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 method[5] 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 ($n^{18}\mathrm{D}$ 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 purified[6] 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, ($n^{18}\mathrm{D}$ 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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[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.

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Hexachlorobenzene from Phthalic Anhydride

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On prolonged chlorination of phthalic anhydride at 170–265° in the presence of ferric chloride[1] 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.

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(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

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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.

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

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