ture and the 1,1-dichloro-1,2-dibromoethane[8] distilled at 175–177° dec., $n^{23}\text{D}$ 1.5554.

Pyrolysis of Acetylene and Trichlorosilane.—Cylinder acetylene, washed and dried, was bubbled (1″ head) through trichlorosilane (40 g.) during 6 hr. and the gas mixture passed into the furnace at 610° to give a recovery of 23 g. Distillation gave some recovered trichlorosilane, 4.7 g. of vinyltrichlorosilane, b.p. 86–89°, active chlorine 64.8%, d^{25} 1.23, and 2.8 g. of more complex silanes boiling at 180–217°.

Pyrolysis of *s*-Dichloroethylene and Trichlorosilane.—A mixture of *trans*-dichloroethylene (42 g.) and trichlorosilane (54 g.) was pyrolyzed at 610° during 600 min. to give 80 g. of product. Distillation through a 12″ packed column gave 36 g. of recovered charge, b.p. 35–60°, an intermediate cut, and the product, β-chlorovinyltrichlorosilane (19.9 g.) b.p. 133–135° (738 mm.), $n^{20}\text{D}$ 1.4735, d^{22} 1.45.

Anal. Calcd. for $C_2H_2SiCl_4$: 3 active Cl, 54.2; Si, 14.3. Found: 3 active Cl, 53.3; Si, 13.6.

The above product (14.5 g.) was treated with bromine (12.3 g.) dropwise at room temperature. Distillation gave α,β-dibromo-β-chloroethyltrichlorosilane, b.p. 131–133° (10 mm.) (22.2 g.).

Anal. Calcd. for $C_2H_2SiCl_4Br_2$: 4 active Cl, 39.9. Found: 4 active Cl, 41.2.

This brominated silane (22 g.) was hydrolyzed by shaking in about 50 cc. of cold water, and then excess base was added. Distillation gave a lower layer which weighed 6.4 g. after drying, and was accompanied by flashes of flame. Distillation gave 3.0 g. of 1-chloro-2-bromoethylene,[9] b.p. 80–85°, d^{20} 1.8, $n^{22}\text{D}$ 1.4956.

Similarly, *cis*-dichloroethylene (22 g.) and trichlorosilane (30 g.) at 610° gave 13.7 g. of β-chlorovinyltrichlorosilane, b.p. 132–134° (707 mm.). Bromination gave the same product as above and side chain cleavage with alkali also gave 1-chloro-2-bromoethylene, b.p. 80–85° (1.8 g.), $n^{23}\text{D}$ 1.4955, d^{20} 1.8.

Pyrolysis of Vinylidene Chloride and Trichlorosilane.—A mixture of vinylidene chloride (34 g.) and trichlorosilane (46 g.) was passed through the furnace at 550° during 100 min. to give 62 g. of product. Distillation gave 48 g. of recovered charge, b.p. 31–35°, an intermediate cut, and a product cut, presumably α- or β-chlorovinyltrichlorosilane, b.p. 115–135° (4.7 g.). Redistillation gave 2.7 g. of product, b.p. 59–63° (63 mm.), $n^{23}\text{D}$ 1.4610.

Anal. Calcd. for $C_2H_2SiCl_4$: 3 active Cl, 54.4; Si, 14.3. Found: 3 active Cl, 54.9; Si, 13.9.

NORTHFIELD, MINNESOTA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ST. OLAF COLLEGE[1]]

Observations on Certain Silanes Containing Bromine in Side Chains

BY COURTLAND L. AGRE AND WALLACE HILLING

RECEIVED JANUARY 10, 1951

Vinyltrichlorosilane readily adds bromine to give α,β-dibromoethyltrichlorosilane. Pyrolysis of this silane is complex and among the products formed are silicon tetrachloride, trichlorobromosilane, α- and β-bromovinyltrichlorosilanes and ethynyltrichlorosilane. The obtainment of silicon tetrachloride is unexpected for trichlorobromosilane only would be expected. Removal of hydrogen bromide from α,β-dibromoethyltrichlorosilane by treatment with quinoline gives α-bromovinyltrichlorosilane and silicon tetrachloride. Various transformations of the silanes encountered are described as their structures are determined mainly by side chain cleavage by alkali. Brief mention is made of the pyrolysis of a mixture of tribromoethylene and trichlorosilane.

Many examples have appeared recently showing that halogen atoms in the side chains of substituted trichlorosilanes encourage side chain cleavage with the net result that a halogen atom from the chain seemingly has become attached to the silicon atom. This research deals with the reactions which are encountered when bromine is present in the side chain, as in α,β-dibromoethyltrichlorosilane.

Hurd[2] treated α- and β-chloroethyltrichlorosilanes with quinoline to prepare vinyltrichlorosilane and obtained also a small amount of silicon tetrachloride. The reaction presumably progressed qualitatively as expressed in the equation

$$ClCH_2CH_2SiCl_3 \xrightarrow{\text{Quinoline}} CH_2{=}CH_2 + SiCl_4 + CH_2{=}CHSiCl_3 + HCl \quad (1)$$

Sommer, Bailey and Whitmore[3] later observed similar results on other silanes when cleavage was effected by heat, aluminum chloride or methylmagnesium bromide—in these reactions it was postulated that the reaction proceeded through the formation of β-carbonium ions. Like Hurd, these authors also observed that silicon tetrachloride accompanied the vinyltrichlorosilane in the dehydrochlorination by quinoline of pure β-chloroethyltrichlorosilane. The preponderance of dehydrohalogenation relative to β-elimination (to give silicon tetrachloride) is suggested to be due to the inability of the quinoline to provide a nucleophilic anion and also to the formation of quinoline hydrochloride. Parallel reactions with other substituted silanes were observed by Sommer, Tyler and Whitmore,[4] and by Gold, Sommer and Whitmore.[5]

By similar reasoning, it would be expected that α,β-dibromoethyltrichlorosilane (II), for example, would decompose thermally to give vinyl bromide and trichlorobromosilane by β-elimination, and a bromovinyltrichlorosilane and hydrogen bromide by quinoline dehydrohalogenation. Actually, in the pyrolysis of this silane, dehydrobromination to give some ethynyltrichlorosilane and a mixture of α- and β-bromovinyltrichlorosilanes is encountered to a major extent. Accompanying this reaction, however, is a side reaction in which silicon tetrachloride and trichlorobromosilane are both obtained. Another complex reaction was encountered in the dehydrohalogenation of II with quinoline for accompanying the α-bromovinyltrichlorosilane was an appreciable amount of silicon tetrachloride. Other similar examples are shown in the flow sheet.

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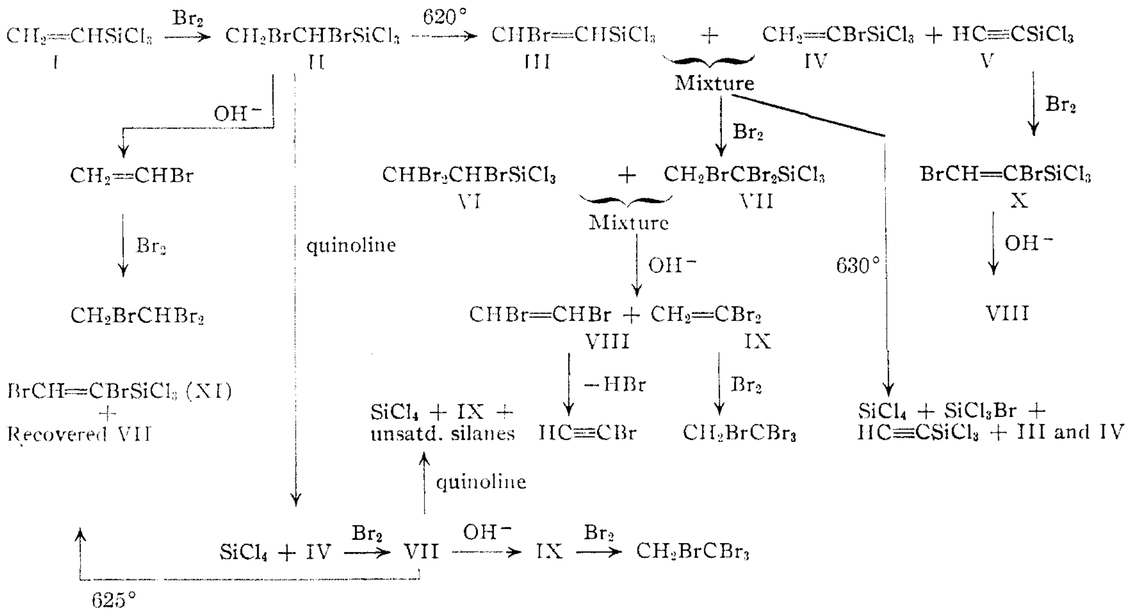
[1] This research was conducted under Contract N8 onr 73700 of the Office of Naval Research.

[2] D. T. Hurd, THIS JOURNAL, **67**, 1813 (1945).

[3] L. H. Sommer, D. L. Bailey and F. C. Whitmore, *ibid.*, **70**, 2869 (1948).

[4] L. H. Sommer, L. J. Tyler and F. C. Whitmore, *ibid.*, **70**, 2872 (1948).

[5] J. R. Gold, L. H. Sommer and F. C. Whitmore, *ibid.*, **70**, 2874 (1948).



Vinyltrichlorosilane I adds bromine readily to give α,β-dibromoethyltrichlorosilane (II). This addition is quite different from the observation of Sommer, Tyler and Whitmore[4] who reported cleavage of the product in the addition of bromine to allyltrimethylsilane. Side chain cleavage of II by excess alkali gives vinyl bromide, identified by the addition of bromine to give 1,1,2-tribromoethane.

Pyrolysis of II gave a complex mixture which was identified, at least in part, as an unsaturated gas (not identified), silicon tetrachloride, trichlorobromosilane, ethynyltrichlorosilane (V), and a mixture of α-bromovinyltrichlorosilane (IV) and β-bromovinyltrichlorosilane (III), and a small amount of recovered II. That a mixture of III and IV was obtained is indicated by the addition of bromine to give a mixture presumed to be α,β,β-tribromoethyltrichlorosilane (VI) and α,α,β-tribromoethyltrichlorosilane (VII). This mixture on treatment with excess alkali gave vinylidene bromide IX, identified as such and also as 1,1,1,2-tetrabromoethane. *s*-Dibromoethylene (VIII) was not isolated but its transitory presence was very strongly indicated by the frequent flashes so characteristic of the bromoacetylene obtained by dehydrobromination of VIII. The inherent thermal instability of III and IV apparently allowed further loss of hydrogen bromide to give ethynyltrichlorosilane (V), which reaction was observed also during a separate pyrolysis of a mixture of III and IV. Ethynyltrichlorosilane (V) was not separated from silicon tetrachloride and trichlorobromosilane as a pure compound because of the proximity of their boiling points but was removed by conversion into α,β-dibromovinyltrichlorosilane (X), at which point bromine addition to V apparently stopped. Distillation then allowed the isolation of small quantities of silicon tetrachloride and trichlorobromosilane. Silane X was identified by the customary side chain cleavage to give *s*-dibromoethylene instead of tribromoethylene which would have been expected had bromination of V given α,α,β,β-tetrabromoethyltrichlorosilane.

Treatment of II with quinoline gave exclusively α-bromovinyltrichlorosilane (IV) (so far as could be determined), silicon tetrachloride and no trichlorobromosilane. No gaseous by-product was observed. Addition of bromine to IV gave α,α,β-tribromoethyltrichlorosilane (VII). The structure of VII was indicated by cleavage to vinylidene bromide. Pyrolysis at 625° showed that VII is relatively stable for a considerable portion was recovered together with a silicon halide and an unsaturated silane believed to be XI. In the pyrolysis of VII, free bromine appeared to be liberated as indicated by the brown vapors at the exit of the furnace, but almost immediately this bromine disappeared and probably added to part of the newly formed unsaturated silane to give VII. This behavior of the silane VII is significantly different from the chlorine analog for with α,α,β-trichloroethyltrichlorosilane[6] essentially complete pyrolytic destruction was encountered.

Treatment of VII with quinoline gave an unsaturated silane (not identified), vinylidene bromide and silicon tetrachloride. It is surprising that silicon tetrachloride was obtained in these reactions for the product of necessity would be trichlorobromosilane if the fourth halogen atom were obtained from the side chain. Pyrolysis and also treatment with quinoline of vinyltrichlorosilane and of ethyltrichlorosilane gave nearly complete recovery of the starting silanes,[6] so halogen in the side chain definitely is necessary to give the complex reactions encountered in these examples.

It is realized that the results observed do not present all the observations required to explain the atypical formation of silicon tetrachloride. It is reasonable to assume that the trichlorobromosilane first formed disproportionates to give silicon tetrachloride. The quinoline dehydrobromination of II to give IV occurs in a directed manner since no isomer was observed. Pyrolysis of II was more complex than the dehydrobromination for a greater

(6) C. I. Agre and Wallace Hilling, THIS JOURNAL, **74**, 3895 (1952).

distribution of products was encountered, in part parallel to the chlorine analogs.[6]

In manner similar to the high temperature reaction of trichloroethylene and trichlorosilane,[6] a mixture of tribromoethylene and trichlorosilane might be expected to give β,β-dibromovinyltrichlorosilane (XIII), which could lose a molecule of hydrogen bromide to yield bromoethynyltrichlorosilane XIV according to the equation

$$\mathrm{Br_2CH{=}CHBr} + \mathrm{HSiCl_3} \xrightarrow[-\mathrm{HBr}]{\Delta}$$

$$\underset{\mathrm{XIII}}{\mathrm{Br_2C{=}CHSiCl_3}} \xrightarrow{-\mathrm{HBr}} \underset{\mathrm{XIV}}{\mathrm{BrC{\equiv}CSiCl_3}}$$

α,β,β-Tribromoethyltrichlorosilane (VI) possibly could be an intermediate addition product but, parallel to previous considerations,[6] quite likely is not formed in the pyrolysis. Actual pyrolysis of a mixture of tribromoethylene and trichlorosilane gave a silane indicated by analysis to be XIV, although its identity has not definitely been established.

Experimental

α,β-Dibromoethyltrichlorosilane.—Vinyltrichlorosilane (275 g.) was placed in a 500-cc. flask cooled by water and irradiated by a 150-watt lamp. Bromine (266 g.) was added during 160 min. at a maximum temperature of about 50°. Distillation through a 500-cc. claisen flask gave 500 g. (91%) of α,β-dibromoethyltrichlorosilane (II), b.p. 91° (11 mm.), 101° (18 mm.), 140° (70 mm.), 215° (735 mm.), $n^{20}\mathrm{D}$ 1.5370, d^{21} 2.05.

Anal. Calcd. for $C_2H_3SiCl_3Br_2$: 4 active Cl, 44.2; Si, 8.75. Found: 4 active Cl, 44.2; Si, 9.0.

Side Chain Cleavage of α,β-Dibromoethyltrichlorosilane.—α,β-Dibromoethyltrichlorosilane (15 g.) was added to 20 cc. of cold water and then excess sodium hydroxide was added to keep gas evolution quite constant. The vinyl bromide was passed into bromine in carbon tetrachloride. Distillation gave 1,1,2-tribromoethane,[7] b.p. 187–190° (721 mm.) (8 g.), d^{20} 2.58, $n^{20}\mathrm{D}$ 1.5890.

Pyrolysis of α,β-Dibromoethyltrichlorosilane.—The silane (372 g.) was pyrolyzed at 620° during 11 hr. to give 264 g. of dark liquid. Traps in an ice-bath failed to remove any low boiling product although a gas was evolved. Titration of the water in the gas absorber showed that 81 g. of hydrogen halide, calculated as hydrogen bromide, was evolved; the aqueous phase gave a positive bromide test. An evolved gas (unidentified) was passed into bromine and reacted with considerable reagent. Distillation of 149 g. of the product through a 12″ packed column gave 18 g. of silanes boiling at 67–95°, d^{20} 1.48, the bulk of the distillate mainly at 140–169° (107 g.), and some higher boiling material. Redistillation of the first fraction (67–95°) failed to separate the constituents but showed that during the distillation the density decreased from 1.40 to 1.31 and the active chlorine from 77.5 to 61.0. This mixture gave a positive test for the acetylenic bond with ammoniacal cuprous chloride solution whereas a control of ethyltrichlorosilane gave a negative test. A portion of the mixture (9.2 g.) was treated with bromine (6.7 g.) at room temperature and product boiling up to 95° was removed. Redistillation then gave 1.3 g. of silicon tetrachloride, b.p. 56–60°, d^{25} 1.40, and 3.9 g. of trichlorobromosilane,[8] b.p. 78–82°, d^{25} 1.79, active halogen (calculated as chlorine) 65.7% (theory 65.5%). The high boiling residue (above 95°) gave 11.3 g. of α,β-dibromovinyltrichlorosilane, b.p. 90° (11 mm.), 210–213° (735 mm.), d^{22} 2.1, $n^{20}\mathrm{D}$ 1.5458, which gave a positive Baeyer permanganate test for unsaturation.

Anal. Calcd. for $C_2HSiCl_3Br_2$: 3 active Cl, 33.5. Found: 3 active Cl, 35.5.

Treatment of a portion of this α,β-dibromovinyltrichlorosilane with excess aqueous alkali gave *s*-dibromoethylene, b.p. 111–114°, d^{25} 2.3, $n^{20}\mathrm{D}$ 1.5432.

The 140–169° portion of the original distillate was redistilled to give 44 g. of the main product, α- or β-bromovinyltrichlorosilane, b.p. 147–165°, $n^{20}\mathrm{D}$ 1.4897, d^{22} 1.8.

Anal. Calcd. for $C_2H_2SiCl_3Br$: 3 active Cl, 44.3. Found: 3 active Cl, 44.8.

The above product (43.8 g.) was treated dropwise at room temperature with bromine (23 g.). Distillation through a modified claisen flask gave a foreshot and then tribromoethyltrichlorosilane (33 g.), b.p. 119–124° (3 mm.), 133–144° (10 mm.), which solidified on cooling, d^{22} 2.2, $n^{20}\mathrm{D}$ 1.566.

Anal. Calcd. for $C_2H_2SiBr_3Cl_3$: 4 active Cl, 35.5. Found: 4 active Cl, 35.5.

This solid silane (27 g.) was treated with excess base and the mixture distilled with occasional flashes characteristic of haloacetylenes. The dry vinylidene bromide (9.9 g.) boiled for the most part at 88–92° (4.5 g.), d^{25} 2.2, $n^{24}\mathrm{D}$ 1.534. On standing, the vinylidene bromide gradually polymerized. Addition of bromine readily occurred and the product, 1,1,1,2-tetrabromoethane,[9] boiled at 213–220° dec., d^{20} 2.84, $n^{20}\mathrm{D}$ 1.620.

Treatment of α,β-Dibromoethyltrichlorosilane with Quinoline.—A mixture of the silane (520 g.) and quinoline (400 g.) was heated gently during 90 min. until the distillation temperature reached 165° to give 328 g. of product. No unsaturated gas was observed. Distillation through a 12″ packed column gave 54 g. of silicon tetrachloride, b.p. 55–57°, $n^{21}\mathrm{D}$ 1.4182, 83% active chlorine, an intermediate cut, and α-bromovinyltrichlorosilane (147 g.) boiling at 146–148° (722 mm.), 60° (36 mm.), $n^{25}\mathrm{D}$ 1.4920.

Anal. Calcd. for $C_2H_2SiCl_3Br$: 3 active Cl, 44.3; Si, 11.6. Found: 3 active Cl, 44.8; Si, 11.2.

α,α,β-Tribromoethyltrichlorosilane.—α-Bromovinyltrichlorosilane (56 g.) in 50 cc. carbon tetrachloride was treated dropwise at room temperature with bromine (37.5 g.). The α,α,β-tribromoethyltrichlorosilane, after removal of solvent, distilled from a Claisen flask at 105–109° (6 mm.) (77 g.) and soon solidified, f.p. 65–70°.

Anal. Calcd. for $C_2H_2SiCl_3Br_3$: 4 active Cl, 35.5; Si, 7.0. Found: 4 active Cl, 35.4; Si, 6.7.

Cleavage of α,α,β-Tribromoethyltrichlorosilane.—The silane (50 g.) was hydrolyzed in cold water and excess base was added. Distillation gave 6.6 g. of vinylidene bromide boiling at 88–89°, d^{25} 2.24, $n^{20}\mathrm{D}$ 1.5305. Polymer gradually separated from the originally clear liquid. This vinylidene bromide on bromination gave 1,1,1,2-tetrabromoethane,[9] b.p. 212–216° dec., 103° (14 mm.), $n^{20}\mathrm{D}$ 1.6317, d^{20} 2.86.

Pyrolysis of α,α,β-Tribromoethyltrichlorosilane.—The silane (70 g.) was passed through the furnace at 625° during 3 hr. to give 45 g. of liquid product and 25 g. of hydrogen bromide. Since it appeared that free bromine separated in the furnace but immediately re-added to the product beyond the heated tube, a strong stream of carbon dioxide was maintained to sweep away some of the bromine. Distillation gave a mixture of silanes (17.1 g.) boiling at 85–190° and 20 g. of product believed to be recovered silane.

Treatment of α,α,β-Tribromomethyltrichlorosilane with Quinoline.—A mixture of 59 g. of the silane and 58 g. of quinoline was allowed to stand for several hours and then was distilled up to 144°. Polymer gradually separated from the distillate. Distillation gave silicon tetrachloride (10.1 g.), b.p. 58–60°, active chlorine 83.6% (theory 83.5%), $n^{20}\mathrm{D}$ 1.4152. Then was obtained 4 g. of vinylidene bromide, b.p. 87–92°, which gradually polymerized. Distillation of the 4 cc. of residual liquid gave a mixture of unsaturated silanes, b.p. 139–213°.

Pyrolysis of α- and β-Bromovinyltrichlorosilane Mixture.—The mixture of these silanes (220 g.), obtained by the pyrolysis of α,β-dibromoethyltrichlorosilane, was pyrolyzed at 630–650° for 8 hr. to give 196 g. of dark liquid. No provision was made to absorb any unsaturated gas possibly evolved. Distillation gave 45.6 g. of product boiling at

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[7] I. M. Heilbron, "Dictionary of Organic Compounds," Vol. III, Oxford University Press, New York, N. Y., 1943, p. 804, gives b.p. 187–188°, d^{20} 2.58, $n^{20}\mathrm{D}$ 1.5890.

[8] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VI, Longmans, Green & Co., London, 1925, p. 980, gives b.p. 80°.

[9] Reference 7, Vol. III, p. 674, gives b.p. 112° (18 mm.), d^{20} 2.87, $n^{20}\mathrm{D}$ 1.6277.

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]

By E. T. McBee and Theodore M. Burton

Received September 4, 1951

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).