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).

nitroethane may be attributed to the stabilizing effect of the trifluoromethyl group. However, on the basis of the interpretation of results from other vapor-phase nitrations, the presence of 1,1,1-trifluoronitroethane would seem to imply the formation of nitromethane, but none could be detected or isolated.

1,1,1-Trifluoro-3-nitropropane was identified by conversion to β,β,β-trifluoropropionic acid, according to the method of Lippincott and Hass[10] for the preparation of carboxylic acids from the corresponding primary nitroparaffins. The physical properties of the acid obtained were comparable to those for β,β,β-trifluoropropionic acid prepared by Scherer[11] following another procedure. Moreover, the 1,1,1-trifluoro-3-nitropropane prepared by vapor-phase nitration had physical constants similar to those for the trifluoronitropropane prepared by Toland.[4] 1,1,1-Trifluoronitroethane was identified by reduction to 2,2,2-trifluoroethylamine with iron and hydrochloric acid. The amine obtained had a boiling point similar to that reported by Benning and Park,[12] and Gilman and Jones[13] for 2,2,2-trifluoroethylamine.

Experimental

Vapor-phase Nitration of 1,1,1-Trifluoropropane.—The apparatus for the vapor-phase nitration was of all-glass construction. Essentially, it was similar to the one developed in this Laboratory and described previously.[5,6] Nitric acid and trifluoropropane were introduced at predetermined rates through calibrated flowmeters. The products were partially condensed by a water-cooled condenser, and trifluoropropane was collected in a receiver cooled by Dry Ice. Etching of the glass system occurred during nitration, but was limited to a small section leading from the nitrator to the condensing system.

In a typical experiment, 1,1,1-trifluoropropane and nitric acid were introduced into the reactor at a rate of 0.42 mole/hr. and 0.52 mole/hr., respectively. A temperature of 395° and calculated contact times of 2.5–3.5 sec. were used. The addition of 334 g. (3.4 moles) of trifluoropropane produced 55.7 g. of nitro compounds of which 21.4 g. was condensed directly. The remaining 34.3 g. of product was obtained as entrained material in the recovered trifluoropropane. A total of 232 g. (2.4 moles) of 1,1,1-trifluoropropane was recovered after scrubbing out the dissolved oxides of nitrogen. The conversion was found to be 11.9% and the yield of nitrated product was 39%. Upon rectification of the final product through a fifty-plate column of the Whitmore–Fenske type, two fractions were obtained: 1,1,1-trifluoronitroethane, b. p. 96°, and 1,1,1-trifluoro-3-nitropropane, b. p. 135.5°. There was no indication of a plateau for nitromethane. The molar ratio of 1,1,1-trifluoronitroethane to 1,1,1-trifluoro-3-nitropropane produced on nitration was approximately 2:3.

Identification of 1,1,1-Trifluoronitroethane.—The fraction boiling at 96° was identified as 1,1,1-trifluoronitroethane, d^{20}_4 1.3914, $n^{20}\mathrm{D}$ 1.3394. A neutralization equivalent of this acidic material could not be determined since decomposition occurred during titration, presumably due to dehydrofluorination. Molecular weight determinations were carried out using the cryoscopic method with benzene as the solvent.

Anal. Calcd. for $C_2H_2F_3NO_2$: N, 10.84; mol. wt., 129. Found: N, 10.50; mol. wt., 127.

The identity of 1,1,1-trifluoronitroethane was established by reduction to the corresponding trifluoroethylamine. The reduction with iron and hydrochloric acid was carried out according to the procedure recommended by Johnson.[14] Five milliliters of concd. hydrochloric acid was added to a stirred suspension of 17.5 g. of 40-mesh iron filings in 37.5 ml. of water. After the evolution of hydrogen had stopped, 10.3 g. (0.08 mole) of trifluoronitroethane was introduced, and with rapid stirring the mass was heated to reflux for thirty-six hours. This mixture was made basic with aqueous sodium hydroxide and the amine and water distilled. Rectification of the aqueous distillate produced about 0.5 g. of amine, b. p. 35°. 2,2,2-Trifluoroethylamine is reported to boil at 37°.[12,13] The amine hydrochloride was formed in ethereal hydrogen chloride at −15° and purified by sublimation.

Anal. Calcd. for $C_2H_5ClF_3N$: Cl, 26.2. Found: Cl, 26.1.

Identification of 1,1,1-Trifluoro-3-nitropropane.—The fraction boiling at 135.5° was identified as 1,1,1-trifluoro-3-nitropropane, d^{20}_4 1.4259, $n^{20}\mathrm{D}$ 1.3525.

Anal. Calcd. for $C_3H_4F_3NO_2$: N, 9.79; neut. equiv., 143. Found: N, 9.48; neut. equiv., 144.

The identity of 1,1,1-trifluoro-3-nitropropane was established by conversion to β,β,β-trifluoropropionic acid, according to the method of Lippincott and Hass.[10] A mixture of 5.7 g. (0.04 mole) of the trifluoronitropropane and 4.6 g. (0.04 mole) of 85% sulfuric acid was heated to reflux. The temperature rose rapidly to 135° and at the end of six hours was 147°. The product was removed under reduced pressure. A total of 4.4 g. (0.034 mole) of crude trifluoropropionic acid was obtained, representing a yield of 86%. The trifluoropropionic acid, purified by rectification, had a boiling point of 145.5°. This is similar to the boiling point of 146° reported by Scherer[11] for the compound prepared by oxidation of 1,1,1-trifluoro-3-propanol. A neutralization equivalent was determined.

Anal. Calcd. for $C_3H_3F_3O_2$: neut. equiv., 128. Found: neut. equiv., 129.5.

The trifluoropropionic acid was converted to its anilide by reaction with thionyl chloride followed by aniline. The melting point of the anilide was 118.5–119°.

Anal. Calcd. for $C_9H_8F_3NO$: N, 6.89. Found: N, 6.90.

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Summary

The vapor-phase nitration of 1,1,1-trifluoropropane has been found to produce 1,1,1-trifluoro-3-nitropropane and 1,1,1-trifluoronitroethane. Although nitromethane was also an expected product, none was detected or isolated. Failure to obtain other nitration products may be attributed to the stabilizing effect of the trifluoromethyl group.

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[15] Original manuscript received October 24, 1949.