[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Trifluoropropyne[1]

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Specific directions are given for the preparation of $CF_3C{\equiv}CH$, by the sequence: $CF_3CH{=}CH_2$ to $CF_3CHBrCH_2Br$ to $CF_3CBr{=}CH_2$ to $CF_3CBr_2CH_2Br$ to $CF_3CBr{=}CHBr$ to $CF_3C{\equiv}CH$. Each step showed a 90% yield or better, and the overall yield was 73%. Three alternate syntheses are given, but not recommended. A boiling point of $-46 \pm 2°$, and a latent heat of vaporization of only 4640 ± 200 calories show that there is no molecular association; this is attributed to the electronegative induction of the CF_3 group which depletes the triple bond electronically. An infrared spectrum is shown and discussed.

The influence of a CF_3 group on an adjacent triple bond has been shown in $CF_3C{\equiv}CCF_3$,[2,3] the symmetry of which facilitates interpretations; for the study of its influence on an acetylene ≡C-H function, trifloropropyne, $CF_3C{\equiv}CH$, was synthesized. While work was underway, a different synthesis was reported[4] from England, with which our final results fully agreed. Interatomic dimensions measured on our samples will be reported in detail by The California Institute of Technology; C≡C is 1.20Å. by microwave measurement.

The synthesis of trifluoropropyne was successfully performed in a variety of ways. Trifluoropropene, $CF_3CH{=}CH_2$, was brominated to $CF_3CHBrCH_2Br$ and the latter treated with an alkali to give exclusively, as expected,[5] $CF_3CBr{=}CH_2$. From this compound, it is possible, but not advised, to remove hydrogen bromide by a vigorous treatment with an alkali; it is, however, much more convenient to add bromine to the double bond to form $CF_3CBr_2CH_2Br$, treat the latter with an alkali to form $CF_3CBr{=}CHBr$, then remove two bromine atoms by means of zinc to complete the $CF_3C{\equiv}CH$ synthesis. This is our recommended procedure, each step of which is easily performed in yield of 90% or better.

Two alternate sequences have also succeeded, but are less convenient, and they are time-consuming. The free radical chlorination of $CF_3CHBrCH_2Br$ should affect the end CH_2Br group preferentially,[6] and it does yield mostly $CF_3CHBrCHClBr$, from which loss of hydrogen bromide gives $CF_3CBr{=}CHCl$, whose treatment with zinc completes the synthesis. In another sequence, the free radical chlorination of $CF_3CH_2CH_2Br$ yielded mostly, as expected,[6] $CF_3CH_2CHClBr$ from which two treatments with an alkali yielded successively $CF_3CH{=}CHCl$ and $CF_3C{\equiv}CH$.

All syntheses depended on $CF_3CH_2CH_2X$ as a starting point, where X is either chlorine or bromine; these derivatives are obtainable by conventional fluorination of $CCl_3CH_2CH_2X$ with antimony fluoride.[7,8] By a modified procedure using methylene chloride or a similar solvent and described in the experimental part, the reported yields were doubled.

Trifluoropropyne forms, from ammoniacal silver oxide, a white silver acetylide which merely darkens on standing but decomposes explosively on heating. The alkyne reacts with great violence with chlorine, when exposed to ultraviolet light; the resulting oil can be further chlorinated to a solid, m. p. 108–109°, which proved identical with an authentic sample of $CF_3CCl_2CCl_3$,[9] m. p. 108–109°. This shows the presence of a CF_3 group and a three-carbon chain in the original alkyne. Analysis by Haszeldine shows 60.1% fluorine (theory 60.6) and our molecular weight determination by vapor density gives the correct value of 94.8.

The boiling point was estimated at $-46 \pm 2°$; better precision was not achieved because the sample superheated with great facility, and differently constructed boilers gave different boiling points. A determination of the vapor tension[10] gave a smooth log p *versus* $1/T$ curve, the slope of which permitted an estimation of the latent heat of evaporation as 4640 ± 200 calories, and from this value, the Trouton constant was found to be about 20. Evidently, there is no intermolecular association, in contrast with plain hydrocarbons. From propane to propyne, the boiling point rises from −42 to −23°, while from $CF_3CH_2CH_3$ to $CF_3C{\equiv}CH$ it drops from −13 to −46°. This is attributed to increased hydrogen bonding involving the electron rich triple bond for hydrocarbons, and elimination of hydrogen bonding to the electron poor triple bond for the fluorinated compounds.

The infrared absorption spectrum was taken at a pressure of 400 mm. with a Baird Spectrophotometer, and is given in Fig. 1.

At 3.04 microns, strong absorption corresponding to the asymmetrical stretching vibration of the C–H bond is observed. It is interesting to note that the analogous stretching vibration for methylacetylene occurs at 2.92 microns.[11] Thus, the substitution of fluorine for hydrogen has apparently resulted in a shifting of the absorption band to longer wave lengths. This appears to be in accord with the anticipated increased acidity of the acetylenic hydrogen in trifluoropropyne.

The weak band at 4.20 microns is attributed to C–F bond over-tone (strong C–F absorption at 8.48 microns).

Three bands fall in the region customarily as-

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(1) Presented at the Chicago Meeting of The American Chemical Society, September, 1950.

(2) A. L. Henne and W. G. Finnegan, THIS JOURNAL, **71**, 298 (1949).

(3) A. L. Henne, J. V. Schmitz and W. G. Finnegan, *ibid.*, **72**, 4195 (1950).

(4) R. N. Haszeldine, *Nature*, **166**, 152 (1950).

(5) A. L. Henne and J. B. Hinkamp, THIS JOURNAL, **67**, 1196 (1945).

(6) A. L. Henne and co-workers, *ibid.*, **64**, 1157 (1942); **67**, 1194, 1197 (1945).

(7) E. C. Ladd and M. P. Harvey, 113th Meeting of The American Chemical Society, Chicago, May, 1948.

(8) S. Adams, Master's Thesis, The Ohio State University, 1949.

(9) A. L. Henne and A. M. Whaley, THIS JOURNAL, **64**, 1157 (1942).

(10) Courtesy of William Sheehan, California Institute of Technology.

(11) G. Herzberg, "Molecular Spectra and Molecular Structure," D. Van Nostrand and Co., New York, N. Y., 1945, Vol. 2, pp. 288-291, 337-339.

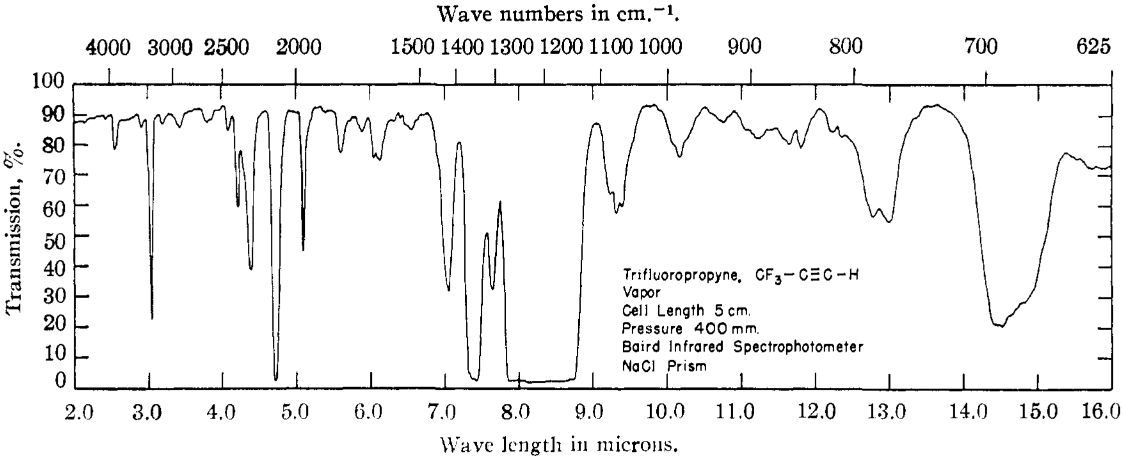

Fig. 1.

signed to the $C{\equiv}C$ and $C{=}C{=}C$ stretching vibrations. These are at 4.4, 4.7 and 5.1 microns. Of these, the band at 4.7 microns is the most intense and it corresponds very closely to the band normally assigned to $C{\equiv}C$.[12] This band in the case of perfluoro-2-butyne has been attributed[2] to partial allenic character of the following nature: $CF_3{=}C{\equiv}C{=}CF_3$, $CF_3{=}CF{=}C{=}CF_2$, $CF_3{=}CH{=}CH{=}CF_3$. It is conceivable that $CF_3{=}C{\equiv}C{-}H$ might also be a contributing structure to the spectrum of trifluoropropyne. The presence of $CF_2H{=}C{\equiv}C{-}F$ is not anticipated. The band at 5.10 microns corresponds to a similar band in the spectrum of perfluoro-2-butyne[2] and is reasonably close to the band assigned to $C{=}C{=}C$.[12] The band at 4.40 microns is unexplained.

Strong C–F bond absorption is noted from 7 to 10 microns. Resolution of this broad band has shown peaks occurring at 7.05, 7.42, 7.65, 8.04 and 8.48 microns. The spectrum of perfluoro-2-butyne[2] also shows strong absorption in this region with peaks at 7.2, 7.4, 7.9 and 8.48 microns.

Experimental

Preparation of $CF_3CH_2CH_2Cl$.—The fluorination of $CCl_3CH_2CH_2Cl$ (a gift of Dr. E. C. Ladd, U. S. Rubber Co., Passaic, N.J.) was carried out in a three-necked aluminum reactor made from a commercial four-quart pressure cooker, and fitted with a mercury seal stirrer, a dropping funnel and a reflux condenser connected to two traps cooled to 0 and −78°, respectively. The reactor was charged with powdered SbF_3 (635 g. or 3.54 moles) and SbF_3Cl_2 (718 g. or 2.87 moles), and methylene chloride (950 ml.) was added while cooling with ice to prevent frothing. $CCl_3CH_2CH_2Cl$ (910 g. or 5.0 moles) was added dropwise over a period of 2 to 3 hours, and with continued cooling in an ice-bath. Only small amounts of hydrogen halides were evolved, and the Dry Ice trap collected only from 50 to 75 g. of difluoromethane mixed with very small amounts of trifluoropropene. After completing the addition, the reaction mixture was stirred for 2 hours longer, then concentrated hydrochloric acid (50 ml.) was added, and the reacted mass was steam distilled. The bottom layer of the distillate was decanted, dried on calcium chloride and distilled, to yield 1552 g. of a mixture of methylene chloride and $CF_3CH_2CH_2Cl$, boiling between 39 and 46°, and 97 g. (or 0.43 mole) of the starting tetrachloropropane.

Preparation of $CF_3CHBrCH_2Br$.—The mixture of halides boiling 39–46° was slowly dripped into a concentrated solution of alkali in alcohol, held in a two-liter flask equipped with a stirrer and a water-cooled reflux condenser. $CF_3CH_2CH_2Cl$ was acted upon at once, to generate trifluoropropene, b.p. −22°, which passed through the reflux condenser and was directed to a flask containing bromine, and strongly illuminated with an ultraviolet lamp. Methylene chloride, which was unaffected, was returned to the reactor by the reflux condenser. After discoloration of the excess of bromine, and drying, distillation gave 1080 g. of $CF_3CHBrCH_2Br$, b.p. 115–117°, $n^{25}D$ 1.4286. The net yield from $CCl_3CH_2CH_2Cl$ to $CF_3CHBrCH_2Br$ is therefore 92.5%.

Preparation of $CF_3CBr{=}CH_2$.—The dehydrohalogenation of $CF_3CHBrCH_2Br$ with alcoholic alkali occurred at 0–5° in 90% yield, to yield $CF_3CBr{=}CH_2$, b.p. 33.0–33.5°, $n^{25}D$ 1.3503; % bromine calcd. 45.68, fd. 45.50. A very small amount of trifluoropropyne was also obtained.

Preparation of $CF_3CBr_2CH_2Br$.—Bromine addition to the preceding olefin occurred quantitatively, to give $CF_3CBr_2CH_2Br$, b.p. 79–81° at 46–47 mm., $n^{20}D$ 1.4831, decomposing slowly on standing with evolution of bromine.

Preparation of $CF_3CBr{=}CHBr$.—Dehydrohalogenation of the preceding compound occurred in 90% yield at 0–5°, with alcoholic alkali, to give $CF_3CBr{=}CHBr$, b.p. 96°, $n^{20}D$ 1.4322; % bromine calcd. 62.95, fd. 62.86.

Preparation of $CF_3C{\equiv}CH$.—A three-necked flask fitted with sealed stirrer, water condenser and dropping funnel was charged with zinc dust (40 g.) and absolute alcohol (350 ml.). The alcohol was brought to vigorous reflux. $CF_3CBr{=}CHBr$ (125 g. or 0.5 mole) was then added dropwise; the debromination started slowly but proceeded smoothly to completion, as the generated propyne passed through the reflux condenser, a calcium chloride tube, and into a trap cooled to −78°, where it liquefied. By rectification of the trap content, 45 g. (or 0.48 mole) of $CF_3C{\equiv}CH$ was collected, amounting to a 97% yield.

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(12) H. M. Randall, *et al.*, "Infrared Determination of Organic Structures," D. Van Nostrand and Co., New York, N. Y., 1949, pp. 46–65.