

Fig. 2.—Infrared spectrum of product: curve A, liquid, 0.025 mm. cell; curve B, gas, sat. vapor, 10 cm. cell; curve C, gas, 60 mm. pressure, 10 cm. cell.

and 3030 cm.^{-1} correspond to those reported for ordinary chloroform.^{5,6} Several very weak minima occurring at 991, 1097 and 1171 cm.^{-1} possibly result from combinations of the fundamentals.

Since the minimum at 1218 cm.^{-1} appeared to persist even in low concentrations of ordinary chloroform, it was decided to use this minimum as a basis for the quantitative analysis of the product. The standard solutions of chloroform in benzene possessed a minimum at this point and obeyed the Beer-Lambert law, as observed in Fig. 3. Transmission of the product (dotted line) corresponded to 6.1 g. of ordinary chloroform in 100 ml. of product or to a 0.960 mole fraction of chloroform-*d*. The average deviation as estimated from the results of three determinations was 0.008 mole fraction units.

Assuming equimolar volumes, the observed density increment of the product as compared to the calculated corresponds to a 0.952 mole fraction, in good agreement with the above analysis.

Acknowledgment.—The authors are indebted to Mrs. Mason H. Earing for preparation of the line drawings.

(6) G. Emschwiller and J. Lecomte, *J. phys.*, **8**, 130 (1937).

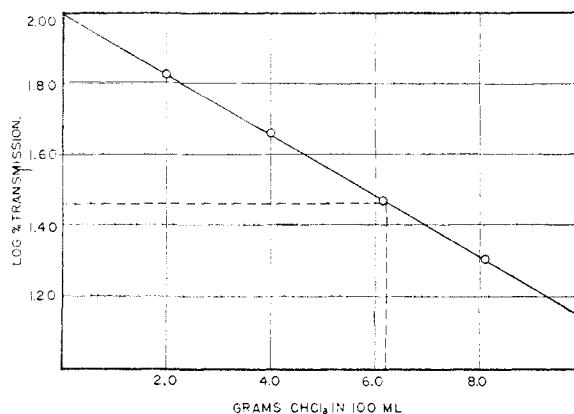


Fig. 3.—Infrared analysis, CHCl_3 in CDCl_3 .

Summary

1. Chloroform-*d* has been prepared in good yield by the action of deuterium oxide on anhydrous calcium trichloroacetate.

2. The infrared absorption spectrum of the product has been measured and the purity quantitatively determined both by this means and by the density increment.

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[CONTRIBUTION FROM THE ILLINOIS INSTITUTE OF TECHNOLOGY AND THE NATIONAL BUREAU OF STANDARDS]

Investigation of the Deuterohaloform Synthesis.^{1a} A New Preparation of Chloroform-*d*

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The preparation of isotopically pure deuteriohalomethanes is of considerable interest. This paper describes an investigation of the deuterohaloform synthesis and reports a new method for the preparation of chloroform-*d*.

Two of the deuterohaloforms, CDCl_3 and CD_2Br_2 , have been reported previously.²⁻⁵

(1) (a) Abstracted from the M.S. Thesis of W. M. Boyer; (b) Wallace A. Erickson & Co., 842 N. Wells, Chicago 10, Illinois; (c) National Bureau of Standards.

(2) F. W. Breuer, *THIS JOURNAL*, **57**, 2236 (1935).

(3) T. W. Newton and G. K. Rollefson, *J. Chem. Phys.*, **17**, 718 (1949).

(4) (a) O. Redlich and F. Pordes, *Monatsh.*, **67**, 203 (1936); (b) O. Redlich and W. Stricks, *ibid.*, **67**, 328 (1936).

(5) R. Truchet, *Compt. rend.*, **202**, 1997 (1936).

These authors, however, made no systematic study of the factors influencing the isotopic purity of their products which were reported to contain the protium-bearing analog in significant, but, in most cases, undetermined amounts. In the present work, mass spectrometric, infrared spectrophotometric and density methods were employed for deuterium analyses in a quantitative investigation of this effect.

Experimental

High vacuum techniques were used in most of the chemical manipulations. A conventional vacuum apparatus was employed.

Chloral (Eastman Kodak Co. White Label), purified by distillation, was further dried by distilling through a heated

TABLE I
 SUMMARY OF CHLORAL EXPERIMENTS

| | Initial D ₂ O | Atom % deuterium in Recovered D ₂ O | Atom % D in hydrogen from Na + D ₂ O | Atom % D in hydrogen from formate | % CHCl ₃ in CDCl ₃ product |
|----------------|--------------------------|--|---|-----------------------------------|--|
| 1 ^a | Stuart | | | | |
| | 98.2 ± 0.5 ^a | 98.9 ± 0.5 ^a | | | 10.5 ± 2.0 ^d |
| | 98.0 ± 0.5 ^b | | | | 13 ± 2 ^c |
| 2 ^a | Same as 1 | 97.5 ± 0.5 ^a | 96.4 ± 0.2 ^c | 0.7 ± 0.1 ^e | 9.3 ± 0.5 ^e |
| | | 98.0 ± 0.5 ^b | | | 9.3 ± 0.5 ^d |
| 3 ^f | Norsk | | | | |
| | 99.8 ± 0.5 ^b | | 98.2 ± 0.5 ^e | 0.4 ± 0.1 ^e | 3.6 ± 0.3 ^e |
| 4 ^f | 90.5 (mixt.) | | | | 12 ± 2 ^d |
| | | | | | 10.6 ± 1.0 ^d |

^a Determined by falling drop density measurement. ^b Determined by mass spectral analysis of gas from electrolyzed sample. ^c Determined by mass spectral analysis. ^d Determined by infrared analysis. ^e Chloral deuterate prepared first, then reacted with NaOD. ^f Anhydrous chloral reacted directly with NaOD.

column of Drierite. It then contained <0.1% moisture, as determined by Karl Fischer titration. Bromal (Eastman Kodak Co.) was vacuum fractionated before use. Trichloroacetophenone was prepared by exhaustive chlorination of acetophenone in an acetate-acetic acid buffer medium. After final purification by distillation at reduced pressure, the product had a boiling point of 135° at 18–20 mm. It was kept over Drierite and further purified with activated charcoal immediately before use. Deuterium oxide from two different sources, Stuart Oxygen Co. ("99.5% D₂O") and Norsk Hydro-Elektrisk ("99.6% D₂O"), was used. Sodium (C.P.) was vacuum melted and refluxed in most cases, and further distilled *in vacuo* for experiment 3.

Four preparations of deuteriochloroform from chloral were made under varying experimental conditions. These experiments were carried out with approximately equimolar quantities of sodium and chloral (*ca.* 0.1 mole) and a total of about 0.6 mole of D₂O.

The experimental procedure producing CDCl₃ of the highest isotopic purity from chloral was as follows. Sodium deuterioxide was formed by distilling D₂O onto cold purified sodium. The evolved deuterium was collected for analysis. After admitting dry nitrogen gas to the apparatus, the anhydrous chloral was slowly added to the NaOD solution at –78°. Upon warming, the CDCl₃ separated immediately and was drawn off, dried with Drierite, and distilled through a small packed column. The yield of purified material was approximately 50%. The aqueous phase of the reaction mixture was distilled to dryness. The specific gravity of the recovered heavy water, after the usual purification with permanganate, was determined by the falling drop density method.⁶ The isotopic purity of this water and of the initial heavy water was also determined by electrolyzing a small sample to dryness and analyzing the gases with the mass spectrometer.

The CHCl₃ content of the CDCl₃ was determined by infrared spectrophotometric analysis using the prominent CHCl₃ band at 3.3 μ, and also by examination of the mass spectrum of the chloroform product.

The solid residue from the reaction mixture was vacuum dried. A portion of this sodium formate residue was titrated electrometrically and found to contain <0.25% alkali (as NaOD). This indicated that the reaction of chloral with NaOD was essentially quantitative. A portion of the residue was decomposed *in vacuo* at 330°. The mass spectrometer was used to analyze the liberated gas, which was found to be essentially pure hydrogen.

Table I summarizes the analytical data for the four experiments with chloral.

Bromoform-*d* was also prepared from bromal by direct reaction with NaOD without first forming the deuterate. A mass spectrometric analysis indicated the presence of 4 ± 1% CHBr₃.

The new method employed for the synthesis of isotopically pure chloroform-*d* consisted in the cleavage of trichloroacetophenone with sodium deuterioxide. The analogous

preparation of chloroform had been reported by Aston, *et al.*⁸ In the present work the synthesis was carried out in the vacuum system following a procedure similar to that employed with anhydrous chloral (experiment 3). Approximately 0.015 mole of trichloroacetophenone and of sodium were each used, together with 0.3 mole of D₂O. This relatively large amount of D₂O was necessary to ensure that all the sodium benzoate remained in aqueous solution throughout the course of the reaction. A yield of approximately 30% chloroform-*d* was obtained after separation and distillation through a small Vigreux column. The mass spectrum of this material showed it to contain 0.8 ± 0.1% CHCl₃ and negligible chemical impurities.

Discussion

Inspection of the results of the chloral experiments in Table I reveals that in every case the chloroform product which separated from the aqueous phase of the reaction mixture contained the protium-bearing impurity in appreciably greater abundance than anticipated from the protium content of the heavy water.

However, the difference in deuterium content between the initial and recovered heavy water is zero, within the experimental error of the isotope measurements. Thus the amount of protium contamination introduced into the reaction mixture from all possible sources (*e.g.*, atmospheric moisture, hydrate in the chloral, hydrogen from the sodium) was not detectable.

Lauder and Wright⁹ have observed the alkaline hydrolysis of chloral in water containing about three atom % deuterium oxide, and found that the sodium formate contained about 0.3 atom % deuterium. They postulated exchange between the hydrogen atom of chloral and heavy water to account for this observation. Such exchange, which would result in protium dilution of the heavy water, was *not observed* in this investigation. The deuterium in the formate residues of experiments 2 and 3 was almost certainly introduced by exchange of formate with the solvent rather than by their mechanism. In any case the total quantity of deuterium in the sodium formate is not nearly sufficient to explain the quantities of CHCl₃ observed in the CDCl₃.

From a consideration of the above it would appear that the hydrogen atom of chloral may be

(6) D. W. Wilson, A. O. C. Nier and S. P. Rieman, "Preparation and Measurement of Isotopic Tracers," J. W. Edwards, Ann Arbor, Michigan, 1946.

(7) S. Tagaki, *J. Chem. Soc. Japan*, **60**, 813 (1939).

(8) J. G. Aston, J. D. Newkirk, J. Dorsky and D. M. Jenkins, *THIS JOURNAL*, **64**, 1415 (1942).

(9) I. Lauder and S. W. Wright, *Nature*, **158**, 381 (1946).

the one which appears in the product as CHCl_3 . This transfer of the hydrogen from the carbonyl carbon atom to the halogen-bearing carbon apparently does *not* occur by an exchange mechanism involving the solvent.

The results obtained in the chloral and bromal experiments suggested that the isotopic purity of the product might be improved if the hydrogen atom were replaced by another group. The preparation of 99.2% CDCl_3 was thus accomplished using trichloroacetophenone. This represents the highest reported isotopic purity for any previous preparation of chloroform-*d*.

Acknowledgments.—The authors are greatly indebted to Professor Eugene Lieber for valuable discussions. Thanks are due to Dr. Sidney Katz

for assistance with the infrared spectrophotometer. The D_2O was obtained through the courtesy of Professor Martin Kilpatrick and the Atomic Energy Commission.

Summary

1. Isotopically pure CDCl_3 is not obtained by the reaction of chloral with sodium deuterioxide.

2. The observed CHCl_3 dilution of the product does *not* occur through the previously advanced mechanism of protium exchange with the solvent.

3. A new synthesis of chloroform-*d* by the reaction of trichloroacetophenone with sodium deuterioxide has produced CDCl_3 of 99.2% isotopic purity.

CHICAGO 16, ILLINOIS

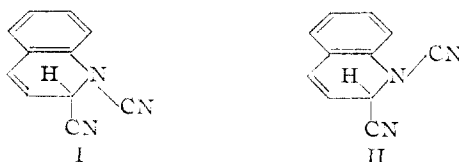
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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF STANFORD UNIVERSITY AND THE UNIVERSITY OF ARIZONA]

The Structure of the Isomeric Quinoline Dicyanides

BY M. G. SEELEY, R. E. YATES AND C. R. NOLLER

Quinoline reacts with bromocyanogen and hydrogen cyanide to form a dicyanide which is isomerized easily by ammonia.¹ The conclusion was drawn² that the isomers must differ stereochemically, and they were assigned the structures of *cis*- and *trans*-1,2-dihydro-1,2-dicyanoquinoline (I and II).



Each of the isomers necessarily would be a racemic mixture, since structures I and II would each have a non-superimposable enantiomorph. If this interpretation of the structure of the isomers is correct, they would constitute the first case in the literature of configurationally stable trivalent nitrogen which is not linked by a double bond as in the oximes,

hydrazones and azo compounds, since their preparation precedes the resolution of Troeger's base.³

Although the chemical evidence is convincing regarding the location of the cyanogen groups, it seemed desirable to examine the two isomers by physical methods to determine whether the results were compatible with the stereochemical explanation. The melting point curve for mixtures of the isomeric quinoline dicyanides (Fig. 1) showed definitely that they are not merely two crystalline forms of the same substance. Next the apparent molecular refractions of the two compounds were determined in bromobenzene solution. The observed values were 45.4 cc. for the low-melting isomer, and 42.9 cc. for the high-melting isomer. The difference of 2.5 cc. is considerably greater than that reported for *cis-trans* ring isomers, for two diastereoisomeric racemic forms, or for *syn* and *anti* oximes. For example, the difference for the *cis* and *trans* decalins is 0.40 cc.,⁴ and for ethyl hexahydrophthalate it is 0.46 cc.;⁵ for the two racemic forms of ethyl *sym*-dimethylsuccinate it is 0.12 cc.;⁵ and for the two mesityl oxide oximes it is 0.64 cc.⁶ Where a choice of several examples was possible, that pair having the highest difference in molecular refraction was selected.

More significant is the difference in the absorption of the two isomers in the ultraviolet. The low-melting isomer has three distinct bands with maxima at 229, 273 and 308 $\text{m}\mu$ and $\log \epsilon_{\text{max}}$ 4.48, 3.67 and 3.32, respectively (Fig. 2). The high-melting isomer has only two maxima at 224 and 284 $\text{m}\mu$ with $\log \epsilon_{\text{max}}$ 4.18 and 3.46, respectively (Fig. 3). It seems unlikely that the spectra of two structurally identical racemic forms would differ to this extent.

Assuming that the above results point to a structural difference in the two isomers, the ques-

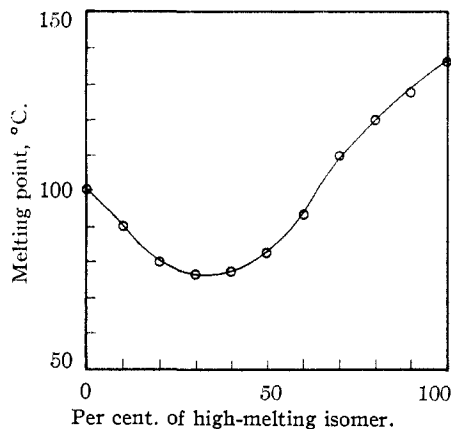


Fig. 1.—Melting point curve for mixtures of isomeric quinoline dicyanides.

(1) Mumm and Herrendörfer, *Ber.*, **47**, 758 (1914).

(2) Mumm and Ludwig, *Ann.*, **514**, 34 (1934).

(3) Prelog and Wieland, *Helv. Chim. Acta*, **27**, 1127 (1944).

(4) Hückel, *Ann.*, **441**, 44 (1925).

(5) Auwers and Ortens, *Ber.*, **57**, 442 (1924).

(6) Auwers and Ottens, *ibid.*, **57**, 458 (1924).