(5) CF_3COSR and Raney nickel led to the alcohol. (6) Hydrolysis of CF_3CHCl_2 by a variety of procedures led nowhere. (7) CF_3CH_2OH was oxidized directly to the acid by sodium dichromate, and was recovered intact after treatment with acetone and aluminum isopropoxide.

Summary

To synthesize an aldehyde bearing a CF_3 group, conventional oxidation of the corresponding alcohol is adequate if the CF_3 is not adjacent to the carbonyl group. For the synthesis of fluoral, CF_3CHO, only the low temperature reduction of CF_3CN with lithium aluminum hydride was found effective. The preparation of CF_3CHO, CF_3CH_2CHO and $CF_3CH_2CO_2H$ are described.

COLUMBUS, OHIO RECEIVED OCTOBER 7, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Oxidative Nitration of 1,1,1-Trifluoropropane. Trifluoroacetaldehyde

BY HAROLD SHECHTER AND FRANKLIN CONRAD[1]

Nitration of alkanes in the vapor-phase at temperatures above 350° yields each nitroalkane derived from the replacement of any hydrogen atom or alkyl group in the hydrocarbon.[2]

In reactions of the "atom-radical" type it has been shown that the trifluoromethyl group has a marked deactivating effect on replacement of hydrogen atoms in alpha positions; however, the effect of the trifluoromethyl group is greatly diminished in beta positions.[3] Since nitration reactions in the vapor-phase usually involve the substitution of nitro groups for hydrogen atoms and alkyl radicals, it is of interest to determine the influence of the trifluoromethyl group on the specificity of nitration of 1,1,1-trifluoropropane.

The reaction of 1,1,1-trifluoropropane, nitric acid, and oxygen at 437–462° yields 1,1,1-trifluoro-3-nitropropane as the only nitrated product; the principal product of reaction is trifluoroacetaldehyde (fluoral).[4]

The yield of 1,1,1-trifluoro-3-nitropropane, based on nitric acid consumed, is 16%; the yield of trifluoroacetaldehyde, as the monohydrate, is 20–24%. No direct evidence was obtained for the formation of nitromethane, nitroethane, trifluoronitromethane, 1,1,1-trifluoro-2-nitroethane, and 1,1,1-trifluoro-2-nitropropane, the products expected from a non-specific nitration reaction. 1,1,1-Trifluoro-3-nitropropane was identified by reaction of its sodium salt with sulfuric acid and 2,4-dinitrophenylhydrazine to yield 3,3,3-trifluoropropionaldehyde 2,4-dinitrophenylhydrazone.[5] The infrared spectrogram of the trifluoronitroalkane is given in Fig. 1.

Trifluoroacetaldehyde, the first completely fluorinated aldehyde to be reported,[6] was isolated from its hydrate by reaction with phosphoric anhydride. The aldehyde was identified by preparing the *p*-nitrophenylhydrazone and the 2,4-dinitrophenylhydrazone. Swarts[7] has reported that oxidation of trifluoroethanol with chromic acid yields trifluoroacetic acid; no trifluoroacetaldehyde was obtained. Whether trifluoroacetaldehyde is produced by oxidation of 1,1,1-trifluoropropane or by decomposition of 1,1,1-trifluoro-2-nitroethane has not been established. Since thermal decomposition of primary nitroalkanes yields the corresponding aldehyde, nitric oxide, and water,[8] it is probable that decomposition of 1,1,1-trifluoro-2-nitroethane yields much of the trifluoroacetaldehyde produced.

Fluoral gives typical reactions of the carbonyl group; however, its properties are greatly influenced by the strong inductive effect of the trifluoromethyl group. The aldehyde, b. p. −18.8 to −17.5°, (infrared spectrum, Fig. 2), dissolves very slowly in water; in dilute acids it forms the expected hydrate. During storage, trifluoroacetaldehyde polymerizes into a clear waxy resin[9] which is slightly soluble in diethyl ether and in acetone. The polymer, insoluble in water, carbon disulfide, chloroform, and carbon tetrachloride, serves as a convenient source of trifluoroacetaldehyde since, upon heating, it decomposes readily into the aldehyde. The polymer is hydrolyzed slowly by concentrated acids, but dissolves rapidly in dilute carbonate solutions to yield fluoral hydrate.

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[1] Abstracted from the thesis of Franklin Conrad, submitted in partial fulfillment of the requirements for the M.S. degree at The Ohio State University, Columbus, Ohio.

[2] Hass, Hodge and Vanderbilt, *Ind. Eng. Chem.*, **28**, 339 (1936); Hass and Shechter, *ibid.*, **39**, 817 (1947).

[3] Henne and Whaley, THIS JOURNAL, **64**, 1157 (1942); Henne and Hinkamp, *ibid.*, **67**, 1197 (1945); McBee, Hass, Elmore, Thomas, Toland and Truchan, *ibid.*, **69**, 944 (1947); Ash and Brown, *Rec. Chem. Prog.*, **9**, 81 (1948).

[4] After submission of this manuscript, McBee and Robinson, 116th Meeting of the American Chemical Society, Atlantic City, N. J., reported that nitration of 1,1,1-trifluoropropane at 390° in the absence of oxygen yields 1,1,1-trifluoro-3-nitropropane and 1,1,1-trifloro-2-nitroethane; no trifluoroacetaldehyde was obtained. It is likely that, at higher temperatures and in the presence of oxygen, trifluoroacetaldehyde is formed at the expense of 1,1,1-trifluoro-2-nitroethane. The conclusions from both studies concerning the effect of the trifluoromethyl group are essentially the same.

[5] Henne, Pelley and Alm, THIS JOURNAL, **72**, 3370 (1950).

[6] Since submission of this manuscript, Husted and Ahlbrecht, 116th Meeting of the American Chemical Society, Atlantic City, N. J., have reported the preparation of perfluorobutyraldehyde.

[7] Swarts, *Bull. soc. chim. Belg.*, **43**, 471 (1934).

[8] Gabriel, *Ber.*, **18**, 1254 (1885); Kon, *ibid.*, **28**, 1861 (1895) Holleman, *Rec. trav. chim.*, **14**, 121 (1895).

[9] Slow distillation of fluoral also yields a crystalline solid, m. p. 47–49°, which has not been identified. The structures of the various polymers of fluoral, perhaps linear and cyclic, are now being studied.

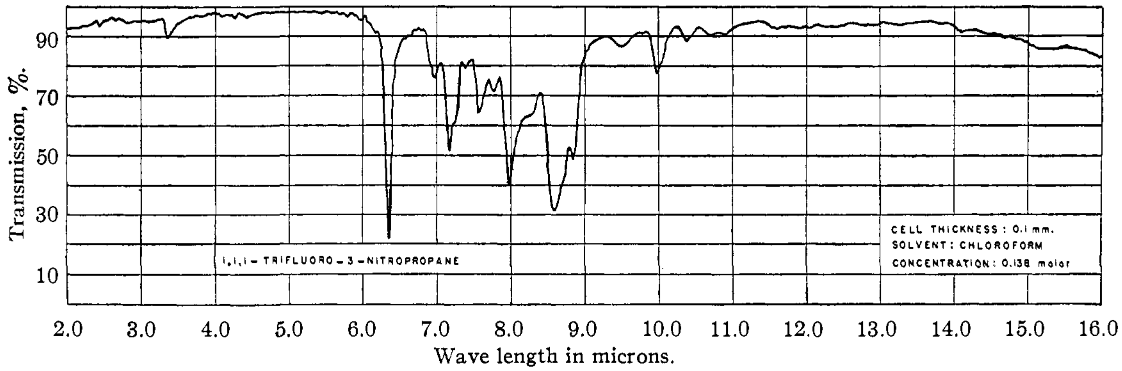

Fig. 1.—Infrared absorption spectra of 1,1,1-trifluoro-3-nitropropane.

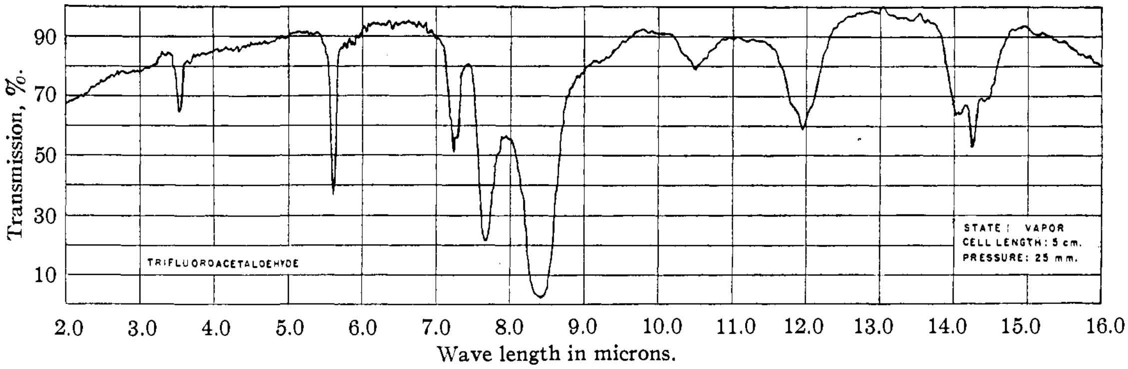

Fig. 2.—Infrared absorption spectra of trifluoroacetaldehyde.

Fluoral hydrate is oxidized by Tollens reagent or dilute potassium permanganate to trifluoroacetic acid. It gives a typical haloform reaction with strong aqueous bases to yield trifluoromethane and salts of formic acid. The hydrate does not form substituted hydrazones readily in neutral or slightly acidic solution; however, sufficient dehydration occurs in concentrated acids to permit formation of the usual derivatives of carbonyl compounds.

Experimental

Apparatus.—The nitration apparatus, based on that described by Hass and Alexander,[10] was constructed of Pyrex tubing (12 mm. o. d., reactor volume 800 ml.) immersed in a fused mixture of sodium and potassium nitrates. Considerable removal of silica from the reactor coil occurred by the etching action of hydrogen fluoride; however, the longevity of the apparatus was not seriously impaired. The products of reaction were condensed in a series of traps immersed in iced water, Dry Ice and acetone, and liquid air, respectively.

Materials.—1,1,1-Trifluoropropane, b. p. −13°, was prepared from 1,1-dichloro-1-propene by the method of Henne and Whaley.[3] Unreacted 1,1,1-trifluoropropane from each nitration experiment was recycled after it had been passed through a series of concentrated sodium hydroxide and sulfuric acid solutions, anhydrous soda-lime and then rectified at low temperatures. Commercial C. P. nitric acid (70% HNO_3, sp. gr. 1.42) served as the nitrating agent.

Nitration of 1,1,1-Trifluoropropane.—1,1,1-Trifluoropropane (1342 g.), nitric acid, and oxygen (mole ratio, 9.9-11.9:1:0.10:0.15) were treated at atmospheric pressure in the gas phase at 437-462° and an exposure time of 1.7-2.0 seconds. The condensate collected at 0°, after an aliquot had been titrated for nitric acid, was extracted immediately with ether. The condensate collected at −80° was distilled at atmospheric pressure to remove unreacted 1,1,1-trifluoropropane, then extracted with ether. The ether extracts were combined, dried over sodium sulfate, and rectified in a column (80 × 1.5 cm.) packed with helices. After removal of the ether, the following fractions were obtained: (1), 72.5 g., b. p. 101-103°; (2), 11.6 g., b. p. 128-134° and (3), 2.7 g. residue, unidentified. The nitric acid recovered was 23.6% of that injected.

Trifluoroacetaldehyde.—Fraction 1 (20-g. aliquot) was extracted with water (20 g.) at 20°; the remaining insoluble liquid (7.6 g.) was combined with Fraction 2. The aqueous extract (12.5 g. aliquot) was added dropwise to phosphoric anhydride (50 g.) and a colorless gas was evolved which solidified in a condenser immersed in liquid air. Considerable decomposition of the reaction mixture occurred during the dehydration. Redistillation of the condensate yielded trifluoroacetaldehyde (3 g.), a colorless hygroscopic liquid, b. p. −18.8 to −17.5°[11] at 748 mm.

Trifluoroacetaldehyde 2,4-Dinitrophenylhydrazone.—The aqueous extract from Fraction 1 (3.5 g. aliquot) was added to 2,4-dinitrophenylhydrazine (2 g.) in 6 *N* sulfuric acid. A solid derivative formed slowly, and the product was allowed to stand overnight. The precipitate was recrystallized from an ethyl alcohol-water mixture to yield the 2,4-dinitrophenylhydrazone of trifluoroacetaldehyde (1.9 g.), orange-yellow needles, m. p. 149.7-151.0°, dec. A derivative prepared by absorbing gaseous trifluoroacetaldehyde in a solution of 2,4-dinitrophenylhydrazine in sulfuric acid is identical with that prepared from the original nitration products. Absorption maxima of the

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[10] Hass and Alexander, *Ind. Eng. Chem.*, **41**, 2266 (1949).

[11] The boiling point was determined by distilling a large sample of trifluoroacetaldehyde. The boiling point is not absolutely correct since the aldehyde polymerizes slowly during the distillation.

hydrazone in ethanol are at 330-334 mμ, ε = 19,800, and at 244-246 mμ, ε = 10,300.

Anal. Calcd. for $C_8H_5N_4O_4F_3$: C, 34.53; H, 1.80; N, 20.15; F, 20.5. Found: C, 35.01; H, 1.80; N, 20.20; F, 19.14.

Trifluoroacetaldehyde *p*-Nitrophenylhydrazone.—The aqueous extract from Fraction 1 (3.5-g. aliquot) was heated with *p*-nitrophenylhydrazine (2.0 g.) in 6 *N* sulfuric acid (200 ml.). The derivative formed very slowly in low yields. Recrystallization of the red-brown solid from alcohol-water gave the *p*-nitrophenylhydrazone (0.4 g.), yellow crystals, m. p. 202-204°, dec. Absorption maxima of the hydrazone in alcohol are at 348-352 mμ, ε = 23,600, and at 236-238 mμ, ε = 8,500.

Anal. Calcd. for $C_8H_6N_3O_2F_3$: C, 41.20; H, 2.58; N, 18.03; F, 24.46. Found: C, 41.52; H, 2.69; N, 18.32; F, 23.10.

1,1,1-Trifluoro-3-nitropropane.—Rectification of Fraction 2, after removal of fluoral hydrate, yielded 1,1,1-trifluoro-3-nitropropane, b. p. 134.0-134.8° at 748 mm., n^{20}_D 1.3558, d^{20}_4 1.4220, MR_D (found) 21.72, MR_D (calcd.) 21.68. Tests for the presence of a carbonyl group in the product with neutral or acidic 2,4-dinitrophenylhydrazine were negative, but evidence for a primary nitro group was obtained when the product dissolved in 10% sodium hydroxide and then gave a nitrolic acid test when treated with potassium nitrite and hydrochloric acid.

Anal. Calcd. for $C_3H_4NO_2F_3$: C, 25.13; H, 2.80; N, 9.77. Found: C, 25.59; H, 3.15; N, 9.67.

3,3,3-Trifluoropropionaldehyde 2,4-Dinitrophenylhydrazone.—1,1,1-Trifluoro-3-nitropropane (1 g., 0.007 mole), dissolved in excess sodium hydroxide, was added, dropwise, with rapid stirring to a cold solution of 2,4-dinitrophenylhydrazine (2 g., 0.01 mole) in sulfuric acid (6 *N*, 200 ml.). (It was observed that an alkaline solution of the trifluoronitroalkane, unless kept cold, is degraded rapidly with considerable evolution of heat.) After the addition was completed, the orange precipitate was filtered, washed with sulfuric acid (6 *N*) and water, dissolved in boiling petroleum ether, and filtered to remove unreacted 2,4-dinitrophenylhydrazine. The solution, when cooled, yielded a yellow powder which after two recrystallizations from an ethyl alcohol-water mixture, treatment with activated carbon, and two recrystallizations from a mixture of benzene and methylcyclohexane gave the 2,4-dinitrophenylhydrazone of 3,3,3-trifluoropropionaldehyde (0.4 g., 0.00137 mole, 19.6%), needles, m. p. 149.6-150.2°. A melting point of a mixture of the hydrazone with an authentic sample,[5] m. p. 150.2-150.8°, gave no depression. The principal absorption maximum of the hydrazone in alcohol is at 348-352 mμ, ε = 17,500.

Anal. Calcd. for $C_9H_7N_4O_4F_3$: C, 36.97; H, 2.38; N, 19.17. Found: C, 37.46; H, 2.28; N, 19.07.

Summary

The nitration of 1,1,1-trifluoropropane with nitric acid in the presence of oxygen at 437-462° yields 1,1,1-trifluoro-3-nitropropane (16%) and trifluoroacetaldehyde (20-24%). The specificity of the nitration reaction is attributed to the inductive effect of the trifluoromethyl group.

Trifluoroacetaldehyde resembles chloral in many of its properties. It forms a stable hydrate, undergoes a typical haloform reaction, and polymerizes during storage. The polymerization is reversed by heat or dilute bases.

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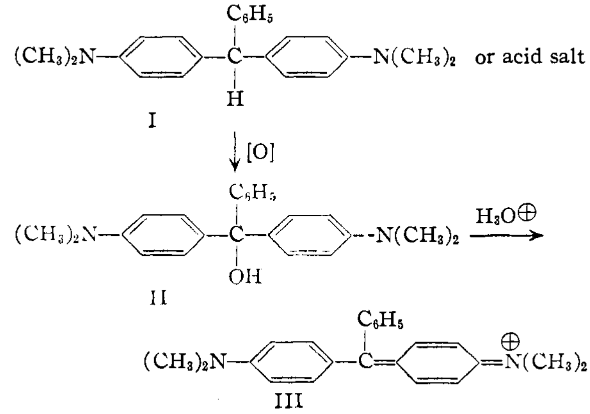
[CONTRIBUTION NO. 1174 FROM THE GATES AND CRELLIN LABORATORIES, CALIFORNIA INSTITUTE OF TECHNOLOGY, AND THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Mechanism of Oxidation of Leuco Malachite Green by Ceric Sulfate[1]

BY C. GARDNER SWAIN AND KENNETH HEDBERG

The mechanism of oxidation of carbon-hydrogen bonds in acid solution by oxidizing agents of high electrochemical potential such as potassium permanganate, ceric sulfate or lead dioxide has never been satisfactorily settled. It is customary to write successive replacements of hydrogen by hydroxyl, splitting out water where possible. For example, the oxidation of leuco malachite green (I) to malachite green (III) by any of these oxidizing agents in acid solution has generally been regarded as yielding first the carbinol or colorless "color base" (II) as the primary oxidation product, which is subsequently dehydrated to the dye (III).[2] Similarly, CH_3-$CH(OH)_2$ is frequently considered as an intermediate in the oxidation of ethanol to acetaldehyde.[3] These hydroxylations have been suggested as merely convenient ways of thinking, enabling one to predict the products obtained; there has been no evidence either supporting or disproving them as actual mechanisms.



The present study proves that carbinol (II) is *not* an intermediate in the conversion of leuco malachite green to dye in aqueous acid solution at room temperature when ceric sulfate is used as the oxidizing agent. The proof rests on the

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[1] Paper presented at 113th Meeting, American Chemical Society, Chicago, Illinois, April 20, 1948.

[2] Conant and Blatt, "Chemistry of Organic Compounds," third ed., Macmillan Company, New York, N. Y., 1947, pp. 532-533; Conant, *ibid.*, first ed., 1933, pp. 504-505.

[3] Fieser and Fieser, "Organic Chemistry," D. C. Heath and Company, Boston, Mass., 1944, pp. 130-131.