

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 methoxymethylmercurial 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 Bourguet's method<sup>5</sup> 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<sub>2</sub>Hg 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 purified<sup>6</sup> 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  $1 \times 10^{-4}$  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

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On prolonged chlorination of phthalic anhydride at 170–265° in the presence of ferric chloride<sup>1</sup> 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.<sup>2</sup> 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.<sup>3</sup> 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

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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.<sup>1</sup> Likewise the role of certain solvents in inhibiting this catalytic decomposition has been shown.<sup>2</sup> 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. Bourguet, *Bull. soc. chim.*, [4] **45**, 1067 (1929).

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

To test this point we have heated DDT at 115–120° in the apparatus previously described.<sup>1</sup> A technical grade of DDT (setting point 91.4°<sup>2</sup>) evolved but 0.02 mole of hydrogen chloride during a four-hour heating period in a U-tube carefully cleaned with nitric and hydrochloric acids followed by water, acetone, and alcohol and then dried in an oven at 110°.

The same lot of technical DDT was then recrystallized twice from alcohol. The alcoholic solution was filtered hot during the first recrystallization. The product was air-dried and was handled with stainless steel spatulas. Although the melting point of this material was 108–109°, it lost 0.45 mole of hydrogen chloride when heated as above.

A sample of this twice-recrystallized DDT was then dissolved in ether and shaken repeatedly with saturated sodium bicarbonate solution and then with water. The ether was distilled and the residue was dissolved in hot alcohol, the solution filtered hot and the crystals which separated on cooling were collected on a Buchner funnel with the aid of a nickel spatula and then dried in vacuum at room temperature. This material melted at 108–109° and lost no hydrogen chloride when heated as above at 115–120° for four hours.

These experiments are viewed as indicating how readily small traces of catalytic material may be picked up by air-drying and by handling with iron or stainless-steel equipment, and how this may lead to the assumption that DDT is not so stable in the pure form as in the crude state. While it is probable that catalytic materials may exist in the technical grade, other impurities such as polymers of chloral and 2-trichloro-1-*p*-chlorophenylethanol (I) inhibit their action to a certain extent. When these inhibitors are removed without taking safeguards against removal of catalytic substances, an apparent instability of DDT is produced.

Thus when 1 part of pure DDT and 2 parts of I were heated together as above for one hour, no hydrogen chloride was evolved. The addition of 0.01% of anhydrous ferric chloride caused the evolution of 0.8 mole of hydrogen chloride during a one-hour heating period, while the heating of I alone with anhydrous ferric chloride produced 0.6 mole. This amount of catalyst completely eliminated 1 mole of hydrogen chloride from pure DDT alone during the course of fifteen minutes heating.

In connection with the study of the catalytic elimination of hydrogen chloride from DDT, several of the isomers and related compounds were tested by the procedure described above. Thus 1,1-dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)-ethylene, m. p. 77–78°, and 1,1-dichloro-2,2-bis-(*p*-bromophenyl)-ethylene, m. p. 123–124°, were prepared by heating the corresponding trichloroethane derivative with 0.01% of anhydrous ferric chloride as outlined above. The melting points of these compounds were not lowered when mixed with authentic material prepared by hydrolysis of the corresponding trichloroethanes with alcoholic caustic.<sup>4,5</sup>

Under similar conditions, anhydrous ferric chloride eliminated 0.95 mole of hydrogen chloride from 1-trichloro-2-(*p*-chlorophenyl)-2-(*m*-chlorophenyl)-ethane. The residue remained an oil, which did not crystallize.<sup>4</sup>

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(3) Fleck and Preston, *Soap and Sanit. Chemicals*, [5] 21, 111 (1945).

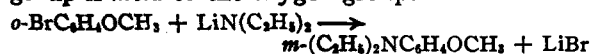
(4) Haller, Bartlett, Drake, Newman, Cristol, Eaker, Hayes, Kilmer, Magerlein, Müller, Schneider and Wheatley, *THIS JOURNAL*, 67, 1591 (1945).

(5) Zeidler, *Ber.*, 7, 1181 (1874).

## Rearrangement in the Condensation of *o*-Bromodimethylaniline with Lithium Diethylamide

BY HENRY GILMAN, ROBERT H. KYLE AND ROBERT A. BENKESER

It was reported recently<sup>1</sup> that lithium dialkylamides underwent reaction, in ether solution, with halogen *ortho* to an ether linkage to give a rearrangement product in which the dialkylamino group is *meta* to the oxygen group.



This type of rearrangement appears to be rather broad in scope, for we have observed that it takes place with *o*-bromodimethylaniline.



An authentic specimen of the *m*-*N,N*-dimethyl-*N',N'*-diethylphenylenediamine was prepared in very satisfactory yield by the following reactions which appear to be of general applicability for the complete alkylation of amines under relatively mild conditions.



In view of the marked similarity in rearrangement reactions of lithium dialkylamides in ether and alkali amides in liquid ammonia,<sup>1,2</sup> it appears reasonable to expect some rearrangement of *o*-halodialkylamines to *m*-ammodialkylamines by reaction with alkali amides in liquid ammonia.

### Experimental

***o*-Bromodimethylaniline and Lithium Diethylamide.**—The lithium diethylamide was prepared by the slow addition in a nitrogen atmosphere of 0.17 mole of methyl-lithium in 64 cc. ether to 0.2 mole of diethylamine in 150 cc. of ether. To the pale, creamy colored mixture which gave a negative color test I,<sup>3</sup> was added 0.17 mole of *o*-bromodimethylaniline and the mixture soon assumed a reddish color. After stirring and refluxing for twenty-four hours, the deep red colored mixture was hydrolyzed by water. Fractional distillation of the dried ether extracts gave 7.3 g. (22%) of recovered *o*-bromodimethylaniline and 2.5 g. distilling at 95–100° (0.5 mm.) and 6.8 g. distilling at 100–102° (0.5 mm.). The last two cuts correspond to a crude yield of 28.5% or, allowing for the recovered *o*-bromodimethylaniline, 37%.

A monopicate prepared from the third fraction and less than one equivalent of picric acid, was orange-red in color and melted at 124.5–125.5° after crystallization from 95% ethanol.

*Anal.* Calcd. for C<sub>12</sub>H<sub>20</sub>O<sub>7</sub>N<sub>2</sub>: N, 16.66. Found: N, 16.0, 15.7, 16.0.

The dipicrate prepared from the third fraction and slightly more than two equivalents of picric acid crystallized from 95% ethanol as yellow prisms melting at 146–147°.

*Anal.* Calcd. for C<sub>24</sub>H<sub>38</sub>N<sub>6</sub>O<sub>14</sub>: N, 17.2. Found: N, 17.1 and 16.95.

(1) Gilman, Crouse, Massie, Benkeser and Spatz, *THIS JOURNAL*, 67, 2106 (1945). See also Bergstrom and Fernelius, *Chem. Rev.*, 20, 437 (1937), and Horning and Bergstrom, *THIS JOURNAL*, 67, 2110 (1945).

(2) Gilman and Avakian, *ibid.*, 67, 249 (1945). Gilman and Nobis, *ibid.*, 67, 1479 (1945).

(3) Gilman and Schulze, *ibid.*, 47, 2002 (1945).