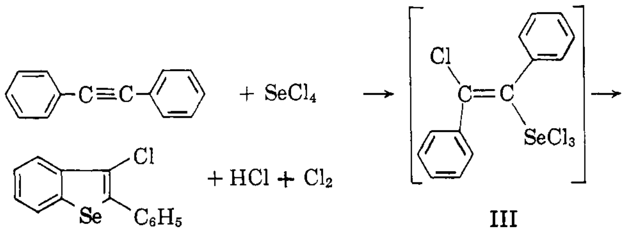
are known to occur[15] produced no other peaks than the ones reported above. Thus, the n.m.r. data also point to the exclusion of structure II.

Since evidence exists for addition of the selenium-trichloride group as a first step in addition reactions of selenium tetrachloride, reaction in this case probably proceeds by cyclization of the intermediate III.



III

Evidence that such an intermediate is involved is provided by the isolation of the tellurium analog of III from the reaction between tellurium tetrachloride and diphenylacetylene.[16] The authors do not report or consider the possibility of further conversion to 2-phenyl-3-chlorobenzotellurophene, so it can be assumed that the tellurium analog of III is more stable. However, it should be possible under appropriate conditions to produce the benzotellurophene analog of I.

Several experiments with sulfur tetrachloride substituting for selenium chloride have not led to an isolatable product, but further work will be carried out with this and other nonmetallic halides.

[12] D. S. Rao and B. D. Tilak, *J. Sci. Ind. Res.*, **18B**, 77 (1959).

[13] E. D. Bergmann and M. Rabinowitz, *J. Org. Chem.*, **25**, 828 (1960).

[14] C. W. Young, *et al.*, *Anal. Chem.*, **23**, 709 (1951).

[15] J. A. Pople, *et al.*, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chap. 5.

[16] M. de Moura Campus and N. Petrognani, *Tetrahedron*, **18**, 521 (1962).

Improved Synthesis of 3,3,3-Trifluoropropyne

William G. Finnegan and William P. Norris

U. S. Naval Ordnance Test Station, China Lake, California

Received November 21, 1962

A novel synthesis of 3,3,3-trifluoropropyne, $CF_3C{\equiv}CH$, has been discovered which gives high product yields (75%) from a readily available starting material in conventional glass apparatus. 1,1,2-Trichloro-3,3,3-trifluoropropene, $CF_3CCl{=}CCl_2$,[1] reacts exothermically with zinc dust in solvents such as dimethylformamide, N,N-dimethylacetamide and N-methyl-2-pyrrolidone to give a zinc salt of 3,3,3-trifluoropropyne. (Anhydrous zinc chloride is normally added to reduce the induction period.) Addition of water liberates 3,3,3-trifluoropropyne in excellent yield and purity.

$$CF_3CCl{=}CCl_2 + 2Zn \xrightarrow[ZnCl_2]{\text{solvent}}$$

$$(CF_3C{\equiv}C)_2Zn \text{ or } CF_3C{\equiv}CZnCl + ZnCl_2 \xrightarrow{H_2O} CF_3C{\equiv}CH$$

Acetic acid and absolute ethanol were relatively ineffective as reaction solvents: yields of about 10% of 3,3,3-trifluoropropyne were obtained in forty-eight-hour reactions at steam bath temperatures and the balance of the starting material was recovered. With dry dioxane no reaction occurred at reflux temperature even after six hours. Solvents such as formamide and 95% ethanol alter the course of the reaction. Yields of 3,3,3-trifluoropropyne varied from 12% to 32% and a variety of partially reduced products were obtained, including the previously uncharacterized *cis*- and *trans*-1,2-dichloro-3,3,3-trifluoropropenes. Similar reductive eliminations of vinylic halogen from 1,1,1,-4,4,4-hexafluoro-2,3-dichlorobutene-2 in a zinc–absolute ethanol mixture[2] and in a zinc–formamide mixture[3] have been observed. The former reaction gave a 30% yield of 1,1,1,4,4,4-hexafluoro-2-chlorobutene-2. The latter yields an appreciable percentage (41.2%) of (*trans*) 1,1,1,4,4,4-hexafluorobutene-2. Dehalogenation to yield 1,1,1,4,4,4-hexafluorobutyne-2 also occurred in each case.

Procedures previously described for the preparation of 3,3,3-trifluoropropyne include the dehydrohalogenations of $CF_3CH{=}CHX$[4–7] and $CF_3CX{=}CH_2$,[6,7] dehalogenations of $CF_3{-}CX{=}CXH$[6,7] and the reaction of sulfur tetrafluoride with propiolic acid.[8] Although yields obtained in these reactions may be comparable with or even superior to those described herein, the usefulness of this new synthesis is readily apparent.

A logical mechanism for this reaction involves dehalogenation of 1,1,2-trichloro-3,3,3-trifluoropropene to yield 1-chloro-3,3,3-trifluoropropyne, which in turn immediately reacts with zinc to yield the zinc acetylide. The ready reaction of the trichlorotrifluoropropene with zinc may be contrasted to the sluggish reaction of 1,2-dichloro-3,3,3-trifluoropropene[6]; the electron withdrawing power of the additional 1-chloro atom apparently facilitates the initial reaction with the zinc.

Experimental

3,3,3-Trifluoropropyne.—Zinc dust (36.0 g., 0.5 mole 90% purity), 3.4 g. (0.025 mole) of fused zinc chloride, and 200 ml. of dry redistilled N,N-dimethylacetamide, were placed in a 500-ml. three-necked flask fitted with a thermometer, addition funnel, stirrer and water cooled condenser leading to a Dry Ice–acetone trap. The reaction mixture was heated to 100° and the slow addition of 50.0 g., (0.025 mole) of 1,1,2-trichloro-3,3,3-trifluoropropene was started. An exothermic reaction usually occurred within 10 min., raising the temperature above 100°. Heating was discontinued and the temperature was maintained at 95–105° by adjusting the olefin addition rate and by directing an air blast on the flask. Addition was complete in approximately 1 hr., and the solution was allowed to cool to 50–60°. An infrared spectrum of the reaction solution showed the presence of a strong $C{\equiv}C$ absorption at 4.65 μ. No product was present in the Dry Ice trap at this time. The slow addition of 100 ml. of water with stirring was started and completed in 30 min.; the temperature was maintained at 50–60° by use of a heating mantle. An immediate vigorous gas evolution commenced and product collected in the Dry Ice trap. Heating was continued for an additional hour.

The product which collected in the Dry Ice trap was distilled directly into a steel sample cylinder and weighed; yield of $CF_3{-}C{\equiv}CH$, 17.7 g. (75.3%), b.p. $-48°$ to $-47°$/705 mm. Identification was based on boiling point, infrared spectrum, and mass spectrographic analysis. The boiling point coincides with that reported in the literature.[5] The infrared spectrum shows a C—H band at 2.99 μ, a strong band at 4.62 μ (—C≡C—), and strong absorptions at 8.0 to 8.5 μ (—CF_3). The mass spectrum gave a parent peak at 94. Analysis by vapor phase chromatography (squalene–Pelletex) indicated a purity of at least 99%.

Reactions run using dimethylformamide and N-methyl-2-

---

[1] A. L. Henne, *et al.*, *J. Am. Chem. Soc.*, **63**, 3478 (1941); $CF_3CCl{=}CCl_2$ is available from Columbia Organic Chemical Co., Columbia, S. C.

[2] A. L. Henne and W. G. Finnegan, *J. Am. Chem. Soc.*, **71**, 298 (1949).

[3] W. G. Finnegan, Ph.D. dissertation, Ohio State University, 1949.

[4] R. N. Haszeldine, *Nature*, **165**, 152 (1950).

[5] R. N. Haszeldine, *J. Chem. Soc.*, 588 (1951).

[6] R. N. Haszeldine, *ibid.*, 2495 (1951).

[7] A. L. Henne and M. Nager, *J. Am. Chem. Soc.*, **73**, 1042 (1951).

[8] W. G. Smith, *et al.*, *ibid.*, **81**, 3165 (1959).

pyrrolidone as solvents gave similar results, except that the latter solution jelled midway during the addition of water and stirring stopped. A 76.5% product yield was obtained nevertheless.

Reaction of $CF_3CCl{=}CCl_2$ with Zinc Dust in Formamide Solution.—The reaction was run as above, using 100 g. (0.5 mole) of 1,1,2-trichloro-3,3,3-trifluoropropene and 200 ml. of dry, redistilled formamide as the reaction solvent. The initial exothermic reaction commenced after about 5 min., low boiling material began to reflux shortly thereafter and condensation of trifluoropropyne and monochlorotrifluoropropene was observed in the trap. The reaction temperature dropped progressively to 60–65°, depending on the rate of addition of trichlorotrifluoropropene. Addition was completed in 1.5 hr. and the reaction mixture was stirred and refluxed for an additional 4 hr.; condensation rate of low boiling products in the trap had markedly decreased by this time. The reaction was worked up by distilling the intermediate boiling products into a Dry Ice–acetone cooled trap at slightly reduced pressure and combining these with the originally trapped product. Distillation of the combined product mixture through a 3-ft. center-rod column (condenser and receivers were cooled to −10°) gave the following fractions: (barometric pressure 702 mm.): $CF_3C{\equiv}CH$ (trap), 10.0 g., 21.3%, b.p −48° to −47°; $CF_3CCl{=}CH_2$,[6] 6.0 g., 9.2%, b.p. 13–15°; midcut, 3.2 g., 4.9%, b.p. 16° −50°, $n^{25}\text{D}$ 1.3511; $CF_3CCl{=}CHCl$ (*trans*-dichloro), 18.5 g., 22.6%, b.p. 51–52°, $n^{25}\text{D}$ 1.3638; mixed (*trans*) $CF_3CCl{=}CClH$ and $CF_3CH{=}CCl_2$, 8.1 g., 9.9%, b.p. 52–58°, $n^{25}\text{D}$ 1.3648; $CF_3CCl{=}CHCl$ (*cis*-dichloro), 5.0 g., 6.1%, b.p. 58°, $n^{25}\text{D}$ 1.3795; and $CF_3CCl{=}CCl_2$, 5.1 g., 5.1% (distillation residue). The material balance amounted to 78.9%. The three dichlorotrifluoropropenes are distinguishable by their proton n.m.r. spectra. 1,1-Dichloro-3,3,3-trifluoropropene, although not isolated from the *trans*-dichloro isomer is recognizable because of the relatively large coupling factor between the C-2 proton and the fluorines on the adjacent CF_3 group giving a quartet with widely separated peaks, τ = 3.85, J_{HF} = 6.4. The *trans* isomer, b.p. 51–52°, exhibits a quartet which is well resolved although the peaks are close together, τ = 2.92, J_{HF} = 1.1. The *cis* isomer, previously unreported, gives only a single broadened peak, τ = 3.35, $J_{HF} < 0.2$, indicating extremely weak coupling between proton and the CF_3 fluorines. The infrared spectrum for the *cis* isomer shows a C=C absorption at 6.22 μ. The mass spectrum shows parent peaks at mass units of 164, 166, and 168 in the expected ratio of 9.6:6.2:1. Vapor phase chromatography indicated a minimum purity of 95%. The major contaminant was identified as 1,1-dichloro-3,3,3-trifluoropropene on the basis of parent peaks at 164, 166, 168, and the absence of mass 116 (CF_3CCl^+) in its mass spectrum.

Anal. Calcd. for (*cis*) $C_3HCl_2F_3$: C, 21.84; H, 0.61; Cl, 42.99; F, 34.56. Found: C, 21.66; H, 0.81; Cl, 40.65; F, 34.34.

New Catalysts for the Oxidation of Sulfides to Sulfones with Hydrogen Peroxide

HERMAN S. SCHULTZ, HARLAN B. FREYERMUTH, AND SAUL R. BUC[1]

Central Research Laboratory, Dyestuff and Chemical Division, General Aniline and Film Corporation, Easton, Pennsylvania

Received April 27, 1962

It has recently become of practical economic importance to have a method available for the oxidation of hydroxyl groups containing sulfides to the corresponding sulfones which eliminates secondary degradative oxidation reactions, gives good yields, simplifies product isolation and purification, and conserves reagents. The method described below using tungsten, molybdenum, and vanadium catalysts with hydrogen peroxide in water substantially meets these requirements.

A large variety of methods for oxidation of sulfides to sulfones has been reported in the literature.[2-4] The desired products are obtained in a wide range of yield, purity, ease of experimental manipulation, and economic applicability. The oxidation of sulfides to sulfones is most generally carried out utilizing 30% hydrogen peroxide in glacial acetic acid. The intermediate sulfoxide is formed readily but the sulfone reaction is slower, generally requiring heat. There are several variations in procedure. An excess over the two moles of hydrogen peroxide needed to satisfy the stoichiometry of the reaction is slowly added with cooling. The mixture is allowed to react at room temperature overnight to form the sulfoxide, and then warmed on a steam bath to give the sulfone. Alternatively, the reaction solution is refluxed for at least one half hour after the hydrogen peroxide addition. The hydrogen peroxide can in some cases be added directly to the refluxing glacial acetic acid solution. In preliminary work on the oxidation of hydroxyethyl sulfides, it was often found that acetic acid esters contaminated the sulfone product. Yields often were not so high as subsequently attained by the new method. It also was found in the case of 2-sulfonylethanols that the use of neutralizing bases during product isolation and purification to remove acetic acid residues resulted in at least some catalyzed dehydration to vinyl sulfones. Very water-soluble products requiring neutralization of acetic acid before removal of water for isolation gave products containing a great amount of acetate salts.

Also in preliminary work, it was found that reactions of 2-thioethanols with hydrogen peroxide in water alone without catalyst required reflux in the presence of a large excess of hydrogen peroxide for a long period (0.5–1 day) to give impure sulfones in poor yields.[5]

The described drawbacks in the use of hydrogen peroxide are eliminated by the use as catalysts of inorganic compounds of tungsten, molybdenum, or vanadium in dissolved or colloidal form in aqueous solutions without the use of glacial acetic acid. The metals are in their highest oxidation state. This improvement is particularly useful for the preparation of 2-sulfonylethanols but has much wider applicability.[6-8]

Generally, the subject reactions are carried out at 60–75° by adding 31% hydrogen peroxide (with efficient stirring) to the molybdenum, vanadium, or tungsten catalyst containing aqueous mixture at such a rate that the peroxide concentration is kept low. The very rapid preferential oxidation of sulfides and sulfoxides at low hydrogen peroxide concentration and moderate temperature, in effect, eliminates the loss of

---

[1] Deceased, June 5, 1960.

[2] C. M. Suter, "Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 660–667.

[3] A. Schoberl and A. Wagner, "Methoden Der Organischen Chemie," Vol. 9, E. Müller, ed., Georg Thieme Verlag, Stuttgart, 1955, pp. 211–215, 227–231.

[4] E. Emmet Reid, "Organic Chemistry of Bivalent Sulfur," Vol. 2, Chemical Publishing Co., Inc., New York, N. Y., 1960, pp. 64–66.

[5] Improved but not best yields can be obtained by the use of small amounts of sequestering agents such as ethylenediaminetetracetic acid which apparently inhibit the secondary oxidation reactions.

[6] H. B. Freyermuth, H. S. Schultz, and S. R. Buc, U. S. Patent 3,005,852 (October 24, 1961) (assigned to General Aniline and Film Corp.).

[7] H. S. Schultz, S. R. Buc, and H. B. Freyermuth, U. S. Patent 3,006,962 (October 31, 1961) (assigned to General Aniline and Film Corp.).

[8] S. R. Buc, H. B. Freyermuth, and H. S. Schultz, U. S. Patent 3,006,963 (October 31, 1961) (assigned to General Aniline and Film Corp.).