Found: N, 6.53%.  $C_{30}H_{26}N_2O_2$  requires N, 6.28%).

**Catalytic Reduction of *cis*-4, 4'-Dinitro- $\alpha$ ,  $\alpha'$ -dimethylstilbene.**—Catalytic reduction of the *cis*-dinitro compound (1.12 g.) gave only an oil (0.8 g., 87%), which was converted into a mixture of *N*, *N'*-disalicylidene derivatives (1.57 g., m. p. 145~171°C). Fractional crystallization from ethanol-benzene gave the *cis*-disalicylidene derivative IV (1.06 g., 61% based on the dinitro compound subjected to the reduction) and the *trans*-isomer III (0.21 g., 12%).

**Deamination of 4, 4'-Diamino- $\alpha$ ,  $\alpha'$ -dimethylstilbenes.**—The *trans*-diamino compound I (0.474 g.) was diazotized with sodium nitrite (0.4 g.) in diluted hydrochloric acid ( $H_2O$  40 ml. and concd.

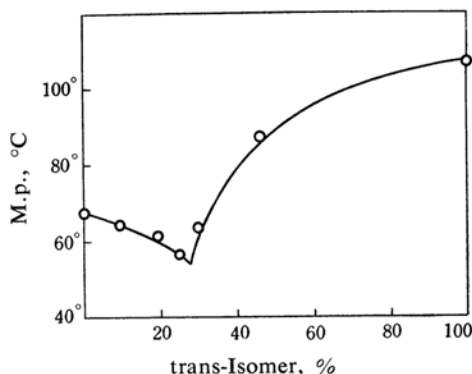


Fig. 1. Melting point—composition curve for a mixture of *cis*- and *trans*- $\alpha$ ,  $\alpha'$ -dimethylstilbene.

HCl 5 ml.) at 0°C. The solution was added to aqueous sodium hypophosphite (10 g. in  $H_2O$  10 ml. and concd. HCl 10 ml.) and the mixture left overnight in a refrigerator. The solution was extracted with ether, the extract washed and dried ( $CaCl_2$ ), and the ether removed. The residue was chromatographed in light petroleum on alumina, giving  $\alpha$ ,  $\alpha'$ -dimethylstilbene (0.277 g., 67.4%), m. p. and mixed m. p. 104.5~107°C.

The product (0.484 g.) from the catalytic reduction of *cis*-4, 4'-dinitro- $\alpha$ ,  $\alpha'$ -dimethylstilbene was subjected to deamination as described above, yielding  $\alpha$ ,  $\alpha'$ -dimethylstilbene (0.246 g., 58%), m. p. 52~60°C. This melting behavior indicates that the dimethylstilbene formed contained about 78% (or 70%) of the low melting isomer (see the accompanying figure).

### Summary

*cis*- and *trans*-4, 4'-Dinitro- $\alpha$ ,  $\alpha'$ -dimethylstilbene were prepared by oxidation of *p*-nitroacetophenone hydrazone with lead dioxide in benzene, followed by treatment with sulphur dioxide. Catalytic reduction of the *trans*-dinitro compound gave at least 64% of *trans*-4, 4'-diamino- $\alpha$ ,  $\alpha'$ -dimethylstilbene, m. p. 157.6°C, and a similar reduction of the *cis*-dinitro compound afforded a mixture of the *cis*- and *trans*-diamino compound which was shown to contain at least 61% of the *cis*-isomer. On deamination, the *trans*-diamino compound yielded  $\alpha$ ,  $\alpha'$ -dimethylstilbene melting at 107°C, and the above mixture of the *cis*- and *trans*-isomer, a mixture of the isomeric  $\alpha$ ,  $\alpha'$ -dimethylstilbenes in which the lower melting form predominated (at least 70%). These findings establish that  $\alpha$ ,  $\alpha'$ -dimethylstilbene, m. p. 107°C, has the *trans*- and the isomer, m. p. 67°C, the *cis*-configuration.

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6) M. J. Allen and A. H. Corwin, *J. Am. Chem. Soc.*, **72**, 117 (1950).

7) "Organic Syntheses", Coll. Vol. 3, (1955), p. 176.