Procedure B.—The hydrocarbon, the chloroalkane and di-*t*-butyl peroxide were weighed into a glass liner (cooled in a bath at −78° when the gaseous hydrocarbons were employed). The liner was sealed into an Ipatieff-type rotating autoclave of 850-cc. capacity, nitrogen was charged to a pressure of 50 atm., and the autoclave was then heated, the temperature being raised gradually during four hours from 130–140°. The autoclave was permitted to stand overnight, after which the gas was discharged to the atmosphere, and the liquid product was washed, dried and distilled.

Identification of Products.—The chlorinated products were identified by means of their boiling points and refractive indices and in many cases by comparison of their infrared spectra with those of authentic samples (see Table I).

Hexachloroethane was isolated from the higher boiling product of a number of experiments and identified by means of its melting point as well as that of a mixture of the material with an authentic sample of hexachloroethane. Thus, for example, in expt. 13, there was obtained 1.5 cc. of the product boiling at 78–90° at 26 mm. (175–193° at 760 mm.). This became partially crystalline on standing and filtration yielded 0.9 cc. of liquid and 0.8 g. of crystals, which were recrystallized from methanol; m. p. and mixed m. p. 184–185° (sealed tube).

Summary

When a saturated hydrocarbon is treated with certain polyhaloalkanes in the presence of a catalytic amount of a decomposing organic peroxide, hydrogen-halogen exchange occurs and the hydrocarbon is converted to a monohaloalkane. Straight chain paraffins of at least three carbon atoms as well as branched chain and cyclic hydrocarbons may be used.

When hexachloroethane is used as the halogen donor, alkyl chloride is obtained in excellent yield, but the other anticipated product, namely, pentachloroethane, is not formed. Instead, tetrachloroethylene and hydrogen chloride are produced.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE GREAT WESTERN DIVISION, THE DOW CHEMICAL COMPANY]

A New Synthesis of Ethyl Trifluoroacetate

BY T. R. NORTON

Various methods have been described for the preparation of trifluoroacetic acid and the esters thereof. According to the method of Swarts,[1] *m*-aminobenzotrifluoride was oxidized with chromic acid. Chlorinated derivatives of $CF_3CH{=}CH_2$ have been oxidized with a permanganate and caustic alkali.[2,3] The oxidation of fluorochlorobutenes, such as $CF_3CCl{=}CClCF_3$, with caustic alkali and a permanganate was described by Babcock.[4]

It has been found that trifluoroacetic acid can be prepared in high yield by a less costly and much less drastic type of reaction involving the simple hydrolysis of 2,4,6-tris-(trifluoromethyl)-1,3,5-triazine (III) with dilute aqueous mineral acid at atmospheric pressure.

The method is made practical by an improved synthesis of the previously described compound (III).[5]

Acetonitrile was chlorinated by one of several known methods[6,7] to give trichloroacetonitrile (I).

The trimerization of trichloroacetonitrile was heretofore carried out by contact with anhydrous halogen acids such as hydrogen chloride or hydrogen bromide.[8,9] In contrast to aromatic nitriles, which are readily trimerized,[10] the reaction with trichloroacetonitrile is extremely slow, the time required for completion being on the order of about 100 hours. It has been found that the addition of a small amount of anhydrous aluminum halide to the reaction mixture of trichloroacetonitrile and hydrogen halides greatly activates the latter in causing trimerization of the trichloroacetonitrile, reducing the time required for completion of the reaction to only a few hours and in many cases to less than one hour. The aluminum halides alone are substantially ineffective to cause the trimerization. Their function appears to be solely to serve as an activator for the hydrogen halide. If either (or both) the aluminum halide or hydrogen halide contains bromine as the halide, the reaction rate is increased and pressure is not required as is the case when aluminum chloride and anhydrous hydrogen chloride are used as catalysts. With increasing proportions of aluminum halide the reaction rate increases, although the yield is decreased slightly. The optimum conditions are described in the two examples in the Experimental Section.

The fluorination of 2,4,6-tris-(trichloromethyl)-1,3,5-triazine has been previously described,[5] using anhydrous hydrogen fluoride and a small amount of antimony pentachloride as catalyst. However, the yield of the completely fluorinated product, 2,4,6-tris-(trifluoromethyl)-1,3,5-triazine, was not given but is assumed to be small in view of the drastic conditions employed. It has now been found that the Swarts reaction using antimony

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[1] Swarts, *Bull. Acad. Roy. Belg.*, **8**, 343 (1922).

[2] A. L. Henne, THIS JOURNAL, **67**, 918 (1945).

[3] A. L. Henne, U. S. Patent 2,371,757 (Mar. 20, 1945).

[4] J. H. Babcock and A. D. Kischitz, U. S. Patent 2,414,706 (Jan. 21, 1947).

[5] E. T. McBee, *et al.*, *Ind. Eng. Chem.*, **39**, 391 (1947).

[6] K. Dachlauer, German Patent 694,479 (Aug. 18, 1942).

[7] J. J. Gray and F. Burgess, U. S. Patent 2,426,091 (Aug. 19, 1947).

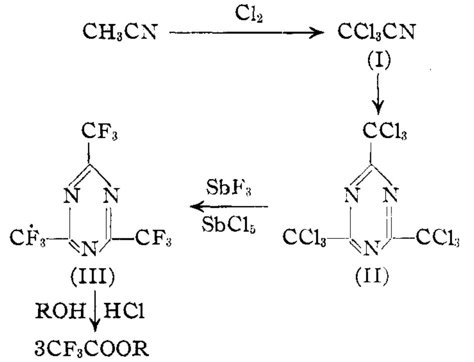
[8] K. Dachlauer, German Patent 682,391 (Oct. 13, 1939).

[9] K. Dachlauer, German Patent 699,493 (Nov. 30, 1940).

[10] M. A. Kunz, *et al.*, U. S. Patent 1,989,042 (Jan. 22, 1935).

trifluoride containing 30% pentavalent antimony works quite well at atmospheric pressure to give the completely fluorinated product in good yields.

Either the esters of trifluoroacetic acid or the trifluoroacetic acid itself can be obtained directly from the 2,4,6-tris-(trifluoromethyl)-1,3,5-triazine. If the ester is desired, the triazine, alcohol and dilute mineral acid are refluxed in a fractionating column, the ester being removed as an azeotrope with water as rapidly as it is formed. The total synthesis may be summarized by the equations



Experimental

2,4,6-Tris-(trichloromethyl)-1,3,5-triazine (II). (a) **Reaction Under Pressure.**—In a steel bomb of 200-cc. capacity was placed 143 g. (0.99 mole) of dry trichloroacetonitrile and 10 g. (0.075 mole) of powdered anhydrous aluminum chloride. The bomb was connected to a cylinder of anhydrous hydrogen chloride and the cylinder valve opened for thirty seconds, while cooling the bomb to absorb the heat of solution. The amount of hydrogen chloride added was 27 g. (0.74 mole). The bomb was rotated for five hours with cooling to maintain the temperature below 75°. At the end of the time the bomb was opened to release hydrogen chloride. It was then heated to melt out the solid contents, and the latter were discharged into one liter of hot water. The aqueous mixture was stirred vigorously, then allowed to cool. The aqueous layer was decanted from the solid product. After being dried in air, it weighed 132 g. (92.5% yield), m. p. 90–92°. After recrystallization from ethanol the product melted at 95–96°.

(b) **Reaction at Atmospheric Pressure.**—Into a 3-liter Erlenmeyer flask was placed 1430 g. (9.9 moles) of dry trichloroacetonitrile and 25 g. (0.094 mole) of anhydrous aluminum bromide, with gentle warming to dissolve the aluminum bromide quickly. The solution was then saturated with dry hydrogen chloride at 25° (cooling was necessary). The flask was placed in a cool water-bath, and the contents gradually increased in temperature to a maximum of 65° after about three hours, at which time the mass solidified. An equal volume of boiling water was then added to the contents of the flask, which was immersed in a steam-bath to melt the solid product. The mixture was stirred vigorously and then cooled to allow the product to solidify again. The water was decanted and the product was recrystallized from ethanol. The yield of trimer was 95%, with a melting point of 93–95°.

Fluorination of (II).—Into a 5-l., 3-neck flask was placed 3.54 kg. (19.8 moles) of anhydrous antimony trifluoride and 468 g. (2.05 moles) of anhydrous antimony trichloride. A stream of chlorine was passed into the mixture heated to about 150° until 454 g. (6.4 moles) of chlorine had been absorbed. The flask holding the fluorinating mixture was then fitted with a water condenser, thermometer, and a ground-in glass stopper and heated with a Glas-Col mantle. A total of 2220 g. (5.12 moles) of dry 2,4,6-tris-(trichloromethyl)-1,3,5-triazine was added in portions of 100, 100, 200, 200, 400, 400, 400, 420 g., with one-half hour separating each addition with just enough heat to cause gentle refluxing. After all of the trimer had been added and the mixture refluxed for an additional two hours, the condenser was replaced with an 11-tray, 25-mm. fractionating column of the sieve-tray type fitted with a liquid-dividing head. The 2,4,6-tris-(trifluoromethyl)-1,3,5-triazine was taken overhead at 98° as rapidly as it was formed. This required about eight hours. The product weighed 1317 g. (90% yield).

Ethyl Trifluoroacetate.—A 50-l., r.-b., pyrex flask was equipped with a 3-in., 20-tray sieve-tray column surmounted by a liquid-dividing head equipped with an automatic reflux ratio timer and three 9-bulb condensers in parallel.[11] The pot was charged with 5.36 kg. (18.8 moles) of 2,4,6-tris-(trifluoromethyl)-1,3,5-triazine, 6.40 l. (110 moles) of 95% ethanol, 8.80 l. (90 moles) of 32% hydrochloric acid and 7.0 l. of water. The mixture was heated to boiling by means of a Glas-Col mantle, and within a few minutes the head temperature dropped to 52.5°. Approximately seven l. of ester azeotrope distilled at 52.5° using a reflux ratio of 3/1. The cut was made at 56° with the reflux ratio increased to 10/1, and the material (about 500 cc.) boiling from 56 to 76° was added to the next charge. The 7.0 l. of azeotrope and 2.5 l. of concd. sulfuric acid were cooled separately to about 5°. They were then poured together into a 12-l., r.-b. flask and thoroughly stirred. The flask was fitted with an 11-tray, 25-mm. sieve-tray column (used merely to remove entrained sulfuric acid). There was no forerun. All of the material boiled at 61.8° giving 7.41 kg. (92.5% yield) of pure dry ethyl trifluoroacetate.

Anal. Calcd. for $C_4H_5F_3O_2$: sapn. equiv., 142.1; F, 40.1. Found: sapn. equiv., 142.1; F, 39.8.

n-Propyl trifluoroacetate was prepared by a similar method in 88.5% yields. It showed the following physical properties: b. p. 82.5°, sp. gr. 25/25 1.1285, $n^{22.5}\text{D}$ 1.3233.

Anal. Calcd. for $C_5H_7F_3O_2$: sapn. equiv., 156.2; F, 36.5. Found: sapn. equiv., 156.2; F, 36.7.

i-Propyl trifluoroacetate was prepared in 79.5% yields. It showed the following physical properties: b. p. 73.5°, sp. gr. 25/25 1.1077, $n^{24}\text{D}$ 1.3165.

Anal. Calcd. for $C_5H_7F_3O_2$: sapn. equiv., 156.2. Found: sapn. equiv., 156.9.

Trifluoroacetic Acid.—To 80 g. (2.0 moles) of sodium hydroxide dissolved in 300 cc. of water heated to *ca.* 90° was gradually added 284 g. (2.0 moles) of ethyl trifluoroacetate (or an equivalent amount of ethyl trifluoroacetate–water azeotrope). The addition required about thirty minutes. The mixture was refluxed and stirred for an additional thirty minutes. The clear solution was evaporated to dryness to give a quantitative yield of sodium trifluoroacetate. The powdered sodium salt was added with stirring and cooling to *ca.* 600 g. of concd. sulfuric acid. By simple distillation a 91% yield of anhydrous trifluoroacetic acid, b. p. 72–74°, was obtained.

Summary

Trifluoroacetic acid and its ethyl, propyl and isopropyl esters have been prepared by a new method. The isolated intermediates are trichloroacetonitrile, 2,4,6-tris-(trichloromethyl)-1,3,5-triazine, and 2,4,6-tris-(trifluoromethyl)-1,3,5-triazine.

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[11] This equipment is manufactured by Glass Engineering Laboratories, Belmont, California.