58–126° and 117 g. of recovered starting silanes. The 58–126° product was treated with bromine (12 g.) to remove ethynyltrichlorosilane. Redistillation of the material boiling below 95° gave 5 g. of silicon tetrachloride, b.p. 58–62°, d^{25} 1.47, 82.5% active chlorine, an intermediate cut, and 4 g. of trichlorobromosilane,[8] b.p. 80–85°, d^{25} 1.82, active chlorine 64.4%.

Pyrolysis of Tribromoethylene and Trichlorosilane.—A mixture of tribromoethylene (26 g.) and trichlorosilane (34 g.) was pyrolyzed at 470° during 110 min. The distillations of the 45 g. of product gave 6.9 g. of product believed to be bromoethynyltrichlorosilane, b.p. 76–80° (11 mm.), $n^{25}\text{D}$ 1.5240.

Anal. Calcd. for $C_2SiBrCl_3$: 3 active Cl, 44.5; Si, 11.7; total halogen (as chlorine), 59.6. Found: 3 active Cl, 44.8; Si, 11.7; total halogen (as chlorine), 59.9.

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[Contribution from the Department of Chemistry of Purdue University]

The Bromination of 1,1,1-Trifluoropropanone[1]

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The direct bromination of 1,1,1-trifluoropropanone was investigated using both acid and base catalysis. The preparation of 3-bromo-1,1,1-trifluoropropanone and of 3,3-dibromo-1,1,1-trifluoropropanone was more successful using acid catalysis, the compounds being prepared in better yield and in higher purity than when prepared by the base-catalyzed bromination. Although 1,1,1-tribromo-3,3,3-trifluoropropanone was obtained by an acid-catalyzed bromination, the compound was prepared more quickly and in better yield by the base-catalyzed bromination of 1,1,1-trifluoropropanone or its partially brominated derivatives.

Discussion

Swarts first prepared 1,1,1-trifluoropropanone by the acid cleavage of either trifluoroacetoacetic acid[2] or its ethyl ester.[3] In attempting to determine the degree of enolization of 1,1,1-trifluoropropanone, Swarts found that it was singularly unreactive toward bromine. Other attempts to halogenate this ketone directly also failed,[4,5] though the preparation of 3-chloro-1,1,1-trifluoropropanone was achieved indirectly by the prolonged chlorination of ethyl trifluoroacetoacetate and then cleavage of the resulting ester with acid.[4] Recently, Henne and Mentcher[5] reported that they had been successful in brominating 1,1,1-trifluoropropanone directly by making use of the basic properties of sodium acetate.

When an attempt was made in this Laboratory to synthesize 3-bromo-1,1,1-trifluoropropanone by the bromination of the parent ketone in the presence of sodium acetate in acetic acid as solvent, it was found to be extremely difficult to obtain the product either pure or in good yield. Since bromination took place with great ease, it was concluded that the principal difficulty involved the separation of a mixture of brominated ketones from the acetic acid. By using higher-boiling acids as solvents and their corresponding salts as basic catalysts, it was found to be easier to effect this separation, but the yields of individual ketones remained small.

In the generally accepted mechanism for the bromination of ketones in the presence of a base such as hydroxyl or acetate ion, the ketone gives up a proton to the base to form the enolate ion.[6] This ion reacts practically instantaneously with bromine to form a brominated ketone. With the very strongly electronegative trifluoromethyl group present, 1,1,1-trifluoropropanone would be unusually acidic for a ketone, as Swarts[7] indeed found to be true, and in the presence of a suitable base, such as the acetate ion, should readily give up a proton to form the corresponding enolate ion, which in turn would react with bromine present in the solution to form 3-bromo-1,1,1-trifluoropropanone. The presence of the electronegative bromine atom should make 3-bromo-1,1,1-trifluoropropanone more acidic than the unbrominated ketone and the mono- and dibrominated ketones should form the enolate ion more readily than trifluoroacetone itself. Thus, the base-catalyzed reaction would be expected to produce the tribrominated ketone in good yield, but it could hardly be expected to produce the other two ketones in satisfactory yields, as was found in practice to be the case.

In the halogenation of acetone, the effect of each halogen introduced on the subsequent ionization of the alpha hydrogen is apparently so large that the sole product formed appears to be the trihalo derivative.[8] In the case of 1,1,1-trifluoroacetone we were successful in isolating yields of the monobromo derivative as high as 32.6%. Apparently in acetone each halogen substituent must have a far greater effect upon the rate of ionization of the alpha hydrogen than is the case in 1,1,1-trifluoroacetone itself.

The difficulties encountered in the synthesis of the monobromo compound by the base-catalyzed reaction led us to examine other methods. Consideration of the mechanism of halogenation under acidic conditions suggested that in the presence of strong acids the reaction might be more easily controlled. In acid catalysis, the fundamental step appears to be the conversion of the ketone into a conjugate acid in which the newly introduced positive electrical field facilitates the removal of a proton by some base too weak in itself to induce rapid ionization of the original ketone. It follows

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(1) This paper contains material abstracted from the thesis of Theodore M. Burton submitted to the faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1951.

(2) F. Swarts, *Bull. sci. acad. roy. Belg.*, [5] **12**, 679 (1926); *Bull. soc. chim. Belg.*, **36**, 313 (1927).

(3) F. Swarts, *Bull. sci. acad. roy. Belg.*, [5] **12**, 692 (1926); *Bull. soc. chim. Belg.*, **36**, 323 (1927).

(4) H. M. Hill, E. B. Towne and J. B. Dickey, This Journal, **72**, 3289 (1950).

(5) A. L. Henne and L. Mentcher, Abstr. of Papers, 118th Meeting, A.C.S., Chicago, Illinois, September, 1950, p. 10 L.

(6) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 97.

(7) F. Swarts, *Bull. soc. chim. Belg.*, **38**, 99 (1929).

(8) P. D. Bartlett, This Journal, **56**, 967 (1934).

TABLE I

PHYSICAL PROPERTIES

Compound	B.p., °C.	Mm.	F.p., ° C.	d^{20}_{20}	n^{20}_D	Molecular refractivity Calcd.[a]	Found[b]	Exaltation
CF_3COCH_2Br	86.6	743.1	< -80	1.8389	1.3750	23.59	23.77	+0.18
$CF_3COCHBr_2$	113.3–113.4	735.5	< -51.0	2.1880	1.4311	31.36	31.93	+0.57
CF_3COCBr_3	69.8–69.9	47	< -39.5	2.4751	1.4785	39.12	39.98	+0.80

[a] Calculated from Eisenlohr values. [b] Observed from Lorentz–Lorenz equation.

that a very strong acid would be required to convert the weak base, 1,1,1-trifluoropropanone, into its conjugate acid.

Since the product, 3-bromo-1,1,1-trifluoropropanone, should be an even weaker base than the original ketone, conversion of the monobromo compound to its conjugate acid should proceed with even greater difficulty. Therefore the bromination of 1,1,1-trifluoropropanone under conditions of controlled acidity offered promise as a means of synthesizing the desired bromo derivatives in high yield.

Accordingly, the bromination of 1,1,1-trifluoropropanone was studied in concentrated sulfuric acid as solvent. Under these conditions the bromination proceeded easily and smoothly—either one or two bromine atoms could be introduced at will to form either the 3-bromo- or the 3,3-dibromo-1,1,1-trifluoropropanone.

A third atom of bromine could not be introduced under these conditions. Evidently, concentrated sulfuric acid is not sufficiently strong to convert the 3,3-dibromo-1,1,1-trifluoropropanone into its conjugate acid. However, the use of anhydrous perchloric acid in acetic acid permitted the conversion of the dibromo ketone to 1,1,1-tribromo-3,3,3-trifluoropropanone. Hence, it follows that the bromination of 1,1,1-trifluoropropanone in the presence of strong acids provides a convenient practical procedure for the preparation of all of the pure bromo derivatives, in contrast to the base-catalyzed reaction which is satisfactory only for the tribromo compound.

It is of interest to point out that the ease of bromination of ketones under acidic conditions correlates well with the basic properties of the ketone. Thus in the case of acetophenone it was observed that a methyl substituent increased both the base strength and the rate of halogenation, whereas a bromine substituent decreased these quantities.[9] Indeed, an examination of the data indicates a simple linear relationship between the two quantities. In the present work the observed ease of halogenation under acidic conditions, $CF_3COCH_3 > CF_3COCH_2Br > CF_3COCHBr_2$, also correlates well with the predicted order of base strengths.

In the bromination reaction only half-molar quantities of bromine are necessary to produce a mole of 3-bromo-1,1,1-trifluoropropanone. Sulfur dioxide was the only gas observed to escape from the reaction mixture. This phenomenon is readily explained by the reaction

$$2HBr + H_2SO_4 \rightleftarrows Br_2 + 2H_2O + SO_2 \qquad (1)$$

The ketone conjugate acid takes up the bromine as fast as it is produced and hence the oxidation of the hydrogen bromide by the sulfuric acid goes to completion.

Krohnke[10] working with monobromoketones found that hydrogen bromide catalyzed the disproportionation of the ketone as shown

$$2RCOCH_2Br \overset{HBr}{\rightleftarrows} RCOCH_3 + RCOCHBr_2$$

Such disproportionation is not catalyzed by sulfuric acid for it was not possible to detect any 1,1,1-trifluoropropanone or 3,3-dibromo-1,1,1-trifluoropropanone following the treatment of 3-bromo-1,1,1-trifluoropropanone with sulfuric acid. This combined with the fact that hydrogen bromide is removed as formed and that trifluoropropanone forms a conjugate acid more readily than the brominated compound presumably account for the excellent yield of 3-bromo-1,1,1-trifluoropropanone.

The physical properties of the brominated ketones are listed in Table I.

Experimental[11]

1,1,1-Trifluoropropanone.—This compound was prepared following the original method of Swarts[2,3] as modified by Milde.[12] The crude ketone was rectified from phosphorus pentoxide in a 26.5-plate, 10-mm., 48" column packed with 1/8" Pyrex glass helices to give an 84.5% yield of pure material, b.p. 21–23° (737.5 mm.). The semicarbazone of 1,1,1-trifluoropropanone was found to melt at 129–130° and the 2,4-dinitrophenylhydrazone melted at 141–142°. An attempt was made to prepare this ketone from trifluoroacetyl chloride[13] and dimethylcadmium following the method suggested by Cason[14] for the preparation of methyl ketones. No 1,1,1-trifluoropropanone could be isolated from the reaction mixture.

3-Bromo-1,1,1-trifluoropropanone. (a) **Base-catalyzed Preparation.**—A mixture of 1.01 moles of 1,1,1-trifluoropropanone in a clear solution of 1.0 mole of anhydrous sodium acetate in 620 g. of glacial acetic acid was brominated by slowly stirring in a mixture of 1 mole of bromine in 100 g. glacial acetic acid over a period of 6 hours at room temperature. The resulting mixture was filtered with suction through a fritted-glass funnel to yield a clear, orange-colored solution. Though separation was difficult, repeated rectification through the 26.5-plate, all-glass column produced 28.2 g. (19.2%) of 3-bromo-1,1,1-trifluoropropanone, b.p. 84.7° (743.8 mm.). The ketone was prepared in a similar procedure using propionic acid as solvent and sodium benzoate as base in 32.6% yield.

(b) **Acid-catalyzed Preparation.**—A solution was made by stirring 210.4 g. (1.872 moles) of 1,1,1-trifluoropropanone into 500 ml. of concentrated sulfuric acid using an all-glass

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(9) L. Zucker and L. P. Hammett, THIS JOURNAL, **61**, 2785 (1939).

(10) F. Krohnke, *Ber.*, **69B**, 921 (1936).

(11) All temperatures reported are corrected. Carbon and hydrogen analyses were made by the Galbraith Microanalytical Laboratories, Knoxville, Tenn. Bromine analyses were made by the Clark Microanalytical Laboratory, Urbana, Ill. Nitrogen analyses were made by Miss Helen D'Agostino at Purdue University. Density determinations were made by Mrs. Margaret Turner at Purdue University.

(12) R. L. Milde, "Some Syntheses from Trifluoroacetone," Ph.D. Thesis, Purdue University, June, 1949, p. 79.

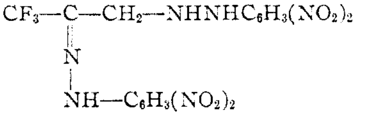
(13) R. G. Jones, THIS JOURNAL, **70**, 143 (1948); A. L. Henne, R. M. Alm and M. Smook, *ibid.*, **70**, 1968 (1948).

(14) J. Cason, *Chem. Revs.*, **40**, 15 (1947).

apparatus. A quantity of 150 g. (0.936 mole) of bromine was then gradually stirred into the solution over a period of about 2 hours at room temperature. A Dry Ice cooled condenser was used to prevent the liberated sulfur dioxide from sweeping the low-boiling ketone out of the solution. The insoluble 3-bromo-1,1,1-trifluoropropanone was separated from the heavier sulfuric acid layer and the latter stripped of volatile components in the 26.5-plate, all-glass column. All material boiling up to 90° was added to the ketone fraction, and the combined products were then rectified in the same column to produce 279.2 g. (79.9%) of 3-bromo-1,1,1-trifluoropropanone, b.p. 85.0–86.8°. In a somewhat larger preparation utilizing 5 moles of 1,1,1-trifluoropropanone, a yield of 87.6% of product was obtained. The fore-run was 1,1,1-trifluoropropanone and the pot residue was 3,3-dibromo-1,1,1-trifluoropropanone. 3-Bromo-1,1,1-trifluoropropanone is a colorless liquid, soluble in water and organic solvents. It is a powerful lachrymator and lung irritant and shows vesicant action in contact with the skin.

Anal. Calcd. for $C_3H_2F_3BrO$: C, 18.87; H, 1.06; Br, 41.85. Found: C, 18.78, 18.73; H, 1.29, 1.25; Br, 41.67, 41.91.

With 2,4-dinitrophenylhydrazine, the ketone formed a complex hydrazone,



$$\begin{array}{ll} CF_3- & C-CH_2-NHNHC_6H_3(NO_2)_2 \\ & \| \\ & N \\ & | \\ & NH-C_6H_3(NO_2)_2 \end{array}$$

of bright-yellow needles from ethyl acetate, m.p. 230° (dec.).

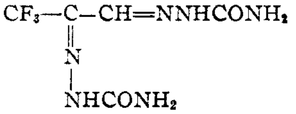
Anal. Calcd. for $C_{15}H_{11}F_3N_8O_8$: C, 36.89; H, 2.27; N, 22.95. Found: C, 37.22, 37.22; H, 2.28, 2.44; N, 22.91, 23.00.

3,3-Dibromo-1,1,1-trifluoropropanone.—This ketone was obtained in small yields from higher-boiling residues of the base-catalyzed preparation of 3-bromo-1,1,1-trifluoropropanone, but was found to be almost impossible to purify by rectification since the ketone and solvent boil so close together. The solvent can be removed from the ketone with concentrated sulfuric acid in which the 3,3-dibromo-1,1,1-trifluoropropanone is insoluble. A more convenient preparation was found in the acid-catalyzed bromination of 1,1,1-trifluoropropanone in concentrated sulfuric acid.

A solution was made by stirring 97.8 g. (0.873 mole) of 1,1,1-trifluoropropanone into 500 ml. of concentrated sulfuric acid using an all-glass apparatus. One mole (160 g.) of bromine was added slowly with stirring at room temperature. The mixture stood overnight and then was refluxed briefly, but the excess bromine failed to react. The heavier ketone layer was separated from the sulfuric acid layer, the latter stripped of volatile components in the 26.5-plate, all-glass column and all low-boiling material up to 125° added to the ketone layer. The ketone layer was then rectified in the same column with bromine as the fore-run. The principal fraction weighed 97.8 g. (86.9%), b. p. 111-113°. The 3,3-dibromo-1,1,1-trifluoropropanone was rerectified in the 26.5-plate, all-glass column and rectified at reduced pressure in a 100-plate, 8 mm., 24" Miniature Podbielniak column with Hastelloy-B packing. The pure ketone is a colorless liquid, soluble in water and organic solvents. It is a strong lachrymator and lung irritant and shows vesicant action in contact with the skin.

Anal. Calcd. for $C_3HF_3Br_2O$: C, 13.35; H, 0.37; Br, 59.23. Found: C, 13.45, 13.41; H, 0.51, 0.48; Br, 58.92, 58.64.

The semicarbazone from ethanol/water was a white, crystalline solid, m.p. 218° (dec.).



$$\begin{array}{ll} CF_3- & C-CH=NNHCONH_2 \\ & \| \\ & N \\ & | \\ & NHCONH_2 \end{array}$$

Anal. Calcd. for $C_5H_7F_3N_6O_2$: C, 25.00; H, 2.94; N, 35.00. Found: C, 25.07, 24.87; H, 3.04, 2.96; N, 34.85, 34.91.

1,1,1-Tribromo-3,3,3-trifluoropropanone.—This ketone was prepared readily by base-catalyzed bromination in organic acids as solvents. Using 90 g. (0.33 mole) of 3,3-dibromo-1,1,1-trifluoropropanone with 30 g. (0.33 mole + 10%) anhydrous sodium acetate, 250 ml. of glacial acetic acid and 58.6 g. (0.33 mole + 10%) of bromine, bromination proceeded readily at room temperature. The solid sodium bromide was filtered off, the clear filtrate dissolved in 450 ml. of concd. sulfuric acid in the cold, centrifuged at 2400 r.p.m. and the denser ketone separated. The crude ketone was rectified in the 26.5-plate, all-glass column at reduced pressure to yield 94.3 g. (81.1%) of 1,1,1-tribromo-3,3,3-trifluoropropanone.

The ketone was also prepared using sodium propionate as a base in propionic acid and using sodium butyrate as base in butyric acid as solvent to produce a 96.5% yield of crude ketone. An attempt to prepare the ketone by bromination of 3,3-dibromo-1,1,1-trifluoropropanone using sodium benzoate as base in diethylene glycol as solvent produced a 63% yield of bromoform, but no ketone.

The 1,1,1-tribromo-3,3,3-trifluoropropanone was purified by extraction of the organic acids with concentrated sulfuric acid in the cold, the ketone being insoluble in that reagent. The ketone was then rerectified at reduced pressure in the 26.5-plate, all-glass column. The ketone is a colorless liquid of slight lachrymatory action and an odor resembling that of bromoform, though somewhat acrid.

Anal. Calcd. for $C_3F_3Br_3O$: C, 10.33; H, 0.00; Br, 68.74. Found: C, 10.15, 10.31; H, 0.04, 0.00; Br, 68.07, 68.06.

The shape of the freezing point curve showed the sample to be of good purity. It was found impossible to prepare a 2,4-dinitrophenylhydrazone. An attempt to form the semicarbazone produced instead a good yield of bromoform. On heating the ketone with freshly distilled aniline, bromoform and trifluoroacetanilide were formed. The latter compound is a solid and was recrystallized several times from an ethanol/water mixture to produce pearly white plates, m.p. 88–89°. The ketone readily forms a solid hydrate with water, m.p. 43–46°, which was not investigated further.

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