Summary

Aldehydes and ketones can be reduced to alcohols by hydrogen and carbon monoxide (synthesis gas) in the presence of a cobalt catalyst, and the reaction can be applied to the reduction of compounds containing sulfur. A free radical mechanism is proposed for the hydrogenation.

When olefins are treated with 150–300 atmospheres of synthesis gas and a cobalt catalyst at 180–185°, alcohols containing one carbon atom more than the olefin are the principal products. Double bonds in some compounds, when treated under these conditions, are hydrogenated rather than hydroformylated.

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

Fluorinated Ethers

BY ALBERT L. HENNE AND MALCOLM A. SMOOK[1]

A fluorinated cluster, such as a CF_3 group, has a pronounced inductive effect on an adjacent function; it increases the acidity of an acid[2] or alcohol,[3] reduces the basicity of an amine,[4] reverses the polarity of a double bond,[5] and protects a CH bond from free radical attack.[6] The present paper considers the influence of fluorinated groups on an ether function,[7] when these groups are on one or on both sides of the oxygen bridge, in alpha or beta position.

In synthesizing new fluorinated ethers, good results were obtained by addition of alcohols to perfluoroethylene, a procedure which is here extended to fluorinated alcohols. Williamson type of reactions also succeeded well. The treatment of a fluorinated alcohol with diazomethane gave the expected methyl ether, but an attempt to use trifluorodiazoethane failed. Attempted acid dehydrations of trifluoroethanol and trifluoropropanol also failed and this was attributed to the loss of basic character of their oxygen, which hampered the formation of positive ions such as $CF_3CH_2OH_2^+$, followed or not by loss of a molecule of water to form $CF_3CH_2^+$; supporting this interpretation is the fact that trifluoroethanol gives only traces of the expected fluoroalkyl sulfate after long heating at 140° with sulfuric acid.[3]

Fluorinated groups lower the basic properties of the oxygen bridge. A group in alpha position is more effective than one further removed, and the presence of fluorinated groups on both sides of the bridge greatly enhances this effect: solubility in concentrated acids, and formation of complexes with Lewis acids such as ferric chloride is depressed by fluorine substitution on one side of the ether function and completely prevented by substitution on both sides. The loss of basic character is also shown in measurements of the heat of mixing with chloroform.[8] The formation of peroxides is, likewise, hampered or prevented.

Fluorinated groups in alpha position are sensitive to hydrolysis[9,10] except when they are protected by a polyfluorinated group such as CF_3 or CHF_2 in beta positions; other halogenated groups in beta position, such as CCl_3, $CHBr_2$, $CHCl_2$ or CHFBr, do not have that protecting effect. Polyfluorinated groups in beta or gamma positions are stable against hydrolysis or hydrogen fluoride removal.

The ether bridge of a beta fluorinated compound such as $CF_3CH_2OCH_2CF_3$ is very easily hydrolyzed. Since this ether is formed from an acidic alcohol, it is somewhat in the nature of an anhydride, and the situation recalls the fact that diaryl ethers are more easily cleaved than dialkyl ethers. The ether bridge of alpha fluorinated ethers could not be tested on account of the sensitivity of the alpha fluorinated group to hydrolysis. The ether bridge of perhalogenated ethers was found completely immune to hydrolysis with concentrated hydrogen iodide or oxidation with fuming nitric acid at high temperature.

The boiling points of several fluorinated ethers

TABLE I

BOILING POINTS, °C.

CH_3OCH_3	−23.6	$C_2H_5OC_2H_5$	34.5
$C_2F_3H_3O$	(30.1)[a]	$C_2F_5OC_2F_5$	5.0[b]
CF_3OCF_3	−59[b]	$CH_3CF_2OC_2H_5$	35.0
		$CH_3CF_2OCH_2CF_3$	37.8
$CH_3OC_2H_5$	10.8	$CF_3CH_2OC_2H_5$	49.8
$CF_2HOC_2H_5$	23.7	$CF_2HCF_2OCH_2CF_3$	56.7
$CH_3OCH_2CF_3$	31.2	$CF_2HCF_2OC_2H_5$	57.5
$CH_3OCF_2CF_2H$	39.5	$CF_2HCH_2OC_2H_5$	66.5
$CH_3OCH_2CF_2H$	47.0[c]	$CF_2HCH_2OCH_2CF_3$	70.5
$CH_3OC_3H_7$	39.0	$C_2H_5OC_3H_7$	63.6
$CH_3OCH_2CH_2CF_3$	54.8	$C_2H_5OCH_2CH_2CF_3$	72.2
$C_4H_9OC_4H_9$	142.0	$CF_2HCF_2OCH_2CH_2CF_3$	88.2
$C_4F_9OC_4F_9$	100.4[b]	$CF_2HCH_2OC_3H_7$	89.0

[a] Booth and Burchfield, THIS JOURNAL, **57**, 2070 (1935), do not give a developed formula; we believe this could not be CF_3OCH_3, but only CF_2HOCH_2F. [b] Data from Minnesota Mining and Manufacturing Co., St. Paul, Minnesota. [c] Swarts, *Bull. Acad. Roy. Belg.*, [3] **37**, 357 (1899).

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(1) Socony-Vacuum Fellow, 1948–1949.

(2) Swarts, *Bull. Sci. Roy. Acad. Belg.*, **8**, 343 (1922).

(3) Swarts, *Bull. Soc. Chim. Belg.*, **43**, 471–481 (1934).

(4) Gilman and Jones, THIS JOURNAL, **65**, 1458 (1943).

(5) Henne and Kay, *ibid.*, **72**, 3369 (1950).

(6) Henne, Hinkamp and Zimmerschied, *ibid.*, **67**, 1906 (1945); J. V. Schmitz, Ohio State Ph.D. dissertation, 1949; H. Schechter and F. Conrad, *ibid.*, **72**, 3371 (1950).

(7) J. D. Park, *ibid.*, **70**, 1550 (1948), gives a good bibliography.

(8) Lacher, McKinley and Park, *ibid.*, **70**, 2598 (1948).

(9) Hanford and Rigby, U. S. Patent 2,409,274 (1946).

(10) Young and Tarrant, THIS JOURNAL, **71**, 2432 (1949), and paper in preparation.

TABLE II

PHYSICAL CONSTANTS OF NEW COMPOUNDS

	p, mm.	B. p., °C.	t, °C.	d^t_4	n^tD	MR	AR_F	Fluorine, % Calcd.	Fluorine, % Found
$CF_2HCF_2OC_2H_5$	740	55.1	25	1.1978	1.294	22.38	1.1		
$CF_2HCF_2OCH_2CF_3$	760	56.7	20	1.4874	1.2728	23.03	1.2	66.5	64.8
$CF_2HCF_2OCH_2CH_2CF_3$	744	88.2	20	1.4087	1.3000	28.41	1.3		
$CF_3CH_2OCH_3$	746	31.2	3	1.1661	1.2942	17.96	1.2	50.0	7442
$CF_3CH_2OC_2H_5$	742	49.9	20	1.0910	1.3042	22.23	1.1	44.5	1443
$CF_3CH_2CH_2OCH_3$	753	54.9	20	1.1129	1.3114	22.27	1.1	44.5	8..8
$CF_3CH_2CH_2OC_2H_5$	746	72.3	20	1.0593	1.3258	27.04	1.1	40.3	.7.3
$CF_3CCl_2OCF_2CF_2Cl$	746	89.6	20	1.6486	1.3303	37.58	1.2	See text	
$C_4F_9OC_4F_9$	741	100.4	20	1.7288	1.2619	43.31	1.24	See text	

The second compound froze at −85.9°. The atomic refraction for fluorine, AR_F, was computed by subtracting from the molecular refraction the customary increments for C, H, O and Cl.

are listed in Table I. The perfluorinated ethers boil at lower temperatures than their unsubstituted analogs, in agreement with the general phenomenon shown by perfluorinated paraffins, acids and aldehydes, and attributed to lack of intermolecular association. Partly fluorinated ethers show internal and external association in varying degrees.

Experimental

Addition of Alcohols to Fluorinated Olefins.—Using the described procedure,[7,8] methanol and ethanol were easily added to $CF_2{=}CF_2$ in improved yields, but for trifluorinated alcohols the operating conditions had to be modified as follows. A 300-ml. autoclave charged with CF_3CH_2OH[11] (50 g. or 0.5 mole), sodium (1.5 g.) and $CF_2{=}CF_2$ (75 g. or 0.75 mole) was rocked for sixteen hours at 180° at a pressure of 40 atmospheres. After cooling, the residual pressure was released through a Dry-Ice trap. The liquid content of the vessel was then distilled to give 75 g. of crude ether, b. p. 51–61°, and the trap gave 3.5 g. more. The solid alcoholate left in the vessel was treated with water and 4 g. of CF_3CH_2OH thus recovered. The yield was 78.5% and the material balance 85%. Several runs were combined, washed with water, dried on calcium sulfate and distilled to give the sample of pure $CF_3CH_2OCF_2CF_2H$ described in Table II.

$CF_3CH_2CH_2OH$[12,13] (39 g. or 0.35 mole) was treated in like fashion, but at 200°. The pressure rose temporarily to 22 atmospheres, then fell back to 20 atmospheres. Working up of the reaction gave 3 g. of cyclo-C_4F_8, 19.7 g., of recovered $CF_3CH_2CH_2OH$, and 17.6 g. of crude ether, b. p. 89–90°. The conversion was 54% and the yield 59%, based on C_2F_4, or 24% and 47%, respectively, based on the trifluorinated alcohol. Purification was done by distillation from sodium, in the hope of freeing the ether of all traces of alcohol, but the AR_F shown in the table indicates that the final product was still slightly contaminated.

Attempted Dehydration of Fluorinated Alcohols.—CF_3CH_2OH was recovered intact after passage through concentrated sulfuric held at 200°, or after having been dripped on potassium hydroxide held at 190°, and it was partly transformed to a sulfonic ester but not to its ether by a treatment with *p*-toluenesulfonyl chloride. $CF_3CH_2CH_2OH$ was recovered intact by distillation from concentrated sulfuric acid.

Treatment with a Diazoderivative.—CF_3CH_2OH (0.32 mole) added at −10° to a diazomethane solution in petroleum ether (boiling range 57–80°) until complete fading of the yellow color gave a 27% of $CF_3CH_2OCH_3$. The reaction was repeated with 2 g. of aluminum isopropoxide in the diazomethane as an acid catalyst; after addition of the reagents, distillation was used to remove all materials boiling below 57°; on cooling, the distillate separated into two layers which were decanted; all fractions were washed with water, and from the combined aqueous portions 1 g. of trifluoroethanol was recovered; the lower layer of the distillate gave 27 g. (0.24 mole) of crude ether, b. p. 30–31° (75% yield and 78% material balance). The ether was contaminated with hydrocarbon; an attempted extraction of the ether with concentrated sulfuric acid gave a product which was still impure, as shown by a deficiency of 5% in the fluorine analysis while this type of analysis gives results which are only 1.5 to 2% too low. The synthesis was then repeated in dicyclohexyl, but gave only a 30% yield of ether slightly better in quality, and a 20% recovery of alcohol.

CF_3CH_2OH did not react with a pentane solution of CF_3CHN_2 containing a little aluminum isopropoxide; the yellow color persisted, and no nitrogen evolution occurred when the mixture was heated to reflux.

Williamson Type of Reactions.—This type of reaction has frequently been observed[14] while treating chlorofluorides and bromofluorides with alcoholic solutions of potassium hydroxide to obtain fluorinated olefins. When so treated, $CClF_2CH_3$ tends to give a mixture of $ROCF_2CH_3$ and $ROCClFCH_3$ rather than $CF_2{=}CH_2$; lower temperatures favor ether formation, while sodium ethylate, a stronger base, favors olefin formation. With CF_3CH_2ONa, a weaker base, ether formation could be expected to proceed favorably.

CF_3CH_2OH (85 g. or 0.85 mole) was treated with sodium (7.5 or 0.30 mole), then placed in an autoclave with CF_3ClCH_3 (20 g. or 0.20 mole). The vessel was rocked at 200°, the lowest effective temperature, for fifteen hours, at a pressure of 36 atmospheres. After cooling, some noncondensable gases and recovered $CClF_2CH_3$ (7.5 g.) were tapped off, and from the residual mass a treatment with ice water removed CF_3CH_2OH (60.5 g.) and separated the ether $CF_3CH_2OCF_2CH_3$ (4.9 g. or 24% yield). In glass, the pure redistilled ether remained clear, but in a stoppered vial it darkened in a few weeks, gave off acid vapors, etched the container, and developed a typical acetate odor.

Other Williamson reactions were similarly performed by heating the reagents in a steel vessel at 100°, unless otherwise stated.

$CHBrF_2$ and potassium hydroxide in absolute ethanol gave in fourteen hours a 31% yield of very impure and unstable $CHF_2OC_2H_5$, b. p. 23.3 to 24.0° at 743 mm., n^{22}D 1.304; this compound is on record[15] as b. p. 45–50°, by observation of a 1-cc. sample.

$CF_3CHClCH_3$ and potassium hydroxide in 95% ethanol gave 47% of a material which distillation separated into a fraction b. p. 65–67° at 752 mm., d^{25}_4 1.024, n^{25}D 1.331, containing fluorine but no chlorine and unsaturated as shown by a permanganate test, and a second fraction b. p. 41–42° at 4 mm. which was saturated and contained both fluorine and chlorine. The first fraction was interpreted

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[11] Henne, Alm and Smook, THIS JOURNAL, **70**, 1968 (1948).

[12] McBee and Truchan, *ibid.*, **70**, 2910 (1948).

[13] Henne, Pelley and Alm, *ibid.*, **72**, 3370 (1950).

[14] Swarts, *Bull. Acad. Roy. Belg.*, 383 (1901), and 563 (1911).

[15] Swarts, *ibid.*, 120 (1910).

as a mixture of $C_2H_5OCF_2CH{=}CH_2$ and $C_2H_5OCH_2CH_2CF_3$,[16] and the second fraction as $C_2H_5OCF_2CHClCH_3$.[17]

CF_3CH_2ONa and methyl iodide gave a compound b. p. 26–27°, $n^{25}D$ 1.3515 which separated into two layers at −78° and was probably a mixture of ether and iodine, in addition to 55% of recovered alcohol. This reaction was repeated with methyl bromide instead of iodide, a modification which permitted the isolation by distillation of the ether, $CF_3CH_2OCH_3$, in 43% conversion or 61% net yield. This is the same ether which the action of diazomethane on trifluoroethanol had given in impure form only.

CF_3CH_2ONa and ethyl chloride gave small amounts of crude ether, b. p. 45.2–47.2°, $n^{20}D$ 1.308. Using ethyl bromide instead of chloride gave 60% of good ether, $CF_3CH_2OC_2H_5$, purifiable by distillation.

$CF_3CH_2CH_2ONa$ and methyl bromide gave 43% of good ether, $CF_3CH_2CH_2OCH_3$; with ethyl bromide a 30% yield of the corresponding ethyl ether was obtained.

The reaction between CF_3CH_2ONa and $BrCH_2CF_2H$ gave an unstable product, b. p. about 70°, which decomposed steadily to give CF_3CH_2OH.

Perchlorination of $CF_3CH_2OCF_2CF_2H$.—This chlorination was performed to obtain a perhalogenated ether at a time when perfluorinated ethers were not yet available: tests were made on both types of materials, and they gave similar results. Chlorination of $CF_3CH_2OCF_2CF_2H$ was done by means of a stream of chlorine through the liquid held in a quartz flask illuminated by an ultraviolet lamp. The escaping gases (mostly hydrogen chloride) were passed through a Dry-Ice trap, the contents of which were periodically returned to the reaction flask. As soon as chlorination had proceeded far enough to raise the boiling point of the sample, heat was applied to maintain reflux. The chlorination was pursued for a whole week, as it had become exceedingly sluggish after the fourth day. The best sample so obtained was still contaminated with some hydrogen containing compound as shown by a chlorine analysis of 33.2% instead of 35.1% for $C_4OCl_3F_7$ and 26.5% for $C_4HOCl_2F_7$.

Examination of $C_4OCl_3F_7$.—This compound was soluble in ether and in 95% ethanol, insoluble in phosphoric or sulfuric acids; it did not dissolve ferric chloride; it did not hydrolyze in sulfuric acid at 90° in fifteen minutes, as shown by negative tests for the chlorine and fluorine ions; it remained colorless after 48 hours of reflux from fuming nitric acid; after completing this test, the refractive index of the organic layer had dropped to only 1.3294, and the acid layer gave negative tests for the chlorine and fluorine ions; a repetition of the nitric acid test, in sealed tube at 150° gave the same negative results; after 24 hours of heating with 48% hydriodic acid in sealed tube at 150°, the compound showed no change in refractive index.

Examination of $C_8F_{18}O$.—After redistillation, a sample of $C_4F_9OC_4F_9$, gift of the Minnesota Mining and Manufacturing Co., showed the physical properties listed in the table. It was insoluble in water and in 95% alcohol, and only partly soluble in ether; it did not dissolve ferric chloride, nor react upon addition of calcium hydride; it did not dissolve in phosphoric acid; it was unaffected by a 48-hour period of refluxing from fuming nitric acid, as shown by the absence of fluorine ions; the hydriodic test at 150° for 24 hours caused no change in refractive index, and did not generate fluorine ions.

Summary

Ethers with polyfluorinated groups on one or on both sides of their oxygen atom have been synthesized. The stability of the halogens, the strength of the oxygen bridge and the loss of basic character of the ether function have been examined and related to the position of the fluorinated groups.

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(16) This mixture was similar to that obtained in the base catalized addition of ethanol to $CF_3CH{=}CH_2$, discussed in a paper now in preparation.

(17) This would be the result of a reaction similar to the formation of $C_6H_5OCF_2CHClCF_3$ from $CF_3CHClCF_3$ and sodium phenate, McBee and Bolt, *Ind. Eng. Chem.*, **39**, 412 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Preparation and Some Reactions of 1,1,1-Trifluoro-2-alkenes[1]

BY KENNETH N. CAMPBELL, JAMES O. KNOBLOCH[2] AND BARBARA K. CAMPBELL

The addition reactions of olefins containing a trifluoromethyl group adjacent to the double bond should be of considerable interest. This group would be expected to exert a strong electron-attracting inductive effect and, as it contains no double bonds, there is no possibility of addition to a conjugated system to complicate the results. Some work has been done on the closely related trichloro methyl ethylenes[3,4] but in this case an allylic shift of one of the chlorine atoms is apt to occur.[3,4,5] The fluorine atoms of the trifluoromethyl group are held so tightly to the carbon atom[6] that a similar allylic rearrangement appears unlikely. Practically no work seems to have been reported on the addition reactions of trifluoromethyl ethylenes. We have therefore, undertaken a study of the addition reactions of olefins containing the group $F_3C{-}\overset{|}{C}{=}C<$, and in the present paper are reporting methods of preparation and preliminary results on some addition reactions.

Very few trifluoromethyl ethylenes have been reported. Henne and Hinkamp[7] have prepared 1,1,1-trifluoro-2-butene by the dehydrohalogenation of 1,1,1-trifluoro-3-chlorobutane, and 1,1,1-trifluoro-2-propene has been prepared in a similar manner.[8,9] This procedure is not practical for the preparation of higher homologs, however, as the intermediate chloro compounds are not readily available.

Swarts[10] synthesized 1,1,1-trifluoro-2-methyl-2-

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(1) From the Ph.D. dissertation of James O. Knobloch, University of Notre Dame, June, 1949. Presented at the Organic Division, Atlantic City meeting of the American Chemical Society, September 1949.

(2) Standard Oil of Indiana Fellow, University of Notre Dame, 1947–1949.

(3) Price and Marshall, *J. Org. Chem.*, **8**, 532 (1943).

(4) Kharasch, Rossin and Fields, THIS JOURNAL, **63**, 2558 (1941).

(5) Jacob, *Bull. soc. chim.*, [5] **7**, 581 (1940).

(6) Gilman, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1943, Vol. I, 956.

(7) Henne and Hinkamp, THIS JOURNAL, **67**, 1194 (1945).

(8) Sherer, I. G. Farbenindustrie A.-G. Report, Frankfurt (Main), April 3, 1941.

(9) Henne and Waalkes, THIS JOURNAL, **68**, 497 (1946).

(10) Swarts, *Bull. soc. chim. Belg.*, **36**, 199 (1927).