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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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Fluorinated Ethers

BY ALBERT L. HENNE AND MALCOLM A. SMOOK¹

A fluorinated cluster, such as a CF_3 group, has a pronounced inductive effect on an adjacent function; it increases the acidity of an acid² 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 trifluorodiazomethane 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 $\text{CF}_3\text{CH}_2\text{-OH}_2^+$, 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 CH_2Br , 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 $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CF}_3$ 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	$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	34.5
$\text{C}_2\text{F}_5\text{H}_2\text{O}$	(30.1) ^a	$\text{C}_2\text{F}_5\text{OC}_2\text{F}_5$	5.0 ^b
CF_3OCF_3	-59 ¹¹	$\text{CH}_3\text{CF}_2\text{OC}_2\text{H}_5$	35.0
		$\text{CH}_3\text{CF}_2\text{OCH}_2\text{CF}_3$	37.8
$\text{CH}_3\text{OC}_2\text{H}_5$	10.8	$\text{CF}_3\text{CH}_2\text{OC}_2\text{H}_5$	49.8
$\text{CF}_2\text{HOC}_2\text{H}_5$	23.7	$\text{CF}_2\text{HCF}_2\text{OCH}_2\text{CF}_3$	56.7
$\text{CH}_3\text{OCH}_2\text{CF}_3$	31.2	$\text{CF}_2\text{HCF}_2\text{OC}_2\text{H}_5$	57.5
$\text{CH}_3\text{OCF}_2\text{CF}_2\text{H}$	39.5	$\text{CF}_2\text{HCH}_2\text{OC}_2\text{H}_5$	66.5
$\text{CH}_3\text{OCH}_2\text{CF}_2\text{H}$	47.0 ^c	$\text{CF}_2\text{HCH}_2\text{OCH}_2\text{CF}_3$	70.5
$\text{CH}_3\text{OC}_2\text{H}_7$	39.0	$\text{C}_2\text{H}_5\text{OC}_2\text{H}_7$	63.6
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CF}_3$	54.8	$\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{CF}_3$	72.2
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	142.0	$\text{CF}_2\text{HCF}_2\text{OCH}_2\text{CH}_2\text{CF}_3$	88.2
$\text{C}_2\text{F}_5\text{OC}_2\text{F}_5$	100.4 ¹¹	$\text{CF}_2\text{HCH}_2\text{OC}_2\text{H}_7$	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 $\text{CF}_2\text{HOCH}_2\text{F}$. ^b Data from Minnesota Mining and Manufacturing Co., St. Paul, Minnesota. ^c Swarts, *Bull. Acad. Roy. Belg.*, [3] **37**, 357 (1899).

(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.

(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.

TABLE II
 PHYSICAL CONSTANTS OF NEW COMPOUNDS

	ρ , mm.	B. p., °C.	t_g , °C.	d_4^4	n_D^{20}	MR	AR _F	Fluorine, %	
								Calcd.	Found
CF ₂ HCF ₂ OC ₂ H ₅	740	55.1	25	1.1978	1.294	22.38	1.1		
CF ₂ HCF ₂ OCH ₂ CF ₃	760	56.7	20	1.4874	1.2728	23.03	1.2	66.5	64.8
CF ₂ HCF ₂ OCH ₂ CH ₂ CF ₃	744	88.2	20	1.4087	1.3000	28.41	1.3		
CF ₃ CH ₂ OCH ₃	746	31.2	3	1.1661	1.2942	17.96	1.2	50.0	74.42
CF ₃ CH ₂ OC ₂ H ₅	742	49.9	20	1.0910	1.3042	22.23	1.1	44.5	14.43
CF ₃ CH ₂ CH ₂ OCH ₃	753	54.9	20	1.1129	1.3114	22.27	1.1	44.5	8.8
CF ₃ CH ₂ CH ₂ OC ₂ H ₅	746	72.3	20	1.0593	1.3258	27.04	1.1	40.3	7.3
CF ₃ CCl ₂ OCF ₂ CF ₂ Cl	746	89.6	20	1.6486	1.3303	37.58	1.2	See text	
C ₄ F ₉ OC ₄ F 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 CF₂=CF₂ in improved yields, but for trifluorinated alcohols the operating conditions had to be modified as follows. A 300-ml. autoclave charged with CF₃CH₂OH¹¹ (50 g. or 0.5 mole), sodium (1.5 g.) and CF₂=CF₂ (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 CF₃CH₂OH 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 CF₃CH₂OCF₂CF₂H described in Table II.

CF₃CH₂CH₂OH^{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-C₄F₈, 19.7 g., of recovered CF₃CH₂CH₂OH, and 17.6 g. of crude ether, b. p. 89–90°. The conversion was 54% and the yield 59%, based on C₂F₄, 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.—CF₃CH₂OH was recovered intact after passage through concentrated sulfuric acid 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. CF₃CH₂CH₂OH was recovered intact by distillation from concentrated sulfuric acid.

Treatment with a Diazoderivative.—CF₃CH₂OH (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 CF₃CH₂OCH₃. 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 mate-

rials 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.

CF₃CH₂OH did not react with a pentane solution of CF₃CHN₂ 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 observed¹⁴ while treating chlorofluorides and bromofluorides with alcoholic solutions of potassium hydroxide to obtain fluorinated olefins. When so treated, ROCCF₂CH₃ tends to give a mixture of ROCCF₂CH₃ and ROCCFCH₃ rather than CF₂=CH₂; lower temperatures favor ether formation, while sodium ethylate, a stronger base, favors olefin formation. With CF₃CH₂ONa, a weaker base, ether formation could be expected to proceed favorably.

CF₃CH₂OH (85 g. or 0.85 mole) was treated with sodium (7.5 or 0.30 mole), then placed in an autoclave with CF₂-CICH₃ (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 non-condensable gases and recovered CClF₂CH₃ (7.5 g.) were tapped off, and from the residual mass a treatment with ice water removed CF₃CH₂OH (60.5 g.) and separated the ether CF₃CH₂OCF₂CH₃ (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.

CHBrF₂ and potassium hydroxide in absolute ethanol gave in fourteen hours a 31% yield of very impure and unstable CHF₂OC₂H₅, b. p. 23.3 to 24.0° at 743 mm., n_D^{20} 1.304; this compound is on record¹⁵ as b. p. 45–50°, by observation of a 1-cc. sample.

CF₃CHClCH₃ 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_4^{25} 1.024, n_D^{20} 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

(11) Henne, Alm and Smook, *THIS JOURNAL*, **70**, 1068 (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).

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