where $\epsilon^*$ is the complex dielectric constant and $\alpha$ is a distribution parameter, varying between zero and unity. In Table VII are recorded values of $\tau_0$, a generalized relaxation time, and $\alpha$ for octanol-1 and 2-methylheptanol-3, which have been calculated from the data of Table VI. Included also are comparable compounds reported by Cole and Cole.[19]

TABLE VII

DISTRIBUTION OF RELAXATION TIMES IN HYDROGEN BONDED LIQUIDS

| Substance | $t$, °C. | $\tau_0 \times 10^{11}$ sec. | $\alpha$ |
|---|---|---|---|
| Water[19] | 19 | 0.94 | 0.09 |
| Methyl alcohol[19] | 19 | 6.4 | 0.13 |
| Ethyl alcohol[19] | 20 | 9.4 | 0.15 |
| Propyl alcohol[19] | 19 | 32 | (0) |
| *n*-Butyl alcohol[19] | 19 | 64 | (0) |
| *i*-Amyl alcohol[19] | 19 | 100 | (0) |
| Octanol-1 | 25 | 133 | 0.494 |
| 2-Methylheptanol-3 | 25 | 5.75 | 0.111 |

With the exception of 2-methylheptanol-3, the relaxation times of the higher alcohols increase uniformly with increasing molecular length. The spread of distribution times, as indicated by $\alpha$, is greater for octanol-1 than that for the other alcohols. However, the parentheses used by Cole and Cole indicate that, for propyl, butyl, and *i*-amyl alcohols, the results were somewhat doubtful. Again it is noted that the more spherical 2-methylheptanol-3 molecule rotates much more easily than the linear octanol-1, being comparable with the methyl alcohol molecule, which is, presumably, somewhat associated.

## Summary

An apparatus has been constructed for the measurement of dielectric constant and absorption with electric waves which *in vacuo* have a length of 9.72 cm. Water has been measured at temperatures from 0 to 100°, and sixteen organic compounds have been measured at 25°. The viscosities of the organic compounds have also been measured.

The relaxation times of the molecules are calculated from the absorptions and used, in the case of water, to calculate the free energies, heats, and entropies of activation for the process of molecular rotation viewed in the light of the absolute reaction rate theory. The values of these thermodynamic quantities are comparable to those for viscous flow. The conclusion is drawn that the polarization of water is due to molecular orientation in the applied field rather than to proton transfer. The relaxation times of the organic molecules increase consistently with their size and the extent of their departure from spherical form. They are related to the behavior of the substances in viscous flow.

PRINCETON, NEW JERSEY RECEIVED AUGUST 25, 1942

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

# Preparation and Properties of Some New Trifluoromethyl Compounds

BY J. H. SIMONS AND EDWARD O. RAMLER[1]

In a previous paper[2] the methods of synthesis of trifluoromethyl compounds were discussed. At this time we can report on the preparation and properties of trifluoroacetyl chloride and trifluoroacetyl bromide. $\alpha$-Trifluoroacetophenone was also prepared and its chemical and physical properties studied. This aromatic ketone is of interest as it is the first ketone of this type reported. Ketones in the aliphatic series containing the trifluoromethyl group have been prepared and studied.[3]

## Preparations and Properties of Compounds

**Trifluoroacetyl Chloride.**—Barium trifluoroacetate was prepared according to the method of Swarts,[4] 36.3 g. (0.10 mole), dried in an oven at 110° for two hours, was placed in the reaction flask and 16 cc. (0.18 mole) of phosphorus trichloride added. An all glass system, consisting of a reaction flask and reflux condenser connected at the top to a dry ice–acetone trap, was used. The phosphorus trichloride was refluxed on a water-bath for eighteen hours. The product was distilled through a small low temperature column previously described by the authors.[5] There was obtained 14 g. (53%) of trifluoroacetyl chloride.

*Anal.* Calcd. for $C_2F_3OCl$: Cl, 26.79. Found: Cl, 27.21.

A small amount of this material was dissolved in about 15 cc. of dry ether, and the amide prepared by the addition

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[1] Present address: E. I. du Pont de Nemours and Co., Arlington, N. J.

[2] Simons, Bond and McArthur, THIS JOURNAL, **62**, 3477 (1940).

[3] Swarts, *Bull. classe sci., Acad. roy. Belg.*, **13**, 175 (1927); Fukuhara and Bigelow, THIS JOURNAL, **63**, 788 (1941).

[4] F. Swarts, *Bull. classe sci., Acad. roy. Belg.*, (5) **8**, 365 (1922).

[5] Ramler and Simons, *Ind. Eng. Chem., Anal. Ed.*, **14**, 430 (1942).

of ammonia. After two recrystallizations from chloroform, it melted at 74.5–75.0° (74.8°)[4].

The melting point of trifluoroacetyl chloride was found to be −146° by means of warming curves in the absence of permanent gases. The boiling point was found to be −27° from the vapor pressure curve. Static determinations of the vapor pressure were made using a mercury manometer connected in an all glass system to a bulb containing the material. The bulb was surrounded with a well insulated copper block and allowed to warm slowly while measurements were made. Temperatures were determined by use of a thermocouple located in a thin walled capillary tube which reentered the bulb from the top and in its center. Measurements of trifluoroacetyl chloride fit the equation $\log_{10} P = -1028/T + 7.07$ with $P$ being pressure in mm. and $T$ being degrees K. The calculated heat of vaporization is 4700 cal. per mole.

**Trifluoroacetyl Bromide.**—In the apparatus described above were placed 36.5 g. (0.10 mole) of barium trifluoroacetate and 20 cc. (0.21 mole) of crude phosphorus tribromide. This was refluxed for nine hours at 190° on an oil-bath. There was obtained after distillation in the described column, 21 g. (59.3%) of trifluoroacetyl bromide.

*Anal.* Calcd. for $C_2F_3OBr$: Br, 45.20. Found: Br, 45.15.

The melting point (−136°), boiling point (−5°) and vapor pressure were determined in the same way as for the acid chloride. Vapor pressure measurements of trifluoroacetyl bromide fit the equation $\log_{10} P = -1069/T + 6.87$ and the calculated heat of vaporization is 4900 cal. per mole.

**Trifluoroacetophenone.**—In a 500-ml. 3-necked flask, equipped with a mercury-sealed stirrer, condenser, thermometer and gas inlet tube, were placed 39 g. (0.50 mole) of benzene, 66 g. (0.50 mole) of technical aluminum chloride, and 100 cc. of carbon disulfide, and cooled to −5°. The condenser was a small Hopkins type cooled by circulating through it acetone cooled in dry-ice. The trifluoroacetyl chloride, 58 g. (0.44 mole), was bubbled into the mixture slowly, the rate depending on the rate of reflux of unused material. Reaction occurred at about 5°. The addition required six hours, and the mixture was stirred four more hours at room temperature. There was recovered 3 g. of unreacted acid chloride. The reaction mixture was poured onto ice and hydrochloric acid mixture and a portion of ether added for extraction. The water layer gave no test for fluoride ion. The ether extractions were dried over anhydrous calcium chloride and distilled through a jacketed 20-in. column, 10-mm. inside diameter, packed with $^1/_8$-in. glass helices, at a reflux ratio of 10 to 1. A fraction of 28 g. (43%) of trifluoroacetophenone was collected at 152° at 730 mm. Distilled from a Vigreux indented Claisen flask at 37 mm., it was found to boil at 75°. Theoretical mol. wt. 174. Found: 163, 180 and 174.

Trifluoroacetophenone, b. p. 152° at 730 mm., f. p. about −40°, $n^{20}_D$ 1.4583, and $d$ 1.279 g./cc. at 20°, dissolves in concentrated sulfuric acid but is recovered by dilution with water. It is soluble in ether, ethanol and benzene.

It dissolves in 10% potassium hydroxide solution with vigorous shaking and is recovered by acidification with sulfuric acid. When allowed to stand for about ten minutes after dissolving in the aqueous alkali, very small bubbles of gas appear and rise to the surface. After several hours the reaction is complete and acidification yields benzoic acid as the sole organic product. This is strong indication that the haloform reaction has taken place, and the gas evolved is probably fluoroform. This solution in alkali is an unusual behavior for an aromatic ketone but is frequently found for aliphatic ketones. In a similar reaction of aliphatic ketones, the formation of a sodium bisulfite addition complex, trifluoroacetophenone dissolves in a 10% aqueous sodium bisulfite solution. Colorless crystals then appear. These do not melt or burn but dissolve readily in water and react with sulfuric acid to evolve sulfur dioxide and regenerate the ketone.

In the haloform reaction trifluoroacetophenone behaves somewhat differently than the other halogenated acetophenones. For the others a common solvent is necessary for the base and ketone, and the reaction is relatively rapid.[6]

Attempts to prepare a cyanhydrin failed. A solution of sodium cyanide added to the bisulfite addition complex did not yield it. The ketone dissolves in a saturated potassium cyanide solution with the evolution of heat, but acidification of such a solution failed to yield the expected alpha hydroxy acid.

A 2,4-dinitrophenylhydrazone, m. p. 94.5–95.5, was readily formed.

Trifluoroacetophenone reacted with phosphorus pentachloride under reflux conditions to form 1,1,1-trifluoro-2,2-dichloro-2-phenylethane.

**1,1,1-Trifluoro-2,2-dichloro-2-phenylethane.**—A mixture of 10 g. (0.0575 mole) of trifluoroacetophenone and 18 g. (0.0865 mole) of phosphorus pentachloride was refluxed for three hours on an oil-bath at 175°. The mixture was distilled through a small Claisen distilling head at 27 mm. The phosphorus oxychloride was removed first at 39. The excess phosphorus pentachloride was removed by filtration with suction. The filtrate was allowed to stand over anhydrous potassium carbonate to remove the sharp hydrogen chloride odor. Continued distillation at 37 mm. yielded 1.8 g. of unreacted trifluoroacetophenone, boiling at 75°, and 5.2 g. of the dichloride boiling at 89–90°.

*Anal.* Calcd. for $C_8H_5F_3Cl_2$: Cl, 31.0. Found: Cl, 30.4.

Thus a 48.5% yield of the desired dichloride was obtained. This material would not form a sodium bisulfite addition compound.

**Diphenyltrifluoromethylcarbinol.**—Phenylmagnesium bromide was prepared in the usual manner from 4.4 g. (0.028 mole) of bromobenzene, 0.7 g. (0.0288 mole) of magnesium turnings, and 14 cc. of dry ether. To this was added 5 g. (0.0287 mole) of trifluoroacetophenone dissolved in 6 cc. of dry ether. The mixture refluxed very slowly of its own accord, and no white precipitate of the complex was formed. The mixture was refluxed on a water-bath for four hours with no apparent change. Water was added to the mixture with stirring. Hydrochloric acid was added to clear the solution, which was then filtered to remove a very small amount of gray powder that was present. The layers were separated and the ether layer dried over anhydrous calcium chloride. The ether was removed on a water-bath and the residue distilled under reduced pressure from a Vigreux indented Claisen flask. A few drops of liquid

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(6) Aston, Newkirk, Dorsky and Jenkins, THIS JOURNAL, **64**, 1413 (1942).

were obtained over a long range until 3.3 g. was collected at 154–157° at 17 mm. There was 1.5 g. of a black tarry residue left in the flask. The material boiling at 157° completely solidified after standing for five days. This was recrystallized from petroleum ether and found to melt at 74.0–74.5°. *Anal.* The material was heated in a sealed tube with potassium metal to 450° for two hours as described by Elving and Ligett,[7] and the product was analyzed for fluorine by the lead chlorofluoride method described by Scott.[8] Calcd. for $C_{14}H_{11}OF_3$: F, 22.62. Found: F, 21.82.

Thus diphenyltrifluoromethylcarbinol was prepared in 46% yield.

*m*-**Bromobenzotrifluoride.**—In a 1-liter, 3-necked flask, equipped with a mercury-sealed stirrer, dropping funnel and condenser, were placed 133 g. (0.91 mole) of benzotrifluoride and 1 g. of iron powder. This was heated on a water-bath to 60° and 3 cc. of dry bromine was added. When the reaction failed to start, it was heated to 70° and 1 g. of iron powder was added. The reaction started and etching was also noticed. The temperature was reduced to 56°, and 21 cc. of bromine was added in the next hour. This was followed by another hour of stirring, and then the last 25-cc. portion of bromine was added over the period of an hour. The temperature was raised to 60°, and the mixture stirred for one more hour. Little etching was noticed with this procedure. The reaction mixture was poured into 700 cc. of water, to which 25 cc. of saturated sodium bisulfite solution had been added. Enough solid sodium bisulfite was added with stirring to decompose all the free bromine. This mixture was steam distilled, collecting two batches of distillate. The first contained the oily *m*-bromobenzotrifluoride which was separated from the water, shaken with dilute potassium hydroxide solution, dried over anhydrous magnesium sulfate, and distilled through a 1-ft. Vigreux indented distilling head. There was collected 12.7 g. of benzotrifluoride (98–102°) and 96 g. of *m*-bromobenzotrifluoride (151–152°) was obtained for a 52% yield.

Upon refluxing with 80% sulfuric acid, this material yielded *m*-bromobenzoic acid, melting point 154° (154°)[9] and neutral equivalent 202 (theoretical 201).

The second batch of distillate contained a white solid which was a mixture of benzoic acid and *m*-bromobenzoic acid, obtained by hydrolysis of the trifluoromethyl group.

**3,4-Dibromobenzotrifluoride.**—If a larger amount of iron powder was used and the temperature kept around 80–85°, the yield of *m*-bromobenzotrifluoride was reduced to 25% and a considerable quantity (8%) of dibromobenzotrifluoride was formed. These conditions were accompanied by excessive etching, and large amounts of the corresponding benzoic acids were obtained. The dibromobenzotrifluoride boiled at 102–104° at 25 mm. When hydrolyzed with 80% sulfuric acid, it yielded 3,4-dibromobenzoic acid, melting at 228–229°,[10] and having a neutral equivalent of 283 (theoretical 280).

*m*-**Methylbenzotrifluoride.**—A Grignard reagent of *m*-bromobenzotrifluoride was prepared in the usual manner from 16 g. (0.66 mole) of magnesium turnings, 143 g. (0.636 mole) of *m*-bromobenzotrifluoride, and 350 cc. of dry ether. The reaction began unaided, and proceeded smoothly to give a clear, brown solution. Titration of a 10-cc. sample indicated a 100% yield of the *m*-trifluoromethylphenylmagnesium bromide. A freshly distilled sample of 85.5 g. (64 cc.) of dimethyl sulfate (b. p. 82° at 19 mm.) dissolved in 65 cc. of dry ether was added to the Grignard reagent. The reaction proceeded smoothly without the aid of heat. The mixture was refluxed on a water-bath for twelve additional hours, then poured onto ice. The ether layer was separated and the milky water layer acidified with concentrated hydrochloric acid. Another layer of ether separated and was removed. The acid layer was extracted twice with ether and the combined ether portions dried over anhydrous calcium chloride. After most of the ether was removed by distillation through the 1-ft. Vigreux head, the residue was distilled through the previously described 20-in. helices packed column. There was collected 59.4 g. of benzotrifluoride (65%) boiling at 100–101° at 734 mm., and 9.3 g. of *m*-methylbenzotrifluoride (9.1%) boiling at 127°, and 5.6 g. of residue. The *m*-methylbenzotrifluoride was hydrolyzed with 80% sulfuric acid to *m*-toluic acid, melting at 106–108° (108–109°)[11] and having a neutral equivalent of 137 (theoretical 136).

The *m*-methylbenzotrifluoride was oxidized to *m*-trifluoromethyltoluic acid melting at 101–102° (103°),[12] and having a neutral equivalent of 192 (theoretical 190).

### Qualitative Test for Fluoride Ion

Two-tenths gram of cerous nitrate is dissolved in 5 cc. of water for use as a reagent. Two drops of acetic acid are added to ensure an acid solution. This reagent will precipitate cerous fluoride from a dilute solution of potassium fluoride. This precipitate is insoluble in excess acetic acid but is soluble in strong mineral acids.

After the sodium or potassium fusion of the organic material has been made and the ions are in solution, 1 cc. of the solution to be tested is made acid with glacial acetic acid and added to an equal volume of the cerous nitrate reagent. A milky white, gelatinous precipitate appears, if fluoride ion is present. This method fits readily into the scheme for qualitative elementary analysis of organic compounds and the test is satisfactory in the presence of chloride, bromide, iodide and cyanide ions.

## Discussion

Both trifluoroacetyl chloride and bromide appear to be normal compounds. Their preparation by means of the action of the appropriate phosphorus trihalide on barium trifluoroacetate is to be expected. An attempt to prepare trifluoroacetyl iodide by a similar method was unsuccessful but this was not unexpected.[13] The reaction of hydrogen iodide on the chloride would probably yield the iodide.

The preparation of trifluoroacetophenone by the

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(7) Elving and Ligett, *Ind. Eng. Chem., Anal. Ed.*, **14**, 449 (1942).

(8) Furman, "Scott's Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, N. Y., 5th Ed., Vol. I, p. 405.

(9) Friedburg, *Ann.*, **158**, 19 (1871).

(10) Cohen and Zortmann, *J. Chem. Soc.*, **89**, 47 (1906).

(11) Kellas, *Z. physik. Chem.*, **24**, 222 (1897).

(12) F. Swarts, *J. Chim. Phys.*, **17**, 32 (1919).

(13) Simons, Sloat and Meunier, THIS JOURNAL, **61**, 435 (1939).

Friedel–Crafts acylation of benzene using the above mentioned acid halides is a result of some interest after the observations of Henne and Newman,[14] that aluminum chloride reacts with organic fluorides to produce aluminum fluoride and an organic chloride. The resistance to this reaction of the fluorine atoms in the trifluoromethyl group in this type of compound is a useful property. Tests revealed no inorganic fluoride in the reaction products.

1,1,1 - Trifluoro - 2,2 - dichloro - 2 - phenylethane failed to react with antimony trifluoride to prepare pentafluorophenylethane. This is unexpected due to the usual reactivity in the Swarts reaction of chlorine atoms adjacent to a phenyl group or a double-bonded carbon atom. The formation of benzotrifluoride by the action of hydrogen fluoride on benzotrichloride[15] (now accomplished in a pressure vessel at higher temperatures in excellent yield) is an indication of the ease of reaction of such a chlorine atom. In fact, even the fluorine atoms in benzotrifluoride are moderately reactive. This compound and related ones hydrolyze readily, if heated with 80% sulfuric acid. This reaction is useful for the identification of trifluoromethyl substituted aromatic compounds, and it is here used to prepare the carboxylic acids from such compounds for this purpose.

Pentafluorophenylethane would be expected to be prepared by the action of mercuric or silver fluoride on the 1,1,1-trifluoro-2,2-dichloro-2-phenylethane.

The Grignard reaction has not previously been reported in the literature for use in connection with fluorine compounds of this type. It is used herein for two purposes. Trifluoroacetophenone reacted with a phenyl Grignard to form diphenyltrifluoromethylcarbinol. *m*-Bromobenzotrifluoride reacted with magnesium in ether to form a Grignard reagent from which *m*-methylbenzotrifluoride was prepared. An unexpected result was obtained in treating this Grignard reagent with dimethyl sulfate. A 65% yield of benzotrifluoride was obtained and only 9% of methylbenzotrifluoride was found.

## Summary

1. Trifluoroacetyl chloride and bromide were prepared and their physical properties studied.

2. Trifluoroacetophenone was prepared by a Friedel–Crafts condensation in the presence of aluminum chloride.

3. Other new compounds reported are: *m*-bromobenzotrifluoride, 3,4-dibromobenzotrifluoride, *m*-methylbenzotrifluoride, trifluoroacetophenone-2,4-dinitrophenylhydrazone, 1,1,1-trifluoro-2,2-dichloro-2-phenylethane and diphenyltrifluoromethylcarbinol.

4. It was found that the Grignard reaction could be used in the synthesis of compounds containing the trifluoromethyl group.

5. A new qualitative test for fluoride ion based upon the precipitation of cerous fluoride is reported.

STATE COLLEGE PA. RECEIVED OCTOBER 31, 1942

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[14] Henne and Newman, THIS JOURNAL, **60**, 1697 (1938).

[15] Simons and Lewis, *ibid.*, **60**, 492 (1938).

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

# The Resolution and Rates of Hydrolysis of *d*,*l*-α-Bromopropionic Acid and its Glycine Derivatives[1]

BY ALBERT F. CHADWICK[2] AND EUGENE PACSU

For the preparation of polypeptides consisting of optically active amino acids relatively large quantities of optically active α-halogen acids are required. One of the latter substances, active α-bromopropionic acid, was prepared by Walden,[3] Purdie and Walker[4] and also by Cowdrey, Hughes and Ingold,[5] from the calcium salt or the ethyl ester of active lactic acid and phosphorus pentabromide. Due to partial racemization during the reaction, the low yields, and also to the fact that it requires the preliminary preparation of pure *d*- and *l*-lactic acids, this method is unsuitable for the preparation of large quantities of

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[1] This work was supported in part by a grant from the Rockefeller Foundation.

[2] This paper is based upon a thesis submitted by Albert F. Chadwick, Allied Chemical and Dye Corporation Fellow in Chemistry, to the Faculty of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Walden, *Ber.*, **28**, 1293 (1895).

[4] Purdie and Walker, *J. Chem. Soc.*, **67**, 914 (1895).

[5] Cowdrey, Hughes and Ingold, *ibid.*, 1208 (1937).