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

# The Preparation of Hexafluoroacetone

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Hexafluoroacetone has been obtained by previous workers in the reaction between acetone and elemental fluorine.[1] The reaction was described as complex, difficult to control and hazardous. We have now devised an alternate synthesis which is more convenient for laboratory preparation and which can be extended to large scale operation. The procedure involves many steps, but uses only readily available intermediates and simple, conventional operations.

The procedure consists in synthesizing a hexafluorinated derivative of isobutene, preferably $(CF_3)_2C{=}CCl_2$, and in oxidizing its double bond to create the ketone function. The synthesis parallels our preparation of trifluoroacetic acid from either $CF_3CCl{=}CCl_2$ or $CF_3CCl{=}CClCF_3$.[2,3]

To obtain the desired carbon skeleton and the first $CF_3$ group, $CF_3C(CH_3)ClCH_2Cl$ was synthesized by two different procedures. In the first sequence, isocrotyl chloride was transformed into $CCl_3(CH_3)ClCH_2Cl$ by successive chlorinations and dehydrochlorinations, and this pentachlorinated compound was treated with antimony fluoride to transform its $CCl_3$ group to a $CF_3$ group. In the second sequence, ethyl trifluoroacetate was condensed with methylmagnesium chloride, and the resulting tertiary carbinol was dehydrated to the corresponding olefin, $CF_3C(CH_3){=}CH_2$; chlorine was then added to the double bond. Cost considerations favor the first sequence for large quantities, and the second sequence for small preparations.

To create the second $CF_3$ group, $CF_3C(CH_3)ClCH_2Cl$ was transformed into $CF_3C(CH_3){=}CCl_2$ by alternated removals of hydrogen chloride and additions of chlorine; by treatment with antimony fluoride in anhydrous hydrogen fluoride; the olefin was easily transformed into $(CF_3)_2CHCH_3$.

The olefin most convenient for the oxidation step is $(CF_3)_2C{=}CCl_2$. It was obtained by chlorination of $(CF_3)_2CHCH_3$ to $(CF_3)_2CHCCl_3$ followed by hydrogen chloride removal. The final oxidation was performed with aqueous potassium permanganate, in neutral or acid solutions only on account of the known sensitivity of hexafluoroketone to alkalies.[1] Isolation of the ketone was complicated by its ability to form a stable hydrate, soluble in water. The pure ketone was ultimately obtained by distilling a concentrated solution of its hydrate from phosphoric anhydride, and its observed properties proved in agreement with those previously recorded.[1]

In the development of a practical procedure, many intermediates were isolated, the more important of which are listed. They have been found valuable as dielectric materials and some of them are under investigation for industrial uses.

## Experimental Details

**Synthesis of $CF_3C(CH_3)ClCH_2Cl$: First Procedure.**—Boiling isocrotyl chloride (2250 g. or 24.8 moles) was treated with a stream of chlorine in the dark; in four hours, the chlorine consumed amounted to 2325 g. (32.7 moles), and the chlorinated mixture weighed 3360 g., a gain of 1110 g. A rough distillation removed 491 g. of a material boiling 65–135° which was rechlorinated at room temperature to give 577 g. of a better product and returned to the main batch. Distillation gave: 20 g. of starting material, b. p. 65–105°; 185 g. of $CHCl_2C(CH_3){=}CH_2$, b. p. 105–128°; 286 g. of $CH_2ClC(CH_3){=}CHCl$, b. p. 128–135°; 206 g. of $(CH_2Cl)_2C{=}CH_2$, b. p. 135–141°; 267 g. of $CHCl_2C(CH_3)ClCH_3$, b. p. 141–147°, and a large amount left in the boiler which is mostly the desired tetrachloride, $CH_2ClC(CH_3)ClCHCl_2$. The first three cuts were then rechlorinated in the dark, at 20° until the weight had increased by 127 g., and this material was then poured back into the boiler. Distillation was then resumed, but at a pressure reduced to 20 mm., to yield 304 g. of mixed compounds boiling below 78°, 2068 g. of the desired tetrachloride $CH_2ClC(CH_3)ClCHCl_2$ b. p. 78–85°, and a residue of mixed pentachlorides. The main fraction (2068 g. or 10.5 moles) represents a 43% yield. It is better to work with this single compound than to disperse efforts on the other chlorides.

Hydrogen chloride was removed practically quantitatively by feeding a cold solution of potassium hydroxide in a 50/50 mixture of water and methanol to the well-stirred tetrachloride carefully kept below 30°; these conditions prevent hydrolysis of the resulting olefin, $CH_2ClC(CH_3){=}CCl_2$. The olefin, an exceedingly unpleasant lacrymator, accepts chlorine at 0° in the dark, to yield $CH_2ClC(CH_3)ClCCl_3$; a quantitative yield is obtained by adding only 60% of the needed amount of chlorine, removing the unreacted olefin by distillation and subjecting it again to chlorination.

The pentachloroisobutane was dehydrohalogenated to the corresponding olefin $CCl_3C(CH_3){=}CHCl$. This olefin hydrolyzed very readily and the best results, obtained by using a deficient amount of alkali, were only a 30% olefin conversion and a 50% recovery of starting pentachloride. The olefin is, however, very easily transformed into $CF_3C(CH_3){=}CHCl$ by "allylic fluorination" with antimony fluoride,[4] and on first trial an excellent sample was obtained in 70% yield, with the following properties: f. p. −120.3°, b. p. 46.4°, $d^{20}_4$ 1.2395, $n^{20}_D$ 1.3489; % chlorine found 24.5, calcd. 24.5; % fluorine found 39.0, calcd. 39.4.

The inefficient passage through the olefin was then short-cut by treating the pentachloride (460 g. or 2 moles) with a fluorinating agent made of commercial antimony trifluoride (2.4 moles) and chlorine (0.7 mole) in a steel vessel heated to 165° in an oil-bath. The working pressure was 10 to 11 atmospheres. This gave 71 g. of a mixture of $CF_3C(CH_3){=}CHCl$ and $CF_3C(CH_2Cl){=}CH_2$, b. p. 41–75°; 145 g. of the desired $CF_3C(CH_3)ClCH_2Cl$, b. p. 90–110°; and 64 g. of insufficiently fluorinated material which could be refluorinated. This is a 40% yield of the main product, and a 25% yield of usable trifluorinated olefins.

**Second Procedure.**—A solution of 4 moles of methylmagnesium chloride in 1500 cc. of ether was treated with a

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[1] Fukuhara and Bigelow, THIS JOURNAL, **63**, 788 (1941).

[2] Henne, Alderson and Newman, *ibid.*, **67**, 918 (1945).

[3] Henne and Trott, *ibid.*, **69**, 1820 (1947).

[4] Henne and Whaley, *ibid.*, **64**, 1157 (1942).

solution of ethyl trifluoroacetate (266 g. or 1.87 moles) in 300 cc. of ether, and the mixture refluxed for four hours. After decomposition with an aqueous solution of ammonium chloride, the ether layer was distilled to give 316 g. of the azeotrope ($C_2H_5OH—C_4F_3H_6OH$) boiling 75–81°; this is a 97% yield of $CF_3C(OH)(CH_3)_2$. Dehydration of this mixture was performed by adding it dropwise to an equal weight of phosphoric anhydride. A lively reaction generated ethylene, but left the fluorinated carbinol unaffected. Later, long, careful heating at 130° formed trifluoroisobutene, b. p. 6.7° in 97% yield; dehydration started at 115°, and much decomposition occurred at 160°. The olefin accepted chlorine rapidly in the dark at 0°, in the presence of a trace of ferric chloride, and the yield was quantitative.

The desired material, $CF_3C(CH_3(ClCH_2Cl$, was very stable and had the following properties: b. p. 93.5° at 760 mm., $d^{20}_{4}$ 1.3899, $n^{20}_{\text{D}}$ 1.3752; % chlorine found 23.6, calcd. 24.5; % fluorine found 39.7, calcd. 39.4.

### Synthesis of $CF_3C(CH_3)=CCl_2$

A solution of $CF_3C(CH_3)ClCH_2Cl$ (431 g. or 2.38 moles) in 300 cc. of ethanol was refluxed under a condenser held at 50°. A solution of potassium hydroxide (2.5 moles) in 600 cc. of alcohol was added dropwise, with vigorous stirring. The resulting olefin, $CF_3C(CH_3)=CHCl$, b. p. 46° was thus able to distil out of the reaction mixture as soon as formed. Working up of distillate yielded 230 g. of the crude olefin, b. p. 43–48°, 51 g. of an intermediate fraction, b. p. 68–71°, presumed to contain $CF_3C(CH_2Cl)=CH_2$ and 73 g. of recovered material. The conversion is therefore 64% and the material balance 98%.

Chlorination of the olefin was performed in the dark, at 0°, with a trace of ferric chloride. By adding only 50% of the theoretical amount of chlorine and reworking the unreacted olefin, a quantitative yield of $CF_3C(CH_3)ClCHCl_2$ was obtained. The removal of hydrogen chloride with an alcoholic solution of potassium hydroxide gave 88% of $CF_3C(CH_3)C=Cl_2$ and 6% of recovered material; no precaution other than to keep the reaction mixture below 25° was needed. The properties of $CF_3C(CH_3)=CCl_2$ are: b. p. 88.4° at 760 mm., $d^{20}_{4}$ 1.4248, $n^{20}_{\text{D}}$ 1.9947; % chlorine found 39.6; calcd. 39.8.

### Synthesis of $(CF_3)_2CHCH_3$

A one-liter steel vessel was loaded with antimony fluoride (331 g. or 1.85 moles) and chlorine (58 g. or 0.81 mole); this mixture corresponds to 44% $SbF_3Cl_2$; it was cooled to −78°, and hydrogen fluoride (80 g. or 4 moles) was added. A mixture of $CF_3C(CH_3)=CCl_2$ (237 g. or 1.33 moles), $CF_3CH(CH_3)CF_2Cl$ (194 g. or 1.06 moles) and $CF_3CH(CH_3)CFCl_2$ (the latter two recovered from a preceding operation) was then poured into the vessel. The vessel was closed, and rocked mechanically at 55° for four hours; the pressure rose to 10 atmospheres. The heating was then raised to 130°, and the pressure rose progressively to 20 atmospheres; by slowly venting hydrogen chloride, the pressure was brought back to a steady 8 atmospheres; heating was continued for five hours, after which the reaction products were worked up to give: 296 g. of the desired $(CF_3)_2CHCH_3$, b. p. 20–30°; 69 g. of $CF_3CH(CH_3)$-$CF_2Cl$, b. p. around 55°; 39 g. of $CF_3CH(CH_3)CFCl_2$, b. p. around 70°; and 14 g. of a clear, higher boiling material. This is a 70% conversion plus a 26% yield of reworkable products. $(CF_3)_2CHCH_3$ is a very volatile liquid, f. p. −106.7°, b. p. 21.5°, $d^{0}_{4}$ 1.3725, $n^{2.9}_{\text{D}}$ 1.2717; % fluorine found 67.2, calcd. 68.6.

### Synthesis of $(CF_3)C_2=CCl_2$

Chlorination of $(CF_3)_2CHCH_3$ was sluggish, but proceeded without decomposition at the boiling point of the reaction mixture, in intense ultraviolet illumination. As the tertiary hydrogen is "protected" by the two flanking $CF_3$ groups,[5] it was not substituted by atomic chlorine. Only two compounds appeared, $(CF_3)_2CHCCl_3$, b. p. 106.5–107.5°, $d^{20}_{4}$ 1.7095, $n^{20}_{\text{D}}$ 1.3690, in 90–95% yield, and a solid, m. p. 111.8–112.4°; % chlorine found 29.6, calcd. 30.3 in 5–10% yield, to which the formula $(CF_3)_2CHCCl_2CCl_2CH(CF_3)_2$ was assigned because it quantitatively lost 2 moles of hydrogen chloride in an alkali treatment to yield $(CF_3)_2C=CClCCl=C(CF_3)_2$, b. p. 123°, $d^{20}_{4}$ 1.6838, $n^{20}_{\text{D}}$ 1.3462; % chlorine found 17.2, calcd. 18.0. Removal of hydrogen chloride from the main product was performed with an alkali in ethanol, and also in a 50/50 methanol–water mixture, at temperatures held below 10°. A conversion of about 50% to $(CF_3)_2$-$C=CCl_2$ was obtained, but the balance was a compound distilling at 127–130°, $d^{20}_{4}$ 1.4364, $n^{20}_{\text{D}}$ 1.3596, which was not the starting material and is still unidentified; however, when the solvent was switched to isopropyl alcohol and only half the theoretical amount of alkali was used, 50% of the material was transformed into the wanted olefin, and the balance proved to be unreacted material which could be retreated; $(CF_3)_2C=CCl_2$, m. p. −98.2°, b. p. 74.5°, $d^{20}_{4}$ 1.6429, $n^{20}_{\text{D}}$ 1.3517; % chlorine found 29.9, calcd. 30.3.

An alternate dehydrohalogenation of $(CF_3)_2CHCCl_3$ was more recently performed by adding 6.5 g. of potassium hydroxide in 50 ml. of water to 31 g. of impure $(CF_3)_2CHCCl_3$ in 50 ml. of $(HOCH_2CH_2)_2O$, with efficient cooling in an ice-bath; soon after the alkali had been added, the solution became neutral. By distilling off up to 100°, drying the distillate and redistilling, 22 g. of a single fraction was obtained which boiled from 71–75°; this would be an 82.5% yield of $(CF_3)_2C=CCl_2$; this material had a low index of $n^{20}_{\text{D}}$ 1.3502, which is a good indication; it was felt that most of the losses were mechanical. The importance of the solvent is thus emphasized, but not explained.

### Synthesis of $CF_3COCF_3$

Several permanganic oxidations were tried; the best results were obtained as follows. A 48-g. batch of crude $(CF_3)_2C=CCl_2$ (0.20 mole), was oxidized for forty-eight hours at room temperature with aqueous acid permanganate. In the Dry Ice trap protecting the system, only one gram of recovered material was found, which had apparently been entrained by the evolution of carbon dioxide. After decolorizing the excess of permanganate with sulfur dioxide, steam distillation was applied until one liter of distillate had been collected, from which 7 g. of starting material was recovered. The amount of oxidized material was therefore no more than 0.17 mole. From this distillate, ether extracted only 2.7 g. of a material, b. p. 93–95°, $n^{20}_{\text{D}}$ 1.3429 and 4 g. of a residual material. Ether extraction was then applied to the main oxidation mixture, and from this came 25.5 g. of material, b. p. 57° at 93 mm., $n^{20}_{\text{D}}$ 1.3288, $d^{20}_{4}$ 1.4085. Since its index of refraction was low and its density high, the chance of it being the fluorinated ketone hydrate was considered good; a test with 2,4-dinitrophenylhydrazine did not succeed, but a test with a semicarbazide solution succeeded well; the semicarbazone softened at 149°, then decomposed brusquely at 153°, in agreement with reported facts.[1] The liquid was then very cautiously dropped into 60 g. of phosphoric anhydride, at a rate such that no cloudy vapors would be evolved. The system was protected by two Dry Ice traps in series, the first of which collected a clear liquid with some solid at the bottom, while the second trap was empty. An Engler distillation of this material gave 16.5 g. of hexafluoroacetone, b. p. −26° (uncor.), and 1 g. of liquid residue forming a semicarbazone, m. p. 190°, still unidentified. During distillation, formation of a solid melting below room temperature was noted wherever moist air would have access. The main fraction consisted of 0.1 mole of the desired $CF_3COCF_3$ and the yield on oxidation is therefore 60%; this could be substantially improved by a better extraction procedure and by handling larger quantities.

**Additional Analyses.**—Percentage chlorine found and calcd.: $CH_2ClC(CH_3)=CH_2$, 66.1 and 66.7; $CCl_3C(CH_3)=CHCl$, 73.0 and 73.1; $CF_3C(CH_2Cl)=CH_2$, 23.6 and 24.5; $CClF_2C(CH_3)ClCH_2Cl$, 53.2 and 53.8; $CF_3C(CH_3)ClCCl_3$, 56.6 and 56.8; $CF_3C(CH_3)ClCF_2Cl$

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(5) Henne and co-workers, THIS JOURNAL, **64**, 1157 (1942); **67**, 1197, 1639 and 1906 (1945).

TABLE OF PHYSICAL CONSTANTS

| | F. p., °C. | B. p., °C., 760 mm. | $d^{20}_4$ | $n^{20}_D$ | $AR_f$ |
|---|---|---|---|---|---|
| $CH_2ClC(CH_3)=CH_2$ | − 78.7 | 158 | 1.3319 | 1.4980 | |
| $CCl_3C(CH_3)=CHCl$ | − 70.0 | 174.8 | 1.4528 | 1.5129 | |
| $CCl_3C(CH_3)ClCH_2Cl$ | 58–63 | 205–210 (98–102 (10 mm.)) | | | |
| $CF_3C(CH_3)=CHCl$ | −120.3 | 46.4 | 1.2395 | 1.3489 | 1.1 |
| $CF_3C(CH_2Cl)=CH_2$ | | 64.1 | 1.2824 | 1.3520 | 0.9 |
| $CF_3C(CH_3)ClCH_2Cl$ | | 93.5 | 1.3899 | 1.3782 | 1.0 |
| $CClF_2C(CH_3)ClCH_2Cl$ | | 131–132 | 1.4441 | 1.4236 | 0.9 |
| $CClF_2C(CH_3)=CHCl$ | | 86–87 | 1.3406 | 1.4023 | 0.8 |
| $CF_3C(CH_3)ClCHCl_2$ | | 123.7 | 1.5201 | 1.4084 | 1.0 |
| $CF_3C(CH_3)=CCl_2$ | | 88.4 | 1.4248 | 1.3947 | 1.1 |
| $CF_3C(CH_3)ClCCl_3$ | 115.6–116.4 | 148–149 | | | |
| $CF_3C(CH_3)ClCF_2Cl$ | | 75.3 | 1.5133 | 1.3440 | 1.1 |
| $(CF_3)_2CHCH_3$ | −106.7 | 21.5 | 1.3725 at 0° | 1.2717 at 2.9° | 1.1 |
| $(CF_3)_2C=CCl_2$ | − 98.2 | 74.5 | 1.6429 | 1.3517 | 1.2 |
| $CF_3C(CH_3)=CH_2$ | | 6–7 | | | |
| $CF_3C(CH_3)=CF_2$ | | 12.8–13.5 (745 mm.) | | | |
| $(CF_3)_2CHCCl_3$ | | 106.5–107.5 | 1.7095 | 1.3690 | 1.0 |
| $[(CF_3)_2CHCCl_2—]_2$ | 111.8–112.4 | | | | |
| $[(CF_3)_2C=CCl—]_2$ | | 123 | 1.6838 | 1.3462 | 1.2 |

32.4 and 32.7; percentage fluorine, $CF_3C(CH_2Cl)=CH_2$, 39.7 and 39.4.

## Summary

Hexafluoroacetone was prepared in 60% yield by permanganic oxidation of $(CF_3)_2C=CCl_2$, in an operation which could easily be improved. The needed olefin was obtained from $CF_3C(CH_3)ClCH_2Cl$ in a sequence of steps, each of which gives a 90–95% yield when the unreacted reagents were reworked. This $CF_3C(CH_3)ClCH_2Cl$ was prepared practically quantitatively from trifluoroacetic acid; it is also obtainable from isocrotyl chloride by a sequence of simple steps which would be cheaper for large quantities.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

# Nitration of 1,1,1-Trifluoropropane[1]

BY E. T. MCBEE, H. B. HASS AND I. M. ROBINSON

This research was undertaken to study the effect of a trifluoromethyl group on the vapor-phase nitration reaction and to make available fluoronitro compounds for further study. Previously, Best[2] had shown that no nitration of 1,1,1-trifluoroethane occurred in the vapor phase at 500° with fuming nitric acid. A description of the preparation of aliphatic fluoronitro compounds appears in a patent on the addition of dinitrogen tetroxide to fluoroölefins.[3] Also, 1,1,1-trifluoro-3-nitropropane has been prepared from the corresponding bromo compound by the Victor Meyer reaction.[4]

From generalizations attending vapor-phase nitrations of hydrocarbons as reported from this Laboratory,[5,6,7,8,9] the vapor-phase nitration of 1,1,1-trifluoropropane might be expected to result in the production of the two mononitro compounds theoretically possible by the substitution of any single hydrogen atom in the molecule by a nitro group, and nitro derivatives of the alkyl radical which could result from the carbon–carbon cleavage of the molecule. The possible products of nitration would be: 1,1,1-trifluoro-3-nitropropane, 1,1,1-trifluoro-2-nitropropane, 1,1,1-trifluoronitroethane, trifluoronitromethane, nitroethane and nitromethane.

Nitration of 1,1,1-trifluoropropane has been found to occur in the vapor phase at 395° with 70% nitric acid. The nitro compounds formed are 1,1,1-trifluoro-3-nitropropane and 1,1,1-trifluoronitroethane. Failure to obtain 1,1,1-trifluoro-2-nitropropane, trifluoronitromethane and

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[1] Taken in part from a doctoral thesis submitted by I. M. Robinson to the faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Presented before the Symposium on Fluorine Chemistry, Division of Industrial and Engineering Chemistry at the 116th meeting of the American Chemical Society.

[2] R. D. Best, M.S. Thesis, Purdue University, 1941.

[3] H. B. Hass and A. C. Whitaker, U. S. Patent 2,447,504.

[4] W. G. Toland, Ph.D. Thesis, Purdue University, 1944.

[5] H. B. Hass, E. B. Hodge and B. M. Vanderbilt, *Ind. Eng. Chem.*, **28**, 339 (1936).

[6] H. B. Hass and J. A. Patterson, *ibid.*, **30**, 67 (1938).

[7] L. W. Seigle and H. B. Hass, *ibid.*, **31**, 648 (1939).

[8] M. H. Danzig and H. B. Hass, THIS JOURNAL, **66**, 2017 (1944).

[9] A. P. Howe and H. B. Hass, *Ind. Eng. Chem.*, **38**, 251 (1946).