water but insoluble in ether and benzene. Upon dissolving in water and neutralizing with dilute hydrochloric acid, the free mercaptan was obtained as an oily precipitate which was very difficult to purify.

**Methylation of the Mercaptan.**—The sodium salt from above operation (2 g.) was dissolved in alcohol (10 ml.) and refluxed for one hour with an excess of methyl iodide (2 ml.). The solution was then diluted with water, when the required thioether crystallized out upon cooling. The wall of the container was rubbed vigorously with a glass rod to facilitate crystallization. The methyl sulfides prepared were soluble in ether, alcohol and benzene but insoluble in water.

In the table are recorded the results of the different products obtained by rearrangement of different sulfanilides under the influence of alkali.

## Summary

Certain sulfanilides have been rearranged by digestion in alcoholic sodium hydroxide solution to give the corresponding *o*-mercaptodiphenylamines, whereas, upon heating alone, the same compound gives *p*-amino sulfides. The free *o*-amino sulfides, so far as examined, do not suffer a rearrangement under the same conditions, hence, the question arises, do the sulfanilides pass through this intermediate stage before forming the *o*-mercaptan derivative. As yet this point has not been clarified.

NEW HAVEN, CONN. RECEIVED JULY 5, 1935

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

# Chloroform-d (Deuteriochloroform)[1]

BY F. W. BREUER

As part of the program on organic compounds of deuterium in progress in this Laboratory,[2] the reaction of chloral with sodium deutroxide has been studied. Chloroform-d, $CDCl_3$, is formed exclusively as shown by the Raman spectrum.[3] The boiling point and freezing point were about 0.5° higher and lower, respectively, than those of ordinary chloroform. No difference was found in the refractive index, $n^{20}_{\mathrm{D}}$ 1.4450. The most significant difference other than the Raman spectrum is in the density, $d^{20}_{4}$ 1.5004 as compared with 1.4888 for ordinary chloroform determined in an identical manner. Assuming identical molecular volumes for $CHCl_3$ and $CDCl_3$, the calculated value is 1.5013.

## Experimental

The various manipulations for making chloroform were first carefully worked out with ordinary water.

**Chloral Deuterate,** $Cl_3CCH(OD)_2$.—Chloral (E. K. Co.) was distilled through a still head (30 × 0.9 cm.) packed with glass helices[4] to give a middle fraction which was redistilled, the vapors being passed over anhydrous calcium sulfate (Drierite)[5] kept at 100°. After a third distillation, the middle cut ($n^{20}_{\mathrm{D}}$ 1.4568) was used. To 14.72 g. (0.1 mole) of the purified chloral was gradually added with cooling 5.47 g. (0.22 mole) of deuterium oxide ($d^{20}_{20}$ 1.1079).

**Reaction of Chloral Deuterate and Sodium Deutroxide.**—In a container permitting the interaction of water vapors with metallic sodium a solution of sodium deutroxide in deuterium oxide was prepared from 2.2 g. (0.096 g. atom) of C. P. sodium metal and 5 g. (0.25 mole) of the deuterium oxide. The oxide was added slowly from a dropping funnel and the deuterium gas evolved collected under a pressure slightly below atmospheric. At first the reaction seemed to proceed at about the same rate as with ordinary water, as evidenced by the amount of gas formed. Soon, however, a coating of sodium deutroxide formed on the metal and the reaction rate decreased considerably. After five days the volume of gas remained constant during a period of twenty hours. A white crystalline precipitate had formed, whereas with ordinary water a clear solution was obtained. Apparently, sodium deutroxide or a deuterate of it is less soluble in deuterium oxide than the proto compounds in ordinary water. This is in accord with the decreased solubility of the chlorides of sodium and barium in heavy water.[6] In the present study chloral deuterate was found to be considerably less soluble in deuterium oxide than chloral hydrate in natural water.

In order to condense vaporized heavy water the reaction flask was cooled to −78° and the gas container heated for five hours with a stream of warm air.

After connection between the two vessels had been severed the reaction flask was equipped with a reflux condenser and the chloral deuterate solution was admitted from a dropping funnel over a period of five hours, the flask being kept below 5°. The first few drops caused a rather vigorous reaction; afterward the formation of chloroform-d continued smoothly. After standing overnight the reaction was completed by gentle warming of the flask for ten minutes. Complete separation into two layers, which occurs with the proto compounds, did not

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(1) Presented before the Division of Organic Chemistry at the New York Meeting, April, 1935.

(2) *Cf.* Whitmore and co-workers, THIS JOURNAL, **56,** 749 (1934).

(3) Wood and Rank, *Phys. Rev.*, [2], **48,** 63 (1935).

(4) Wilson and others, THIS JOURNAL, **55,** 2795 (1933).

(5) Hammond and Withrow, *Ind. Eng. Chem.*, **25,** 653, 1112 (1933).

(6) Taylor and others, THIS JOURNAL, **56,** 5334 (1934); Bingham and Stephens, *J. Chem. Phys.*, **2,** 107 (1934).

occur even after two days. The separation was finally effected by centrifuging. The reaction product was dried over freshly ignited calcium oxide, distilled, and redistilled. The yield of $CDCl_3$ was 7.85 g.

**Boiling Point, Freezing Point, Density, Refractive Index and Raman Spectrum of Chloroform-d.**—The difference in boiling points of the product and of ordinary chloroform prepared by the same reaction was determined with a set of two micro Cottrell apparatus,[7] each of a capacity of 5 cc., one junction of the thermopile being inserted in each of the instruments. At 732 mm. the deuteriochloroform boiled 0.5° higher than its light analog. Good checks were obtained with Emich's micro boiling point determination.[8]

In order to ascertain the degree of purity of the compound freezing and melting point determinations on a 1.5-cc. sample were run, and compared with the constants of highly purified chloroform and also of ordinary chloroform prepared from chloral hydrate and sodium hydroxide. The determinations were carried out in a double-jacketed container with air insulation. A copper–constantan thermopile of 2 couples enclosed in a flattened platinum tube was used with a glass container of similar shape which by the reduced volume allowed the entire thermopile to be covered with the liquid. The determinations were carried out under a pressure of 3 mm. to ensure removal of all gases which might have been formed by partial decomposition of chloroform during the Raman exposure.

| | M.p. or range, °C. | F. p., °C. | |
|---|---|---|---|
| $CHCl_3$, esp. pure | −63.62 | ............ | |
| $CHCl_3$, from chloral hydrate | −63.77 to −63.33 | −63.49 | −63.62 |
| $CDCl_3$ | −64.69 to −64.15 | −64.12 | −64.12 |

The melting range of the samples of light and heavy chloroform prepared on a small scale indicates that these compounds are not quite pure. Refractionation was not possible because of the small quantities obtained.

However, the observed values indicate that the deuteric compound melts definitely lower, which is in accordance with the lower melting points of other organodeuterium compounds.

A density determination of a middle fraction, using a 0.5-cc. pycnometer, gave $d^{20}_4$ 1.5004.

The index of refraction was determined by means of a new carefully calibrated Bausch and Lomb refractometer of the Abbe type with temperature control at 20 ±0.05°: $n^{20}_D$ for $CDCl_3$ 1.4450, for $CHCl_3$ 1.4450.

Because of the close similarity in properties of $CHCl_3$ and $CDCl_3$ it would have been most difficult to determine the nature of the product except for the Raman spectrum obtained and analyzed by Professor R. W. Wood of Johns Hopkins University and Dr. D. H. Rank of this Laboratory.[3] All lines appearing on the plates correspond to those for $CDCl_3$. No evidence of any $CHCl_3$ lines was detected.

Grateful acknowledgment is made to Professor Wood and Dr. Rank and to Mr. G. H. Fleming of this Laboratory for his help in portions of the work.

## Summary

1. Chloroform-d, $CDCl_3$, free from ordinary chloroform, has been prepared.

2. The properties of the new substance closely resemble those of ordinary chloroform.

STATE COLLEGE, PENNA. RECEIVED AUGUST 5, 1935

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[7] To be published elsewhere by Mary L. Willard and Delcena E. Crabtree of this Laboratory.

[8] Emich-Schneider, "Microchemical Laboratory Manuel," John Wiley and Sons, Inc., 440 Fourth Ave., New York City, 1932.