

50° for one hour. The reaction mixture was cooled and poured onto ice; the resulting solid was filtered, washed, and dried. The product was recrystallized from acetone-ethanol and melted at 181.5–183.5° (cor.).

Anal. Calcd. for $C_{14}H_7Cl_2Br_2N_2O_4$: C, 29.09; H, 1.22. Found: C, 29.32; H, 1.23.

1-Tribromo-2,2-bis-(*p*-bromophenyl)-ethane (II).—This compound was prepared in the same manner as I, with substitution of 330 g. of bromobenzene for the chlorobenzene. Three layers were formed in the ether extraction, the center layer containing about 110 g. of crude bromobenzenesulfonic acid. The ether and excess bromobenzene (210 g.) were removed under reduced pressure and the residual oil was crystallized from Skellysolve B. The yield of crude solid, m. p. 136–160°, was 34.5 g. (16.5%). Several recrystallizations from Skellysolve B gave about half of this material as pure compound melting at 173–174° (cor.) and crystallizing as rhombs or needles.

Anal. Calcd. for $C_{14}H_3Br_3$: C, 29.15; H, 1.57. Found: C, 29.19; H, 1.76.

The compound was quite unstable; ethanolic solutions became acidic rapidly, and crystallization from ethanol or from benzene-ligroin resulted in products decomposing at 140–150°.

1,1-Dibromo-2,2-bis-(*p*-bromophenyl)-ethylene was prepared by the treatment of II with ethanolic potassium hydroxide (as given above for I) in 76% yield. The product recrystallized from 95% ethanol was obtained as pale-yellow, prismatic needles melting at 121.8–122.7° (cor.).

Anal. Calcd. for $C_{14}H_3Br_2$: C, 33.91; H, 1.63. Found: C, 33.49; H, 1.36.

A hundred and ten mg. of the olefin was oxidized in 80% yield with chromic anhydride, as described above, to *p,p'*-dibromobenzophenone, m. p. 174–175° (cor.) after recrystallization from 95% ethanol, and the melting point was not depressed when the sample was mixed with an authentic sample prepared by the oxidation of bis-(*p*-bromophenyl)-methane according to Goldthwaite.⁴

Dinitro Derivative of II.—To 5 ml. of fuming nitric acid cooled in an ice-bath 500 mg. of II was gradually added. After one hour in the ice-bath and one hour at room temperature, the reaction mixture was poured onto ice. The precipitate was filtered, washed and dried. After recrystallization from acetone-ethanol, the product melted at 203–205° (cor.).

Anal. Calcd. for $C_{14}H_7Br_2N_2O_4$: C, 25.22; H, 1.06. Found: C, 25.53; H, 1.09.

(4) Goldthwaite, *Am. Chem. J.*, **30**, 445 (1903).

BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE
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Observations on the Equilibrium between *cis*- and *trans*-Stilbene

BY D. C. DOWNING AND GEORGE F. WRIGHT

The thermal equilibrium between *cis*- and *trans*-stilbene has been reported as 92–94% *trans* at 340°,¹ as 96% *trans* at 214°,² and 93% *trans* at 25°.³ In order to test this apparent independence with respect to temperature we applied the method of methoxymercuration⁴ to a sample of *trans*-stilbene isomerized at 330–340° and found

(1) G. B. Kistiakowsky and W. Smith, *THIS JOURNAL*, **56**, 638 (1934).

(2) T. W. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938).

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

(4) (a) G. F. Wright, *ibid.*, **57**, 1993 (1935). (b) W. H. Brown and G. F. Wright, *ibid.*, **62**, 1991 (1940). (c) A. M. Birks and G. F. Wright, *ibid.*, **62**, 2412 (1940).

(Fig. 1) that the rate of mercury consumption versus time was identical (curve A) with that shown by pure stilbene (curve B), whereas a 92:8 *trans-cis* mixture and an 8:92 *trans-cis* mixture consumed mercury according to curves C and D, respectively. These data indicate that the melting point lowering observed by Kistiakowsky and Smith was not owing to the presence of 8% *cis*-stilbene.

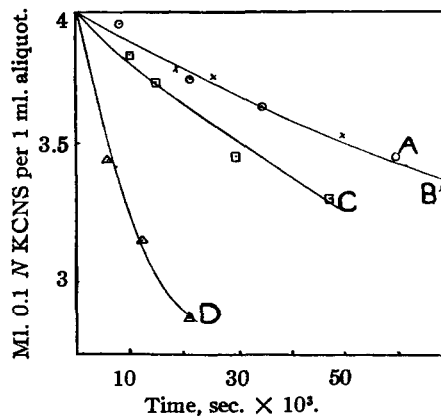


Fig. 1.—Mercury consumption by *cis-trans* mixtures vs. time.

The methoxymercuration was carried out without a catalyst⁴ in order to accentuate the difference in reaction rate between *cis* and *trans* isomers. The slight solubility of *trans*-stilbene in the reaction medium also exaggerated this difference.

We were unable to test the 93:7 equilibrium reported at 25° because we could not repeat the catalytic isomerization of Price and Meister with boron trifluoride in carbon tetrachloride or as its etherate. In our hands no isomerization occurred with either *cis*- or *trans*-stilbene, nor did benzoyl peroxide or peracetic acid act as a co-catalyst.

It would appear that the isomerizing action of boron trifluoride is not so simple as Price and Meister supposed it to be. We are continuing to search either for a co-catalyst in their system or for an inhibitor in our own.

Experimental

Thermal Isomerization of *trans*-Stilbene.—A bomb tube, 10 × 150 mm., containing 1.80 g. (0.01 mole) of *trans*-stilbene was heated for eight hours at 330–340°. The gas was turned off and the tube was dropped from the furnace directly into ice and water. The organic material was taken up in chloroform, washed with ferrous sulfate, dried with magnesium sulfate, and the solvent evaporated under 15 mm. The residue softened at 95° and melted completely at 109°.

Analysis for Mercury.—The procedure reported previously^(4c) was adapted to a semimicro procedure employing one-tenth of the former quantities. Methoxymercuration was carried out at 35° in a fresh 0.2 M mercuric acetate solution freed from mercurous salt by centrifugation. The 1-ml. aliquots, diluted into aqueous potassium nitrate, were extracted five times with chloroform before titration with thiocyanate using ferric sulfate indicator.

Methoxymercuration.—When a 0.2 M solution of *trans*-stilbene is stirred or shaken in catalyst-free methanol suspension, also 0.2 M in mercuric acetate, the mercury is

consumed according to curve B (Fig. 1), and a 6% yield of 1-methoxy-2-chloromercuri-1,2-diphenylethane (*trans* isomer modification) is obtained upon dilution into aqueous sodium chloride after two days. Hydrobenzoin dimethyl ether and mercurous acetate also are produced.

cis-Stilbene under the same conditions reacts rapidly to give more than a 70% yield of the diastereoisomeric methoxymercurial in less than one day. Since neither *trans*-stilbene nor the impurities arising from its thermal isomerization are very soluble in methanol, the ready solubility of *cis*-stilbene in this medium indicates that its presence ought easily be detected in mixtures after, say, two thousand seconds' reaction time.

Preparation of *cis*-Stilbene.—Most of our *cis*-stilbene was prepared directly by Bourguel's method⁵ and was purified readily by distillation. Occasionally a mixture of diphenylethane with *cis*- and *trans*-stilbene was obtained because of over-active catalyst or prolonged hydrogenation time. We have been successful in separation of these disagreeable mixtures by treating them with an excess of methanolic mercuric acetate in absence of peroxide. Crystallization of the product from ethanol yields the pure 1-chloromercuri-2-methoxy-1,2-diphenylethane corresponding to *cis*-stilbene. Regeneration of this geometric isomer from the mercurial is tricky. Reduction with hydrazine hydrate, sodium stannite or formic acid precipitates some mercury, but the remainder is evidently present as the non-isolable R_2Hg compound. Reduction with sodium thiosulfate is better but does not reliably decompose the intermediate halogen-free mercurial to the ethylene. Reaction of the diastereoisomer from *cis*-stilbene with ethyl Grignard reagent causes complete isomerization to *trans*-stilbene. A *cis*-stilbene which is over 90% pure (n_D^{20} 1.6234) can, however, be obtained by shaking the diastereoisomer from *cis*-stilbene with concentrated hydrochloric acid and ether at 25° until no more mercury is freed. Distillation under 10 mm. yields the pure isomer. This demonstrates for the first time that the geometric isomer from which a diastereoisomeric methoxychloromercurial is prepared can be regenerated without conversion to an equilibrium mixture of geometric isomers.

Isomerization of *cis* and *trans*-Stilbenes with Boron Trifluoride.—When 1.80 g. (0.01 mole) of *cis*-stilbene in 8 cc. of purified⁶ carbon tetrachloride was treated with 450 cc. of boron trifluoride over fifty min., no precipitate was formed. The solution was washed with aqueous solutions of sodium carbonate and ferrous sulfate, and, after drying with potassium carbonate, was evaporated under 25 mm. to leave unchanged *cis*-stilbene, (n_D^{20} 1.6225). Identical results were obtained when 1×10^{-4} mole of either benzoyl peroxide or peracetic acid was added to the original mixture.

A solution of 1.80 g. *trans*-stilbene in 15 ml. of boron trifluoride etherate plus 25 ml. peroxide-free anhydrous ether was aged for five days, then washed with aqueous sodium carbonate, ferrous sulfate and water, dried with magnesium sulfate and evaporated under 30 mm. pressure. The residue was shaken with 0.01 mole of 0.2 *M* methanolic mercuric acetate over a three day period during which aliquots were withdrawn. Finally 1.6 g. of mercurous acetate was filtered off and the filtrate added to 2% aqueous sodium chloride. The 1.25 g. portion which precipitated was crystallized from ethanol to melt at 134–136°. This was identified as almost pure hydrobenzoin dimethyl ether. No mercurial could be isolated, although previous experience (ref. 4 c, page 2418) has shown that it is easily separable from the ether by crystallization from ethanol and petroleum ether (b. p. 60–70°). This experiment was repeated except that the diluent ether was replaced by an equal volume of absolute ethanol. The recovered stilbene in this case contained peroxide and therefore reacted fairly rapidly when shaken with methanolic mercuric acetate. The rate was not followed analytically since undissolved *trans*-stilbene was present. After three days, 0.05 g. of mercurous acetate was filtered off and the

filtrate drowned in 2% sodium chloride. The product, 1.05 g., melted at 129° after crystallization from a quantity of ethanol just sufficient to remove the *trans*-stilbene. A second crystallization raised this melting point to 130°.

Identity with the 1-chloromercuri-2-methoxy-1,2-diphenylethane (m. p. 130–131°), obtainable from *trans*-stilbene was established by mixed melting point.

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Hexachlorobenzene from Phthalic Anhydride

BY M. N. DVORNIKOFF, D. G. SHEETS AND F. B. ZIENTY

On prolonged chlorination of phthalic anhydride at 170–265° in the presence of ferric chloride¹ a weight increase greater than that corresponding to the formation of the tetrachloro derivative is observed, and finally the weight decreases again, while carbon dioxide and phosgene (identified as diphenylurea) are being evolved. The final product, obtained in 95% yield, is hexachlorobenzene.

The formation of hexachlorobenzene from *unsym*-tetrachlorophthaloyl chloride by chlorination at 300° has been recorded in the literature.² The conversion of tetrachlorophthalic anhydride into hexachlorobenzene by exhaustive chlorination is analogous also to the production of decachlorobiphenyl by chlorination of *o*-nitrobiphenyl at high temperature in the presence of ferric chloride.³ Each of the reactions mentioned involves replacement of functional groups by chlorine.

Experimental

An agitated mixture of 148 g. (1 mole) of phthalic anhydride and 2.2 g. of anhydrous ferric chloride was chlorinated starting at 170°, gradually increasing the temperature to 265° during ninety hours, and maintaining that maximum temperature for an additional fifty hours. Then 3 g. of calcium oxide was added and the product was distilled, yielding 272 g. (95%) of slightly yellow solid, b. p. 248–255° (160 mm.) and m. p. 214–224°. On crystallization from chloroform, 79% of hexachlorobenzene, m. p. 226–227.5°, was obtained; mixed m. p. with an authentic sample of hexachlorobenzene, 226–227°. All melting points are corrected.

(1) Dvornikoff, U. S. Patent 2,028,383 (January 21, 1936).

(2) Kirpal and Kunze, *Ber.*, **62**, 2103 (1929).

(3) Jenkins, U. S. Patent 2,354,813 (August 1, 1944).

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Stability of DDT and Related Compounds

BY ELMER E. FLECK AND H. L. HALLER

The action of catalysts such as iron, chromium, anhydrous ferric and aluminum chlorides in eliminating hydrogen chloride from DDT (1-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane has been demonstrated.¹ Likewise the role of certain solvents in inhibiting this catalytic decomposition has been shown.² Nevertheless, the idea is widely held that pure DDT is less stable toward heat than is the technical grade.

(1) Fleck and Haller, *THIS JOURNAL*, **66**, 2095 (1944).

(2) Fleck and Haller, *Ind. Eng. Chem.*, **37**, 403 (1945).

(5) M. Bourguel, *Bull. soc. chim.*, [4] **45**, 1067 (1929).

(6) Fieser and Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, Boston, 1935, p. 308.