To test this point we have heated DDT at 115–120° in the apparatus previously described.[1] A technical grade of DDT (setting point 91.4°[3]) 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.[4,5]

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.[4]

UNITED STATES DEPARTMENT OF AGRICULTURE
AGRICULTURAL RESEARCH ADMINISTRATION
BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE
BELTSVILLE, MD.

RECEIVED NOVEMBER 9, 1945

---

[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[1] 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.

$$o\text{-BrC}_6\text{H}_4\text{OCH}_3 + \text{LiN(C}_2\text{H}_5)_2 \longrightarrow m\text{-(C}_2\text{H}_5)_2\text{NC}_6\text{H}_4\text{OCH}_3 + \text{LiBr}$$

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

$$o\text{-BrC}_6\text{H}_4\text{N(CH}_3)_2 + \text{LiN(C}_2\text{H}_5)_2 \longrightarrow m\text{-(C}_2\text{H}_5)_2\text{NC}_6\text{H}_4\text{N(CH}_3)_2 + \text{LiBr}$$

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.

$$m\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{NH}_2 \xrightarrow[\text{(2) C}_2\text{H}_5\text{I}]{\text{(1) CH}_3\text{Li}} m\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{N(C}_2\text{H}_5)_2$$

In view of the marked similarity in rearrangement reactions of lithium dialkylamides in ether and alkali amides in liquid ammonia,[1,2] it appears reasonable to expect some rearrangement of *o*-halodialkylamines to *m*-aminodialkylamines 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 methyllithium 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,[3] 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 monopicrate 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 $C_{18}H_{22}O_7N_5$: 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 $C_{24}H_{26}N_8O_{14}$: N, 17.2. Found: N, 17.1 and 16.95.

---

[1] Gilman, Crounse, 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**, 349 (1945). Gilman and Nobis *ibid.*, **67**, 1479 (1945).

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

The dipicrate (m. p., 146–147°) showed no depression of m. p. in a mixed m. p. determination with the dipicrate of *m*-N,N-dimethyl-N′,N′-diethylphenylenediamine prepared by the ethylation of *m*-N,N-dimethylaminoaniline.

The orange-red plates of the mono-picrate when treated in 95% ethanol with additional picric acid gave the yellow prisms of the dipicrate (m. p., 145–146°).

In a check experiment the crude initial yield of *m*-N,N-dimethyl-N′,N′-diethylphenylenediamine was 24%; b. p., 102–104° (0.3 mm.), n^{20}_{D} 1.5632; d^{20}_{4} 0.982; *MR* calcd., 63.55; found, 63.7. The picrates of this compound melted at the same points as the picrates prepared from the other experiment.

Ethylation of *m*-N,N-Dimethylaminoaniline.—To a solution of 5 g. (0.037 mole) of *m*-dimethylaminoaniline in 15 cc. of ether was added in an atmosphere of dry nitrogen, 0.04 mole of methyllithium in 25 cc. of ether. After stirring and refluxing for sixteen hours, 6.25 g. (0.04 mole) of ethyl iodide in 10 cc. of ether was added over a fifteen-minute period, and the mixture was then refluxed for one hour. Then 0.05 mole of methyllithium in 30 cc. of ether was added over a period of twenty minutes. The mixture was refluxed for twenty minutes and a heavy tan precipitate formed. Then in succession, by related procedures, there was added 7.8 g. (0.05 mole) of ethyl iodide in 15 cc. of ether; 0.02 mole of methyllithium in 12 cc. of ether; and 3.1 g. (0.02 mole) of ethyl iodide in 15 cc. of ether. Subsequent to hydrolysis by water, and drying of the ether extracts, there was obtained 5 g. (71%) of *m*-N,N-dimethyl-N′,N′-diethylphenylenediamine.

The authors are grateful to Dr. J. B. Dickey for some *m*-nitrodimethylaniline, and they wish to acknowledge the help of Dr. L. A. Woods for the dialkylation procedure using methyllithium and an organic halide.

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA
RECEIVED SEPTEMBER 29, 1945

The Synthesis of *dl*-Methionine

BY DALE GOLDSMITH AND MAX TISHLER

Recently, Albertson and Tullar reported a synthesis of *dl*-methionine from acetamidocyanoacetic ester and 2-methylmercaptoethyl chloride.[1] We should like to record a similar synthesis of *dl*-methionine consisting of alkylating diethyl acetamidomalonate with the 2-methylmercaptoethyl chloride and of subjecting the resulting compound to hydrolysis and decarboxylation. Our synthesis is an extension of the newly developed route to the α-amino acids from diethyl acetamidomalonic ester.[2] The direct yield of pure *dl*-methionine from the above mentioned reagents is 60% using *t*-butyl alcohol as the solvent for the alkylation step and omitting the isolation of the intermediate diethyl acetamido-(2-methylmercaptoethyl)-malonate. Alkylation in absolute ethanol is almost as satisfactory so far as the yield (56% over-all) is concerned, but the purification of the crude methionine is more difficult. Alkylation in isopropyl alcohol is definitely less satisfactory, and alkylation in either dioxane or xylene leads to poor yields and tarry by-products.

Experimental

Diethyl Acetamido-(2-methylmercaptoethyl)-malonate.—To 1200 cc. of freshly distilled *t*-butyl alcohol was added 14.8 g. of sodium strips and the mixture, protected from air, was refluxed and stirred until the sodium was entirely dissolved. Diethyl acetamidomalonate, 130 g., was added to the warm stirred solution in a few minutes time followed by 82 g. of 2-methylmercaptoethyl chloride. The mixture was stirred and boiled under reflux for six hours, at which time it was neutral to litmus. The completed reaction mixture was concentrated to dryness under reduced pressure and the residue was extracted well with absolute ethanol. The combined extracts and washings were distilled to dryness under reduced pressure and the crude residue (171 g.) was ready for hydrolysis and decarboxylation to *dl*-methionine.

The condensation product can be isolated in a pure form by recrystallizing the residue from a mixture of ether and petroleum ether. After recrystallization, the product melts at 50–52°.

Anal. Calcd. for $C_{12}H_{21}O_5NS$: C, 49.47; H, 7.27; N, 4.81. Found: C, 49.51; H, 7.31; N, 4.66.

***dl*-Methionine.**—A mixture of the crude diethyl acetamido-(2-methylmercaptoethyl)-malonate (above residue), 478 cc. of water and 122 cc. of concentrated hydrochloric acid was boiled under reflux for six hours during which time the ester dissolved. At this time an additional quantity of dilute hydrochloric acid (478 cc. of water and 122 cc. of conc. hydrochloric acid) was added and the mixture was boiled three hours longer. The mixture was concentrated to dryness under reduced pressure; about 150 cc. water was added to the residue and the concentration was repeated. The residue was dissolved in about 800 cc. of absolute ethanol and clarified with a small amount of charcoal. To the resulting solution was added 125 cc. of pyridine and after twenty-four hours storage at 5° the product was collected; wt. 59.3 g. (66.4% yield).

The crude product was purified by dissolving in 450 cc. of water, clarifying the solution with charcoal, concentrating the filtrate to 350 cc. and allowing the resulting solution to crystallize. After four hours an equal volume of ethanol was added and the mixture was stored at 0–5° for twelve hours. The weight of pure *dl*-methionine was 54.1 g.; yield 60.5%.

Anal. Calcd. for $C_5H_{11}NO_2S$: N, 9.39. Found: N, 9.46.

When the *t*-butyl alcohol in the alkylation step was replaced by 280 cc. of absolute ethanol, the yield of crude *dl*-methionine was 63% and of pure product 56%.

RESEARCH LABORATORIES
MERCK AND CO., INC.
RAHWAY, N. J.
RECEIVED OCTOBER 23, 1945

---

[1] Albertson and Tuller, THIS JOURNAL, **67**, 502 (1945).

[2] Albertson and Archer, *ibid.*, **67**, 308 (1945); Snyder, Shekleton and Lewis, *ibid.*, **67**, 310 (1945).

The Quantum Yield in the Photo-reaction between Methyl Iodide and Nitric Oxide

BY T. IREDALE AND E. R. MCCARTNEY

Because of its continuous absorption spectrum, and because the products of its photodecomposition are mainly iodine, methane, with small amounts of other hydrocarbons, methyl iodide is presumed to dissociate by light absorption in the near ultraviolet into $CH_3 + I$. The quantum yield is very low because of the high probabilities of the reverse reactions $CH_3 + I = CH_3I$ and $CH_3 + I_2 = CH_3I + I$. These matters are fully discussed in recent textbooks and papers.[1,2,3,4]

---

[1] Noyes and Leighton, "Photochemistry of Gases," p. 334.

[2] Spence and Wild, *Proc. Leeds Phil. Lit. Soc. Sci.*, **3**, 141 (1936).

[3] Iredale and Stephan, *Trans. Faraday Soc.*, **33**, 800 (1937).

[4] Iredale, *ibid.*, **35**, 458 (1939).