259. *Some Reactions of the Stilbenes in the Presence of Metal Halides.*

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Contrary to the claim of Price and Meister (*J. Amer. Chem. Soc.*, 1939, **61**, 1595) neither boron trifluoride nor titanic chloride could be made to isomerise *cis*-stilbene, pure or in solution. Without a co-catalyst there was no reaction; in the presence of a co-catalyst, such as water, *cis*-stilbene polymerised; *trans*-stilbene reacted similarly. Both isomers were polymerised by concentrated sulphuric acid. Experiments in a high-vacuum apparatus showed that both isomers reacted reversibly with titanic chloride to give deep red complexes. The *trans*-stilbene complex was more easily decomposed than the *cis*-stilbene complex and became colourless when cooled in liquid nitrogen; the *cis*-stilbene complex did not. Complex formation did not isomerise *cis*-stilbene. Water, and possibly hydrochloric acid, acted as co-catalysts in the system stilbene–titanic chloride and caused polymerisation of both isomers. The polymers were mixtures of dimers and trimers which included unsaturated compounds, and substituted indanes, but not 1 : 2 : 3 : 4-tetraphenyl*cyclo*butane.

1. *The Isomerisation of* cis-*Stilbene.*—The isomerisation of *cis*-stilbene in carbon tetrachloride solution by boron trifluoride and its ether complex was reported by Price and Meister (*J. Amer. Chem. Soc.*, 1939, **61**, 1595) who stated that both catalysts produced a maximum of 92—93% conversion. In view of the large theoretical superstructure which has been built upon this alleged observation, it seemed pertinent to attempt its reproduction, especially because it could not be confirmed by Downing and Wright (*ibid.*, 1946, **68**, 141). The present authors were unable to isomerise *cis*-stilbene by boron trifluoride. Under dry conditions *cis*-stilbene (pure or in carbon tetrachloride solution) was unaffected by boron fluoride (test by refractive index and ultra-violet spectrum); in the presence of water it polymerised to a tacky resin. Similar results were found with *trans*-stilbene, and with both isomers when titanic chloride was used as the catalyst. These findings are in agreement with those of Meier (*J.*, 1950, 3656) who studied the interaction of boron trifluoride with *cis*-but-2-ene and found that either polymerisation or no reaction at all occurred.

Conditions under which cis-*stilbene has been isomerised.* When *cis*-stilbene was mixed in approximately equimolar proportion with crystalline trichloroacetic acid, a solution was formed which, after three weeks in the dark, gave a purplish crystalline mass. From this, *trans*-stilbene could be isolated. When a hexane solution 0·04M in trichloroacetic acid and 0·4M in *cis*-stilbene was left for 56 hours at room temperature, or refluxed for 3 hours, no *trans*-stilbene was formed.

The isomerisation of *cis*-stilbene by bromine atoms described by Kharasch, Mansfield, and Mayo (*J. Amer. Chem. Soc.*, 1937, **59**, 1155) and by iodine and ultra-violet light, reported by Zechmeister and McNeely (*ibid.*, 1942, **64**, 1919), was confirmed. We found that *cis*-stilbene neither isomerised nor polymerised when kept for a week at room temperature over floridin activated at 300° for 2 hours. Lebedev and Filonenko (*Ber.*, 1925, **58**, 163) found that molten *trans*-stilbene is not polymerised by activated floridin.

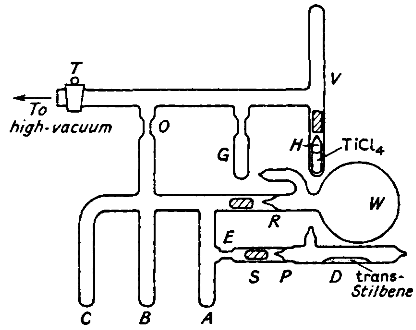
Polymerisation of cis- *and* trans-*stilbene by sulphuric acid.* The literature contains no reference to the polymerisation of either *cis*- or *trans*-stilbene by concentrated sulphuric acid. The addition of a drop of concentrated sulphuric acid to about 1 ml. of *cis*-stilbene produced a light yellow dispersion, considerable heat evolution, and a great increase in the viscosity of the mixture. From this a colourless, glassy transparent resin was isolated. A similar product was obtained from *trans*-stilbene by an analogous procedure.

2. *Interaction of* cis- *and* trans-*Stilbene with Titanic Chloride* in vacuo.—Preliminary experiments demonstrated that *cis*-stilbene was not isomerised in the presence of Friedel–Crafts catalysts but that, depending on the presence or absence of a suitable co-catalyst, either polymerisation or no reaction at all occurred. As a result of these observations it was decided to investigate the interaction of the stilbenes with titanic chloride under more rigorously defined conditions.

EXPERIMENTAL

Experiment with trans-*Stilbene.—Materials. trans*-Stilbene was prepared by Ballard and Dehn's method (*J. Amer. Chem. Soc.*, 1932, **54**, 3969) and recrystallised from *n*-hexane to constant m. p. (124°). It was purified by vacuum-sublimation through a series of five phials until it was contained in phial *D* (see Figure). The titanic chloride was a colourless commercial product which was fractionated *in vacuo*, and distilled into phials. One of these (*H*) with a magnetic phial-breaker was sealed into limb *V* of the apparatus.

Apparatus and procedure. When assembled, the whole apparatus was flamed at intervals and evacuated for 24 hours to produce a " black " vacuum ($<10^{-4}$ mm. of Hg). Then tap *T* was closed. Seal *P* was broken and most of the *trans*-stilbene sublimed into *B*, but some was left in *A*. Constriction *E* was then sealed and vessel *D* removed. With liquid nitrogen round *G*, phial *H* was broken. The first fraction coming off the titanic chloride from *H* was condensed in *G*. Then, with liquid nitrogen round *C*, *G* was sealed and pulled off, the remainder of the titanic chloride from *H* was condensed in *C*, and then *O* was sealed.



Observations. Immediately after the phial *H* was broken, some volatile substance came into contact with the upper portion of the film of *trans*-stilbene in *B* and produced a series of brown bands about 1—1·5 cm. wide. The remainder of the contents of *B* and *A* remained white. However, most of the more volatile portion from the titanic chloride, probably hydrochloric acid, had condensed in *G*. When the titanic chloride had attained room temperature, no change took place in *A* or *B*. By means of liquid nitrogen some of it was distilled into *A* and *B*. As soon as the region where it was in contact with the *trans*-stilbene warmed up, a deep red liquid was formed. Then the titanic chloride was distilled back from *A* and *B* into *C*. The red complex was thereby decomposed and the system reverted to its original condition. Even after the red complex had been thus formed and decomposed six times, the white solid in *A* or *B* could be sublimed, thus proving that no polymerisation had occurred. The brown ring formed in *B* immediately after the breaking of phial *H* could not be sublimed. Therefore this was probably some polymeric material. When cooled in liquid nitrogen the red complex of *trans*-stilbene and titanic chloride became colourless, but the colour returned when it warmed up again. When seal *R* leading to the water-vapour bulb *W* was broken, an immediate brown colour, similar to that produced at the beginning of the experiment at the top of *B*, appeared wherever any white *trans*-stilbene had been present. Since it was impossible to sublime away this brown material, polymerisation must have occurred.

Experiment with cis-*Stilbene.—Apparatus and procedure.* The apparatus was similar to that used for *trans*-stilbene. The main modification was a device for fractionating the titanic chloride after breaking of phial *H*, without letting it come in contact with the *cis*-stilbene.

The *cis*-stilbene, prepared as described previously (Brackman and Plesch, *J.*, 1952, 2188), was distilled once in a high vacuum and sealed off in *D*. After the whole apparatus had been flamed and pumped out for 24 hours, seal *P* was broken, the *cis*-stilbene distilled into *A*, and constriction *E* sealed off. The heat of this operation isomerised some *cis*-stilbene to the *trans*-isomer which adhered as a thin white crystalline film to the wall of *A* near *E*. The phial *H* was then broken, a first small volatile fraction condensed and sealed off in *G*, and the remainder of the titanic chloride put in communication with the three-limbed reaction vessel *A*, *B*, *C* by breaking a glass seal. With the *cis*-stilbene in *A* at room temperature, the titanic chloride was condensed into *C* : only a trace of titanic chloride got into *A*. Finally constriction *O* was sealed.

Observations. As the titanic chloride in *C* warmed to room temperature a deep red colour spread through the *cis*-stilbene in *A*. The film of *trans*-stilbene near *E* remained white. When titanic chloride was condensed on to it the red complex was formed, as in the previous experiment. When *C* was cooled in liquid nitrogen the red *trans*-stilbene complex near *E* was decomposed as before, but the red colour of the contents of *A* did not disappear, except where the *cis*-stilbene was present as a thin film on the wall above the bulk of liquid. By means of this thin layer of *cis*-stilbene it could be shown that the complex formation is reversible. Even after many cycles it showed no sign of isomerisation or polymerisation. When the deep red mixture in *A* was cooled in liquid nitrogen the colour did not change. About an hour after the start of the experiment a very dark red substance with a matt surface had formed in *A*. It could be shown that it contained unpolymerised *cis*-stilbene.

After condensation of the titanic chloride into *A*, water vapour was admitted by breaking seal *R*, and the dark mass in *A* started to bubble, becoming more viscous and leaving colourless shreds of the collapsed bubbles. On warming, the bubbling became more vigorous and a honeycomb structure of semi-solid polymer was formed.

At no time after the admission of the titanic chloride did any evidence appear which indicated that the *trans*-isomer had been produced.

The Structure of the Polymers.—The photo-dimer of stilbene (1 : 2 : 3 : 4-tetraphenyl*cyclo*butane), m. p. 163°, was prepared as a reference compound by a modification of the method of Pailer and Müller (*Monatsh.*, 1948, **79**, 615). On hydrogenation over platinum in acetic acid this absorbed 1·3 moles of hydrogen per mole of dimer. This indicates that the *cyclo*butane ring is opened by hydrogenation. The infra-red spectrum of the photo-dimer showed that it was absent from the reaction products obtained from *cis*-stilbene (A) and from *trans*-stilbene (B) by the action of sulphuric acid, and from the product (C) obtained in the high-vacuum experiment with *cis*-stilbene.

Product (A) had a molecular weight of 370 (cryoscopic in *cyclo*hexane) [Found: C, 92·8; H, 6·9. $(C_{14}H_{12})_2$ requires *M*, 360; C, 93·3; H, 6·7%]. It absorbed 0·4 mole of hydrogen per mole of dimer. The ultra-violet spectra of (A) and (B) were very similar. They showed peaks near 2650 and 3000 Å. The latter peak was removed by hydrogenation; it indicates the presence of a substance in which a double bond is conjugated with two phenyl groups. Quantitative comparison with the spectrum of *trans*-stilbene itself showed that there was only 5—10% of this conjugated material in the reaction products. A plausible structure for it is 1 : 2 : 3 : 4-tetraphenylbut-1-ene. Comparison of the infra-red spectra of (A) and (B) and of those obtained after their hydrogenation, with each other and with that of polystyrene, indicated that a major constituent of (A) and (B) was probably 3-benzyl-1 : 2-diphenylindane, that (B) contained appreciably more of this than did (A), and that the indane ring was probably opened by our hydrogenation technique. The nature of the unhydrogenatable constituent(s) is still obscure.

Product (C) was a brittle, transparent, pale yellow resin of molecular weight 438. It was therefore probably a mixture of dimers and trimers (Found : C, 93·2; H, 6·7%). The ultra-violet spectra before and after hydrogenation showed that this reaction product also contained a small proportion of double bonds conjugated with benzene rings. These are again ascribed to the but-1-ene and/or the corresponding stilbene trimer. The structure of the main constituents of the mixture is not known, but by analogy with products (A) and (B), and with those obtained in benzene solution by the action of titanic chloride and trichloroacetic acid (Brackman and Plesch, " Cationic Polymerisation and Related Complexes," W. Heffer and Sons, Cambridge, 1953, p. 103), the indane structure seems likely. This would also be analogous to the dimer of 1 : 1-diphenylethylene obtained by Schoepfle and Ryan (*J. Amer. Chem. Soc.*, 1930, **52**, 4021) by the action of stannic chloride and hydrogen chloride in benzene solution, to which they assigned the structure 3-methyl-1 : 1 : 3-triphenylindane. In the absence of deliberately added hydrogen chloride these workers obtained the 1 : 1 : 3 : 3-tetraphenylbut-1-ene.

Discussion.—The present experiments, in agreement with those of Downing and Wright (*loc. cit.*), show that *cis*-stilbene is not isomerised by the action of boron fluoride or titanic chloride. Price and Meister (*loc. cit.*), who first reported this reaction, do not give any evidence that the solid isolated by them after the interaction of *cis*-stilbene and boron fluoride was indeed *trans*-stilbene; it is quite possible that they mistook a polymer for the *trans*-isomer. Thus, there is now no evidence for the direct interaction of boron fluoride with double bonds, and there is much evidence against it (A. G. Evans and Weinberger, *Nature*, 1947, **159**, 437; A. G. Evans and Meadows, *J. Polymer Sci.*, 1949, **4**, 359; A. G. Evans, *J. Appl. Chem.*, 1951, **1**, 240; *op. cit.*, p. 20; Meier, *loc. cit.*). Any theories based upon such interaction must therefore be revised.

The high-vacuum experiments described above show that *cis*- and *trans*-stilbene react reversibly with titanic chloride, in the absence of a third substance, to give two different complexes. Both complexes are deep red, but the colour of the *trans*-stilbene complex is destroyed reversibly by cooling in liquid nitrogen. The complex from *cis*-stilbene is appreciably more stable than that from the *trans*-isomer. There was no evidence that *cis*-stilbene was isomerised by complex formation. In the presence of a suitable co-catalyst (water, and possibly hydrochloric acid) both isomers formed polymers under the influence of titanic chloride. Thus, during complex formation with titanic chloride the two isomers retain their identity and therefore the hydrocarbon cannot be fully ionised in the complex, as was postulated for the (hypothetical) boron fluoride complex of *cis*-stilbene by Price and Meister (*loc. cit.*). Our results are also in contrast to those of Euler and Willstaedt (*Arkiv Kemi, Mineral., Geol.*, 1929, **10**, *B*, No. 9; *Chem. Abs.*, 1929, **23**, 4465) who found that by reaction in anhydrous chloroform both isomers gave the same complex with antimony trichloride, $(C_6H_5\cdot CH{:})_2,2SbCl_3$ (m. p. 106—107°), and with ferric chloride, $(C_6H_5\cdot CH{:})_2,2FeCl_3$, which could be heated to 326° without melting. The complexes from both halides were colourless. These two halides have a greater similarity to aluminium chloride than to the Group IV halides and the properties of these complexes, which differ from those of the titanic chloride complexes, may well be further evidence for Plesch's suggestion (*J. Appl. Chem.*, 1951, **1**, 269) that there is a fundamental difference between the mode of action of boron fluoride and the Group IV halides on the one hand, and the other tervalent halides on the other. The present results also add yet another to the list of polymerisations catalysed by metal halides, for which it has been shown that the presence of a co-catalyst is essential.

The structure of the polymers indicates that chain growth probably stops predominantly by an internal Friedel–Crafts reaction. This seems to be a general feature of the cationic polymerisation of arylenes, since polystyrenes and poly-α-methylstyrenes produced in this way also lack unsaturation (Dainton *et al.*, *op. cit.*, p. 80). This is in contrast to cationically produced polyalkenes in which unsaturated end-groups predominate.

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