

that both the three-membered ring character and double bond character at ring carbons 1 and 2 might retard to some degree abstraction of a proton from these positions to give 1-phenylcyclohexene. There will, however, be hydrogens on atoms 3 and 6, with respect to the methyl sulfite anion and  $\alpha$  to the partially unsaturated 1- and 2-positions, which might therefore be readily removable to produce 3-phenylcyclohexene. Cram<sup>26</sup> has presented some evidence that this mechanism is inoperative for E<sub>1</sub> reaction with 3-phenyl-2-butyl tosylates.

The mixture of methanes obtained in the pyrolysis of *l*-menthyl methyl sulfite (VIII) compared rather closely with that formed in the Chugaev reaction on *l*-menthol.

### Conclusions

The experiments described suggest that the pyrolysis of methyl alkyl sulfites may be a useful procedure for dehydration, although the reaction has to be investigated further before its scope and limitations as a preparative reaction for olefins can be stated. Nevertheless, at this stage the following can be safely said.

(a) Yields are usually higher than in the Chugaev reaction. In the few cases so far studied several yields of better than 90% have been realized, while in the Chugaev reactions 70 to 80% is considered a good yield.

(b) The Chugaev reaction involves several steps (preparation of the sodium alcoholate, which in the case of secondary carbinols can be quite time-con-

suming, reaction with carbon disulfide and then with methyl iodide), and the xanthates are often difficult to purify. The preparation of methyl alkyl sulfites requires only one step, since methyl chlorosulfinate can be prepared separately and stored under refrigeration.

(c) The pyrolysis of xanthates is made very unpleasant by the evolution of carbon oxysulfide and methyl mercaptan. The product usually still contains substantial amounts of sulfurated impurities, and requires a lengthy purification. In the case of the sulfites, the only gas evolved is sulfur dioxide, which can be absorbed completely in alkali solutions; the olefinic product is quite pure and can be easily freed from the small amounts of dimethyl sulfite that may be present.

(d) The pyrolysis temperature of the sulfites, although higher than those of the corresponding xanthates, are much lower than those of the acetates. The latter require temperatures from 450 to 550°, with consequent preparative difficulties and lower yields.

On the other hand, unfavorable features of the pyrolysis of sulfites are its apparent lack of stereospecificity and the fact that the yields drop sharply with primary substituents. The latter point, however, is a draw-back of all pyrolytic elimination reactions.

(27) J. P. Wibaut and A. J. van Pelt, *Rec. trav. chim.*, **57**, 1055 (1938); **60**, 55 (1941).

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

## The Polymerization of Stilbene in Boron Fluoride Etherate

BY CHARLES C. PRICE AND GIANCARLO BERTI<sup>1</sup>

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The previous report by Price and Meister<sup>2</sup> that *cis*-stilbene is isomerized to *trans*-stilbene by boron fluoride has been found to be in error. In the absence of a proton donor, no reaction occurs; in the presence of a proton donor, the reaction observed is the formation of a low-molecular weight polymer. When heavy water was employed as cocatalyst, the polymer contained about one deuterium atom, the recovered stilbene only a minor amount of deuterium.

### Introduction

Price and Meister<sup>2</sup> in 1939, reported that boron fluoride would isomerize *cis*-stilbene to *trans*-stilbene. These findings have been questioned by Downing and Wright<sup>3</sup> and recently by Brackmann and Plesch,<sup>4</sup> who were unable to repeat this isomerization. The latter authors state that, if the reagents are dry and pure, no reaction at all takes place between *cis*-stilbene and boron fluoride. In the presence of a proton-donating co-catalyst, they report that *cis*-stilbene is transformed not into the *trans*-isomer, but into a low molecular weight polymer. We have therefore repeated our previous work, reinvestigating the behavior of *cis*- and *trans*-stilbene in boron fluoride etherate solution, a convenient homogeneous medium.

(1) E. I. du Pont de Nemours and Co. Fellow, 1952-1953. Abstracted from a part of the Ph.D. dissertation of G. Berti. Presented at the 124th Meeting of the American Chemical Society, Chicago, Ill., September 7, 1953.

(2) C. C. Price and M. Meister, *THIS JOURNAL*, **61**, 1595 (1939).

(3) D. C. Downing and G. F. Wright, *ibid.*, **68**, 141 (1946).

(4) D. S. Brackmann and P. H. Plesch, *J. Chem. Soc.*, 1289 (1953).

### Experimental

***cis*-Stilbene.**—This compound was prepared by decarboxylation of  $\alpha$ -phenylcinnamic acid with copper chromite in quinoline, according to Taylor and Crawford.<sup>5</sup> For the purification the directions of Brackmann and Plesch<sup>6</sup> were followed, with some modifications. The crude product of the decarboxylation was distilled once at 0.005 mm., keeping the bath temperature at 90°. All of the distillate, except the first milliliter, was recrystallized twice from Skellysolve F, cooling in a Dry Ice-acetone-bath. In this way a 70-75% yield of a nearly colorless product, melting around 0°,  $n_D^{20}$  1.6200,  $n_D^{20}$  1.6218, was obtained, which was considered sufficiently pure for our purposes. Pure *cis*-stilbene, according to Brackmann and Plesch,<sup>6</sup> melts at 5-6° and has  $n_D^{20}$  1.6214  $\pm$  0.0005, but they report that after a few days the melting point drops to 0.6°. When the distillation was conducted at higher pressure a somewhat less pure product was obtained. Thus, using a pressure of 10 mm., a product was formed melting between -10 and -5°,  $n_D^{20}$  1.6208. The slightly lower refractive index found for our product did not indicate the presence of *trans*-stilbene, as was shown by the following observation. A sample of *cis*-stilbene,  $n_D^{20}$  1.6208, after saturation with *trans*-stilbene, had  $n_D^{20}$  1.6230, showing that impurities of *trans*-isomer would in-

(5) T. W. J. Taylor and C. E. J. Crawford, *ibid.*, 1130 (1934).

(6) D. S. Brackmann and P. H. Plesch, *ibid.*, 2177 (1952).

crease and not decrease the refractive index of *cis*-stilbene.

**Analysis of Reaction Products.**—The analysis of the reaction mixtures was based both on their solubility in ethanol and on ultraviolet data.

(a) **Solubility.**—The solubility of *cis*-stilbene in ethanol at room temperature is higher than 10%, while that of *trans*-stilbene is only 0.8% at 17° and that of the polymer even less. Thus, the solubility, although not distinguishing between *trans*-stilbene and polystilbenes, gave an indication of the extent of transformation of the *cis*-stilbene.

(b) **Ultraviolet Data.**—The absorption curves of *cis*-stilbene, *trans*-stilbene and polystilbene are quite different. *cis*-Stilbene shows two maxima at 223 m $\mu$  ( $\epsilon$  1.9  $\times$  10<sup>4</sup>) and 274 m $\mu$  ( $\epsilon$  1.12  $\times$  10<sup>4</sup>). *trans*-Stilbene shows two maxima at 226 m $\mu$  ( $\epsilon$  1.57  $\times$  10<sup>4</sup>) and 294 m $\mu$  ( $\epsilon$  2.85  $\times$  10<sup>4</sup>). Polystilbene shows only one maximum at 262 m $\mu$  ( $\epsilon$  500).

In all cases a solution in 95% ethanol, containing 0.0036 g./l. of the mixture to be analyzed, was prepared (corresponding to a 2  $\times$  10<sup>-6</sup> M solution, based on pure stilbene) and its optical density at 274 and 294 m $\mu$  was determined in 1-cm. cells in a Beckman spectrophotometer.

	$D_{274}$ m $\mu$	$D_{294}$ m $\mu$	Ratio
Pure <i>cis</i> -stilbene	0.224	0.174	1.29
Pure <i>trans</i> -stilbene	.367	.572	0.64
Polystilbene	.0175	.0118	1.48

In the following,  $D_{274}$  and  $D_{294}$  will stand for the optical densities of the above concentration at the stated wave length. The ratio of these two values is an indication of the amount of isomerization to *trans*-stilbene taking place.

The approximate percentage of polymerization was calculated by the expression

$$\% \text{ polym.} = 100 - \frac{D_{274} - 0.0175}{0.224 - 0.0175} \times 100$$

in which it is assumed that nothing but *cis*-stilbene and polymer are present. Of course it can only be safely applied in cases in which the ratio  $D_{274}/D_{294}$  is close to 1.29. A similar expression gives the percentage of polymerization in samples containing only *trans*-stilbene and polymer.

**Experiments with Boron Fluoride Etherate.** (1).—A solution of 1 ml. of *cis*-stilbene in 8 ml. of boron fluoride etherate (b.p. 125°) was sealed in a test-tube. After one month in the dark, the solution had turned slightly yellow, but no precipitate had formed. The boron fluoride was neutralized with sodium carbonate solution, the ether layer dried over magnesium sulfate and evaporated. The residue had the following properties: m.p. between -8 and -4°; completely soluble in 10 ml. of ethanol at 25°;  $D_{274}$  0.192,  $D_{294}$  0.150; ratio 1.28; polymerization 15%.

(2).—Three drops of water was added to 2 ml. of *cis*-stilbene in 16 ml. of boron fluoride etherate. After 24 hours in the dark, some colorless resinous material started to separate. After 48 hours, the solution was treated as described above. The residue was a glassy colorless resin. Ten ml. of ethanol dissolved only 0.02 g. of it at 25°;  $D_{274}$  0.02,  $D_{294}$  0.01.

(3).—A similar solution containing water was heated at 95–100°. After 30 minutes a sample of 4.5 ml. was withdrawn and treated as described above. The residue was a resin very similar to that obtained in expt. 2. Ten ml. of ethanol dissolved 0.06 g. at 25°;  $D_{274}$  0.020,  $D_{294}$  0.025. Another sample taken out after 3.5 hours at 100° gave similar results.

(4).—To a solution of 3 g. of *cis*-stilbene in 24 ml. of boron fluoride etherate was added three drops of water. Portions of 8 ml. were taken out at given intervals and worked up in the usual manner.

The products had the following properties: After one hour: solidification point -10°;  $D_{274}$  0.220,  $D_{294}$  0.170; ratio 1.29. After six hours: viscous liquid, not solid at -10°; much insoluble residue was left on treatment with ethanol;  $D_{274}$  0.137,  $D_{294}$  0.108; ratio 1.27; polymerization 45%. After 24 hours: soft glass; 10 ml. of ethanol dissolved only 0.08 g.;  $D_{274}$  0.045,  $D_{294}$  0.040; ratio 1.12; polymerization 90%.

(5).—A suspension of 1 g. of *trans*-stilbene in 8 ml. of boron fluoride-ether complex and 1 drop of water was shaken for one hour. The solid was then filtered off on a sintered glass funnel: 0.8 g. of pure *trans*-stilbene, m.p. 124°. The solution, after the usual treatment, gave 0.19 g. of almost pure *trans*-stilbene, m.p. 118–120°.

Using double amounts of material and shaking for 24 hours, 1.6 g. of pure *trans*-stilbene was removed by filtration. The solution, after the usual treatment, gave 0.27 g. of crystalline material, m.p. 100–115°;  $D_{274}$  0.300,  $D_{294}$  0.470; ratio 0.64; polymerization 20%. The over-all polymerization including recovered *trans*-stilbene was only about 3%.

(6).—To 2 g. of *cis*-stilbene in 16 ml. of freshly-distilled boron fluoride etherate was added six drops of 98% deuterium oxide. The solution was left in the dark for 12 hours, then was treated as usual. The product was a viscous liquid; 0.102,  $D_{294}$  0.080; ratio 1.28; polymerization 60%; deuterium analysis, 1.305  $\pm$  0.005 atom % D.

(7).—To a solution of 2 g. of *trans*-stilbene in 56 ml. of boron fluoride-ether complex was added 21 drops of deuterium oxide and the solution was left in the dark for 12 hours, then was subjected to the usual treatment;  $D_{274}$  0.347;  $D_{294}$  0.535; ratio 0.65; polymerization 8%; deuterium analysis, 0.320  $\pm$  0.005 atom % D.

(8).—*cis*-Stilbene (15 g.) was dissolved in 100 ml. of boron fluoride etherate containing 3.4 g. of 98% deuterium oxide, and the solution was placed in a shaker. After seven hours of shaking, the solution started to become turbid and some oil precipitated. The mixture was treated as usual and a viscous oil was obtained;  $D_{274}$  0.0575,  $D_{294}$  0.048; ratio 1.20; polymerization 80%.

The crude product was dissolved in a small amount of ether and an excess of methanol was added; a viscous oil separated. The solution was decanted, the residue dissolved in Skellysolve B and precipitated with ethanol. The solvent was decanted again, the residue of polymer extracted with boiling ethanol and then dried at 110° (2 mm.) over phosphoric anhydride in a pistol desiccator. This sample of polystilbene contained 5.44  $\pm$  0.1% deuterium; mol. wt. 500 (cryoscopically in dioxane). The specific viscosity in benzene ( $\eta_{sp}$  0.66 at 0.133 mole/l.) give a molecular weight of 990, assuming the value of the Staudinger constant,  $K_m$ , to be 5  $\times$  10<sup>-4</sup>.

The solvent was eliminated from the mixed mother liquors and the residue distilled under reduced pressure; a fraction, b.p. 112–118° (2 mm.), was collected; it melted between -10 and -5° and was almost pure *cis*-stilbene; 0.333  $\pm$  0.003% deuterium.

Part of the distillate was dissolved in acetone and solid potassium permanganate was added portionwise to the refluxing solution, until a persistent purple color was obtained. The mixture was diluted with water, filtered and the filtrate was concentrated to 100 ml., filtered again and acidified with hydrochloric acid. The precipitate of benzoic acid was recrystallized twice from Skellysolve B; m.p. 121–122°; 0.087  $\pm$  0.005% deuterium.

Non-deuterated polymer (1.5 g.) was shaken for 16 hours with 10 ml. of boron fluoride etherate and 0.3 g. of deuterium oxide, then treated as usual. This polymer contained 0.602  $\pm$  0.003% deuterium.<sup>7</sup>

## Discussion

From the experimental data it clearly appears that the results previously reported by Price and Meister<sup>2</sup> were improperly interpreted. The precipitate obtained by them and assumed to be *trans*-stilbene by virtue of its insolubility in ethanol must have been polystilbene, also insoluble in ethanol. In the present experiments the ratio  $D_{274}/D_{294}$  never was such as to indicate the presence of more than a trace of *trans*-stilbene at most. The lack of reactivity of *cis*-stilbene in boron fluoride etherate in the absence of a proton donor is in agreement with previous statements<sup>8–11</sup> that boron fluoride and similar substances do not catalyze olefin polymerization except in the presence of a cocatalyst.

(7) The authors are grateful to Dr. W. H. Urry and Frank Stacey for the deuterium analyses by combustion and flotation density.

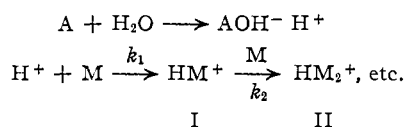
(8) A. G. Evans, D. Holden, P. H. Plesch, M. Polanyi, H. A. Skinner and M. A. Weinberger, *Nature*, **157**, 102 (1946).

(9) A. G. Evans and M. Polanyi, *J. Chem. Soc.*, 252 (1947).

(10) F. S. Dainton and R. H. Tomlinson, *ibid.*, 151 (1953).

(11) P. H. Plesch, *ibid.*, 1662 (1953).

Our observations concerning the incorporation of deuterium in the polymer formed with heavy water as cocatalyst, are all in agreement with the concept that the initiating process is donation of a proton to the olefin.<sup>10</sup> Using A for catalyst and M for olefin we may represent the reaction as



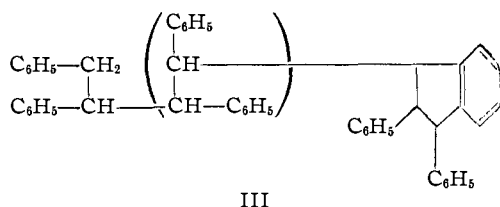
The protonated olefin I might be assigned either a classical cationic structure IA or a bridged or  $\pi$ -complex structure IB.



To account for the much greater proportion of deuterium in the polymer than in recovered *cis*-stilbene, as well as the absence of isomerization of *cis*- to *trans*-stilbene, structure IA for the protonated intermediate requires that  $k_2$ , the reaction of I with a second olefin, must be very much faster than  $k_{-1}$ , the loss of a proton from IA. Since this seems somewhat implausible, we prefer to regard the intermediate as having the structure IB.

Our observations and conclusion are in accord with those of Levy, Taft and Hammett<sup>12</sup> who found no interconversion of 2-methyl-2-butene to 2-methyl-1-butene or *vice versa* when either olefin was partially hydrated to *t*-amyl alcohol in sulfuric acid.

The ultraviolet spectrum of the polymer showed that the absorption characteristic of stilbene had disappeared, while a benzenoid type of curve was obtained, with only one maximum at 262  $m\mu$ . If the extinction coefficient is calculated per benzene ring, a molar extinction coefficient of 500 is obtained, which compares rather closely with that of toluene ( $\lambda_{\max}$  262  $m\mu$ ,  $\epsilon_{\max}$  300<sup>13</sup>). The low extinction coefficient suggests that the polymerization was terminated by cyclization of II with formation of 3-aryl-1,2-diphenylindane end-groups (III), rather than by formation of olefinic double bonds by loss of a proton.



The polymers obtained by Brackmann and Plesch<sup>4</sup> had peaks at 265 and 300  $m\mu$ . Our data indicate that the latter peak was probably due to the presence of some *trans*-stilbene, rather than to

(12) J. B. Levy, R. W. Taft and L. P. Hammett, *THIS JOURNAL*, **75**, 1253 (1953).

(13) E. A. Braude, *Ann. Reports (Chem. Soc.)*, **42**, 124 (1945).

1,2,3,4-tetraphenylbutene as suggested by these authors. More recent work by Plesch<sup>11</sup> on the polymerization of styrene by stannic chloride and by Dainton and Tomlinson<sup>10</sup> on  $\alpha$ -methylstyrene indicated no unsaturation in the resulting polymers.

The experiments with heavy water showed clearly that the rate of exchange of hydrogen with deuterium in stilbene in the presence of boron fluoride etherate is slow. The formation of the  $\pi$ -complex with the deuterium should not lead to exchange. If it is assumed that only one deuterium atom is found per molecule of polymer and that no deuterium exchange takes place with the unreacted monomer, the following results are obtained. One deuterium atom per stilbene unit ( $C_{14}H_{12}$ ) would correspond to  $100/12 = 8.3$  atom %. In the case of *cis*-stilbene the material was 60% converted to polymer of 2.8 units per molecule. This would give

$$\frac{8.3 \times 0.60}{2.8} = 1.78\%$$

as the expected percentage deuterium. In the case of *trans*-stilbene, the same calculation gives

$$\frac{8.3 \times 0.08}{2.8} = 0.24 \text{ atom } \%$$

deuterium expected. These values are in fairly good agreement with the experimental values (1.3 and 0.3 atom %, respectively), so that the assumptions on which they are based appear to be reasonable.

The effect of the dilution of the deuterium oxide by water during these experiments can be neglected, as it is calculated that in experiment 6 at the end more than 90% of the initial amount of deuterium oxide was still present in the reaction mixture. In experiment 7, where a much larger amount of deuterium oxide was used, the error was even smaller.

In experiment 8, the polymer was separated from the unreacted stilbene and each was analyzed for deuterium separately. As expected, the deuterium content of the polymer was much higher (about 16 times) than that of the monomer. This proved that the rate of exchange of the monomer with deuterium is negligible in comparison with that of introduction of deuterium into the polymer and that most of the deuterium enters the molecule during the polymerization.

The fact that the benzoic acid obtained in the oxidation of the recovered monomer contained only 0.087 atom % of deuterium, as compared with 0.333 mole in the recovered monomer itself, shows that in the monomer exchange reaction, only about 25% of the deuterium exchange occurs with the five hydrogens of each of the two benzene rings, while 75% of it takes place in the two  $\alpha$ -positions.

It is also shown that the rate of exchange of the polymer with deuterium is not much different from that of the monomer, as a sample of non-deuterated polymer that had been in contact with boron fluoride etherate and deuterium oxide for 16 hours contained only about twice as much deuterium as the monomer recovered after seven hours of reaction.