Some Observations on the Reactions of α,α'-Dimethylstilbene and Related Compounds

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F. v. Wessely and H. Welleba[2] reported that α,α'-dimethylstilbene of m. p. 67° was not isomerized to the geometrical isomer by the action of iodine in benzene solution. Therefore in view of the well established fact that thermally or photochemically activated halogen can cause the cis-trans interconversion of various ethylenic compounds, it seemed of interest to study the actions of various agents which are known to be effective in causing the stereoisomerization of the ethylenic compound on the geometrical isomers of α,α'-dimethylstilbene.[3] The present paper gives an account of some observations made during this investigation.

Ramart-Lucas and Salmon-Legagneur[5] heated α,α'-dimethylstilbene with a little concentrated sulfuric acid and found that the isomerization of the trans to the cis isomer took place only to a very limited extent, but that the reverse reaction could not be effected. The re-examination of the action of sulfuric acid (for 20 hours at 210°) revealed that the isomerization, in fact, occurred from either isomer yielding an equilibrium mixture consisting of about 55 % of the trans and 45 % of the cis isomer. The implication of this result has already been discussed[4] in terms of the steric effect of substituents on the stabilization of the molecule due to the conjugation of unsaturated systems.

We repeated Wessely and Welleba's experiment[2] by boiling 0.1 g. of *cis*-dimethylstilbene and 14 mg. of iodine in 5 cc. of benzene for 4.5 hours and recovered the unchanged material, thus confirming their results. H. J. Barber et al.,[6] however, effected the isomerization of *cis*-4,4'-dibromo-α,α'-dimethylstilbene to the trans isomer by boiling in the presence of traces of iodine in nitrobenzene. When trans-α,α'-dimethylstilbene was heated at 210° for 19 hours with a little iodine an oily product was formed, from which 22 % of *meso*-2,3-diphenylbutane[7], m. p. 129-129.5°, was isolated. The cis isomer gave the same result. In none of the experiments carried out was any isomerized product detected. Part of α,α'-dimethylstilbene was apparently hydrogenated at the ethylenic double bond by the action of iodine at the expense of the remainder. No products expected from the dehydrogenation could be isolated. A similar treatment of stilbene with iodine yielded 38 % of bibenzyl.

As evidence has been obtained to show that bromine atoms can isomerize dimethyl-

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[2] F. v. Wessely and H. Welleba, *Ber.*, **74**, 777 (1941).

[3] α,α'-Dimethylstilbene exists in two geometrically isomeric forms, one with m.p. 107° and the other with m.p. 67°; the former was assigned the trans and the latter the cis configuration on the basis of the dielectric constant measurements by Wessely and Welleba[2], but relevant numerical data have never been available. Recently, a confirmation of this assignment has been obtained by one of us[4] from theoretical considerations concerning the ultraviolet absorption spectra of the two isomers; accordingly, in this paper the higher melting isomer will be designated as the trans and the lower melting one as the cis isomer.

[4] H. Suzuki, This Bulletin **25**, 145 (1952).

[5] Ramart-Lucas and Salmon-Legagneur, *Bull. Soc. Chim. France*, [4] **45**, 718 (1929).

[6] H. J. Barber, R. Slack and A. M. Woolman, *J. Chem. Soc.*, **1943**, 99.

[7] A small amount of this substance was also obtained as a by-product in the reduction of 3,3-diphenyl-2-butanone with sodium and alcohol to 3,3-diphenyl-2-butanol in the course of an attempted synthesis of dimethylstilbene from acetophenone. W. Thorner and Th. Zincke (*Ber.*, **11**, 1988 (1878)) claimed to have prepared 2,2-diphenylbutane, m.p. 127.5~128.5°, by the action of phosphorus and hydrogen iodide on acetophenone and pointed out the identity of the substance with 2,3-diphenylbutane formed from (1-bromoethyl)benzene by the action of zinc or sodium (Br. Radziszewsky, *Ber.*, **7**, 140 (1874); C. Engler and H. Bethgef, ibid,. **7**, 1125 (1874)). It is highly probable that 2,2-diphenylbutane of Thorner and Zincke is *meso*-2,3-diphenylbutane.

stilbene, as will be described later, it is only because of the steric repulsion exerted by large groups at the ethylenic linkage on an attacking iodine atom which is larger than a bromine atom that iodine is ineffective in causing the isomerization at lower temperatures. On the other hand at higher temperatures, at which the isomerization catalyzed by iodine atoms might take place, the disproportionation of dimethylstilbene by iodine becomes prevailing, so that any isomerization would be completely masked.

According to Barber et al.,[6] *trans*- and *cis*-4,4'-dibromo- α,α'-dimethylstilbenes are different from each other in their behavior towards bromine in chloroform at room temperature; the latter adds bromine to give 2,3-dibromo-2,3-bis-(*p*-bromophenyl)-butane, while the former does not. Further, J. Lévy[8] reported the formation of dibromide, m. p. 150-155°, from dimethylstilbene. The results of the present experiments on the action of bromine are noteworthy. When bromine was added to a carbon tetrachloride solution of *trans*- or *cis*-dimethylstilbene in diffuse room light at night the decolorization occurred and the evolution of hydrogen bromide took place immediately. Thus, one mole of dimethylstilbene consumed ultimately about two moles of bromine, approximately two moles of hydrogen bromide being evolved. Evidently, the substitution by bromine took place rather than the addition to the double bond. The product was, besides traces of α-bromoacetophenone, the same 1,4-dibromo-2,3-dimethyl-2-butene, m. p. 153.5-155°, whether the starting material was the trans or the cis isomer. The structure of this compound, which seems to be identical with that obtained from bromine and 2,3-diphenylbutadiene[9], was established on the basis of analytical data and the result of ozonolysis which gave α-bromoacetophenone. It is probable that Lévy obtained this compound and described it as dimethylstilbene dibromide. The crude product from this reaction, melting at 134-150°, contained some crystals which decomposed with effervescence at about 130°. It is suspected that dimethylstilbene dibromide may have been formed, although it could not be actually isolated. When one mole of bromine was allowed to react with one mole of *trans*-dimethylstilbene in carbon tetrachloride in the dark, about 42 % of the dimethylstilbene was converted to a crystalline mixture, melting at about 130° to 150°, the bromine content of which corresponded approximately to the calculated value for 1,4-dibromo-2,3-diphenyl-2-butene, and about 27 % was recovered as a crystalline mixture, melting at 50° to 77°, consisting of *cis*- and *trans*-dimethylstilbenes. When a similar experiment was carried out in a quartz flask in direct sunlight, there was a vigorous evolution of hydrogen bromide, giving a complex mixture of products from which 1,4-dibromo-2,3-diphenyl-2-butene (6 %) and a small amount of α-bromoacetophenone (as 2,4-dinitrophenylhydrazone) were isolated.

The observation that the cis-trans isomerization of dimethylstilbene took place and that the intervention of oxygen occurred as revealed by the formation of α-bromoacetophenone suggests that the action of bromine on dimethylstilbene involves bromine atoms and, consequently, radicals at some stage of the reaction, because it is well established that bromine atoms induce the cis-trans isomerization of ethylenic compounds, and that the addition of bromine to a double bond can take place through a radical mechanism involving bromine atoms.[10] A bromine atom adds to one carbon atom of the central double bond of dimethylstilbene forming a radical intermediate which contains a single bond between the α,α' carbon atoms. The radical can then react in three ways: (1) cis-trans isomerization by the rotation of the groups round the single bond between the α,α' carbons followed by the expulsion of the bromine atom to regenerate a double bond between the α,α' carbons; (2) reaction with a bromine molecule to give dimethylstilbene dibromide and another bromine atom; and (3) reaction with oxygen to give an oxygenated radical which decomposes in a manner generally postulated for peroxides[11] with the fission of the bond between α,α' carbons producing eventually a molecule of acetophenone which is then brominated to α-bromoacetophenone. The mechanism of the formation of 1,4-dibromo-2,3-diphenyl-2-butene is not clear. There are two possibilities. One involves dimethylstilbene dibromide and 2,3-diphenylbutadiene as intermediates. Inspection of a model of the former constructed with Taylor-Hirschfelder atom models shows that there is considerable steric strain due to the crowding of the bulky substituent groups. Accordingly dimethylstilbene dibromide may be so unstable a substance as to decompose readily. If any decomposition takes place at a low temperature during the present reaction to yield

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[8] J. Lévy, *Bull. Soc. Chim. France*, [4] **29**, 878 (1921).

[9] C. F. H. Allen, C. G. Eliot and A. Bell, *Can. J. Research*, **17**B, 75 (1939); *C. A.*, **33**, 6284 (1939).

[10] O. Simamura, This Bulletin, **17**, 274 (1942).

[11] J. E. Leffler, *Chem. Rev.*, **45**, 385(1949); C. E. Frank, ibid., **46**, 155 (1950).

hydrogen bromide and 2,3-diphenylbutadiene, then the latter would give dibromodiphenylbutene through the 1,4-addition with bromine. It is possible that oxygen may intervene at the stage where 2,3-diphenylbutadiene adds bromine, the latter attaching itself to the terminal carbon and oxygen to the α carbon atom, and the subsequent decomposition yielding α-bromoacetophenone. The other mechanism involves the substitution by bromine at the methyl group through a radical chain mechanism: a bromine atom abstracts a hydrogen atom from a methyl group of dimethylstilbene, producing a radical stabilized by a mesomeric structure, which in turn gives, by reacting with a molecule of bromine, 1-bromodiphenylbutene and a bromine atom. That 1-bromodiphenylbutene could not be isolated from the reaction mixture might suggest either that it is substituted by bromine at the remaining methyl group to give dibromodimethylstilbene much more rapidly than dimethylstilbene is substituted to give the monobromo derivative or that the bromine atom is unable to attack the methyl group as postulated above.

The action of bromine on dimethylstilbene leading to the facile substitution at the methyl group rather than the addition at the double bond seemed to be attributable to the steric effect in the molecule caused by the crowding of bulky groups; consequently, in order further to ascertain the effect of substituents in the α,α' positions on the bromination of stilbenes the following experiments were conducted. To a solution of 0.33 millimole of an α,α'-disubstituted stilbene in 5 cc. of carbon tetrachloride was added 0.16 millimole of bromine in carbon tetrachloride (about 0.17 cc.) in diffuse light, and the time required for decolorization was compared. In Table I where the results are summarized, the figures in the column headed I denote the time which had elapsed before the red color of the reaction mixture just matched that of a standard bromine solution in carbon tetrachloride, which was approximately 6 millimolar in bromine; the figures in columns II and III denote the time when the reacting solution was faintly pale yellow and completely colorless, respectively. The number of plus signs in the fifth column indicate the approximate intensity of the evolution of hydrogen bromide visually observed. The values in the last column were determined by separate experiments.

TABLE I

ACTION OF BROMINE ON VARIOUS STILBENES

	Consumption of bromine (time in min.)			Evolution of HBr	Approximate number of moles of bromine reacted
	I	II	III		
Stilbene	2-3 (hrs.)	—	—	0	1
trans-α-Methylstilbene	1-2	—	—	++	1
trans-α,α'-Dimethylstilbene	6	10	13	++++	2
cis-α,α'-Dimethylstilbene	7-9	35–45	—	+++	2
α-Methyl-α'-ethylstilbene	30	50	65	++	2
trans-α,α'-Diethylstilbene	40	60	—	+	2
cis-α,α'-Diethylstilbene	60	115	—	+	2
Methyltriphenylethylene	2-2.5 (hrs.)	—	—	+	1

Of the compounds shown in Table I stilbene and methylstilbene add bromine to the double bond, the former more slowly than the latter; this is probably due to the retarding action of atmospheric oxygen. Methylstilbene appears to react faster because a little hydrogen bromide formed by the substitution accelerates the addition of bromine by producing, in co-operation with oxygen, bromine atoms which start the chain addition reaction of bromine[10].

Methyltriphenylethylene did not add bromine, but was substituted at the methyl group only slowly in spite of the evolution of hydrogen bromide; the absence of the addition is probably due to the steric hindrance caused by the large substituents as in the case of tetraphenylethylene which also adds no bromine. The slowness of the substitution is also attributable to the steric hindrance which prevents the double bond from producing bromine atoms from hydrogen bromide and oxygen.

Experimental

Materials Dimethylstilbene was prepared according to Ott[12] by dehydration and rearrangement of 100 g. of 3,3-diphenyl-2-butanol, b. p. 172-3° at 14 mm., n_D^{21} 1.5822 (synthesized by the method of Lévy[8]), by boiling with 13 g. of concentrated sulfuric acid in 400 g. of glacial acetic acid for 20 hours. Recrystallization of the crude product from petroleum ether yielded 34 g. of the trans

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[12] E. Ott, *Ber.*, **61**, 2135 (1928).

isomer, m. p. 107°. The purification of the cis isomer proved to be difficult. The best method was to grow large crystals and to pick out hexagonal plates in which the cis isomer had crystallized. Repeated recrystallization from petroleum ether gave 10 g. of the cis isomer, m. p. 67–67. 3°.

α-Methylstilbene was prepared according to Hell[13] and Ley.[14] Dehydration of 43 g. of 1, 2-diphenyl-2-propanol by doiling with 80 g. of acetic anhydride and 40 g. of acetyl chloride gave an oil containing crystals. The crystals were filtered, and recrystallization from petroleum ether gave 20 g. of *trans*-α-methylstilbene, m. p. 83–83. 5° The oily product was fractionally distilled in vacuo to yield 4 g. of an oil, b. p. 151–155° at 14 mm., which consisted mainly of *cis*-α-methylstilbene as revealed by the ultraviolet absorption spectrum.[4]

α-Methyl-α′-ethylstilbene was prepared by the method of Lévy.[8] The isomer which crystallized, m. p. 47–8°, was found to be the trans form by means of the ultraviolet absorption spectrum. The cis isomer could not be freed from contamination with a considerable amount of the trans isomer, as revealed by ultraviolet spectrum,[4] and formed an oily specimen.

α, α′-Diethylstilbene was prepared similarly to the synthesis of the dimethyl analogue. α, α-Diphenylbutyraldehyde, b. p. 185–190° at 18 mm. and ethylmagnesium iodide in ether gave 4, 4-diphenyl-3-hexanol, b. p. 185° at 14 mm., which, boiled with a little concentrated sulfuric acid in glacial acetic acid, yielded an oily mixture of the cis and trans forms, b. p. 166° at 12 mm. On cooling, the oil deposited crystalline trans isomer, which melted at 77–78° after repeated crystallizations from petroleum ether. The mother liquor was further fractionated and gave an oil, b. p. 177–8° at 22 mm., which was shown to consist mainly of *cis*-α, α′-diethylstilbene by measurement of the ultraviolet absorption spectrum.[4]

Methyltriphenylethylene was prepared according to Meisenheimer[15] by the action of phenylmagnesium bromide on 2, 2-diphenylpropanal, b. p. 170° at 15 mm., followed by dehydration and rearrangement of the resulting carbinol with concentrated sulfuric acid. The product melted at 88–9°, b. p. 210° at 14 mm.

Isomerization by Sulfuric Acid *cis-* or *trans*-Dimethylstilbene (about 0. 8 g.) was heated for 20 hours at 210° with a few pieces of biscuit chips impregnated with concentrated sulfuric acid in a sealed tube. It was cooled, the crystals were pressed on a porous plate to remove some adhering oily matter, and the isomeric composition of the product was determined by comparing its fusing behavior with that of a standard sample of known composition. The isomerization occurred from either isomer giving an equilibrium mixture consisting of about 55% of the trans and 45% of the cis isomer. No isomerization took place at 100° for 20 hours, and only a slight isomerization in the absence of sulfuric acid at 210° for 20 hours.

Action of Iodine A sealed tube containing 1. 45 g. of *trans*-dimethylstilbene and 0. 03 g. of iodine was heated for 19 hours in boiling nitrobenzene. The reaction mixture, taken up in ether (with active charcoal), filtered, and the ether removed from the filtrate, gave an oil, from which 0. 315 g. of *meso*-2, 3-diphenylbutane, m. p. 129. 0–129. 5°, crystallized, the melting point being not depressed on admixture with an authentic specimen prepared by hydrogenating *cis*-dimethylstilbene with one mole of hydrogen in the presence of palladium-barium sulfate in ether. An experiment with the cis isomer gave the same result. Similarly stilbene gave 38% of bibenzyl, m. p. 48–51°, identified by the mixed melting point with an authentic specimen.

Action of Bromine Bromine (14. 5 millimoles) was added to 1. 503 g. of *trans*-dimethylstilbene in 15 cc. of carbon tetrachloride. After decolorization the carbon tetrachloride was removed in vacuo at room temperature and 2. 496 g. of a crystalline compound, m. p. 134–150°, was obtained. Repeated crystallizations from carbon tetrachloride gave 0. 974 g. of 1, 4-dibromo-2, 3-diphenyl-2-butene, needles, m. p. 153. 5–155° (Found: Br, 43. 6. Calcd. for $C_{16}H_{14}Br_2$: Br, 43. 72%). This substance (0. 42 g.), on ozonization in 50 cc. of chloroform followed by decomposition with water, gave 0. 41 g. of α-bromoacetophenone. It was observed under a microscope that the crude product melting at 134–150° contained some crystals which decomposed with effervescence at about 130°. It may be suspected that dimethylstilbene dibromide was also formed. In some experiments carried out similarly to those above, the crude product was washed with a little alcohol and the alcoholic solution deposited, on addition of 2, 4-dinitrophenylhydrazine solution, a very small amount of α-bromoacetophenone 2,4-dinitrophenylhydrazone, m. p. 220°.

The action of bromine on *cis*-dimethylstilbene gave similar results. *trans*-Dimethylstilbene (0. 375 g., 1. 8 millimoles) in carbon tetrachloride, added in the dark with 1. 8 millimoles of bromine in the same solvent (1: 20), and the solvent removed in vacuo, gave a crystalline mass, which was extracted with petroleum ether. The insoluble residue, melting at 130 to 150°, weighed 0. 23 g. (Found: Br, 42. 4, Calcd. for $C_{16}H_{14}Br_2$: Br, 43. 72%), which on repeated crystallizations from carbon tetrachloride gave 0. 138 g. of 1, 4-dibromo-2, 3-diphenyl-2-butene. Evaporations of the petroleum extract gave about 0. 1 g. of a crystalline mixture, m. p. 50–77°, consisting of *cis-* and *trans*-dimethylstilbenes.

trans-α-Methylstilbene consumed about 1 mole of bromine with evolution of hydrogen bromide and gave 1, 2-dibromo-1, 2-diphenylpropane, m. p. 126–7°, as isolable compound.

Methyltriphenylethylene reacted with bromine in carbon tetrachloride only slowly in the dark, but, very rapidly in sunlight, about 1 mole of bromine being taken up with the evolution of hydrogen bromide in accordance with the observation of Meisenheimer[15]. The only product isolated was 3-bromo-1, 1, 2-triphenylpropene, m. p. 121° (from petroleum ether).

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[13] C. Hell, ibid., **37**, 453 (1904).
[14] H. Ley, ibid., **50**, 243 (1917).
[15] J. Meisenheimer, *Ann.*, **436**, 126 (1927).

cis-Diethylstilbene (2.668 g.) in 30 cc. of carbon tetrachloride reacted with nearly 2 moles of bromine in the course of a few days in the dark, hydrogen bromide being evolved. The removal of the solvent gave viscous matter and 0.78 g. of 2, 5-dibromo-3, 4-diphenyl-3-hexene, m. p. 156–8° (from carbon tetrachloride).

Summary

cis- and *trans*-α, α'-Dimethylstilbene, heated with a little sulfuric acid at 210°, were isomerized to an equilibrium mixture consisting of 55% of the trans and 45% of the cis isomers. Heated with iodine at 210°, they yielded *meso*-2, 3-diphenylbutane. The action of bromine produced 1, 4-dibromo-2, 3-diphenyl-2-butene; under certain experimental conditions the concurrent cis-trans isomerization was observed. This fact, together with the isolation of a small smount of α-bromoacetophenone as a by-product, supports the view that the reaction proceeds by a mechanism involving bromine atoms. The action of bromine on some α, α'-disubstituted stilbenes was examined. The reactions observed were discussed in terms of the steric effect exerted by the bulky groups at the ethylenic linkage.

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