methyl difluoroacetate, and 24 g. of dimethyl difluoro-malonate (*Anal.* Calcd.: F, 22.6. Found: F, 22.5), a 67% yield. A solution of 2 g. of this ester in 8 g. of ethyl ether was treated at 0° with anhydrous ammonia. White crystals formed at once, and 1.6 g. of amide, m. 206.5-206.7°, was collected, the theoretical yield. Nitrogen analysis indicated 20.1% (calculated, 20.3%).

The same amide (as determined by mixed melting point) was also obtained by oxidation of CCl_2=$CClCF_2CCl$=CCl_2 but this oxidation was slow; it required long heating, and the yield was poor. Better operating conditions were not worked out.

Summary

Diethyl ketone was transformed into 3,3-di-fluoropentane and the latter subjected to chlorination. The directing effect of the CF_2 group upon the first two chlorine atoms entering the organic molecule was ascertained, before perchlorination was allowed to proceed. From saturated derivatives, two non-conjugated dienes were prepared, CH_2=$CHCF_2CH$=CH_2 and CCl_2=$CClCF_2CCl$=CCl_2, both of which were oxidized to difluoromalonic acid. The latter was transformed into its dimethyl ester by means of diazomethane, and characterized as its crystalline diamide.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

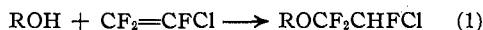# Polyfluoro Alkyl Ethers and their Preparation

BY J. D. PARK, D. K. VAIL, K. R. LEA AND J. R. LACHER

Alkyl ethers containing fluorine were previously prepared by Swartz[1-3] by the action of alcoholic caustic or metallic carbonate on polyfluorohalo-ethanes. This procedure was later modified by Gowland.[4] Aryloxy alkanes containing fluorine also were prepared by McBee and Bolt[5] by a similar reaction. In the present work, alkoxy-2-chloro-1,1,2-trifluoroethanes were prepared by the base-catalyzed addition of alcohol to chlorotrifluoroethylene carried out at room temperature and atmospheric pressure. This type of addition to fluoroolefins was first carried out by Hanford and Rigby[6] under autogenous pressure and at elevated temperatures in the presence of sodium alkoxide as a catalyst.

Starting Materials.—The various alcohols and chemicals used in this study were of technical grade. When deemed necessary they were purified by distilling before using. The compound, CF_2ClCCl_2F, used as an intermediate in the preparation of chlorotrifluoroethylene was of "refrigerant-grade" furnished us through the courtesy of Mr. R. J. Thompson of the Kinetic Chemicals, Inc. Chlorotrifluoroethylene was obtained by dehalogenation of CF_2-$ClCCl_2F$ with ethanolic zinc according to a known method.[7] Fractionation of the product showed the pure olefin to boil at −34 to −35° at 630 mm. pressure.

Preparation of Ethers.—The general reaction involved is

$$ROH + CF_2{=}CFCl \longrightarrow ROCF_2CHFCl \quad (1)$$

According to Pauling's[8] bond energies, the vapor phase reaction should be exothermic to the extent of 5.7 kcal. The entropy change is not known but may be estimated by analogy with similar reactions,[9-12] to be around −28 e. u. The free energy change at 298°K. is +2.6 kcal. and becomes zero at 200°K. It is apparent, therefore, that an equilibrium would be favored by low temperatures and high pressures. Since the reaction was quite rapid at room temperature and slightly above, it was not necessary to employ high pressures. An excess of alcohol was used in all cases.

In the experimental arrangement finally chosen, the olefin, CF_2=$CFCl$, from a cylinder was bubbled through a dispersion disk at the bottom of a long vertical tube filled with a potassium hydroxide saturated solution of the alcohol. The outlet end of the tube was connected to an upright water condenser. The unreacted olefin escaping through the condenser was led into a second potassium hydroxide–alcohol solution. The flow of organic through the disk was so regulated that most of the reaction took place in the first reactor. The reaction was quite slow at first. However, as soon as some ether was formed, the rate increased quite rapidly with a resultant rise in temperature. After the necessary amount of olefin had reacted with the alcohol, the reaction mixture was poured into water. The excess alcohol was completely removed by washing with water and the heavier ether layer separated. The ether was then dried over "Drierite" and fractionated in a laboratory precision column.

The addition of alcohols to chlorotrifluoroethylene may proceed to give the product listed in equation I or the structure may be $ROCClFCHF_2$. It is believed that the structure containing the —$CHFCl$ group is the more probable. This is indicated by the formation of $CHFCl$-$COOH$ in the catalytic hydrolysis of the ethyl ether in the presence of silica gel.[8] The second structure is not consistent with the relative stabilities of the ethers (with the possibile exception of the isopropyl derivative). This structure would permit the elimination of hydrochloric acid quite easily with the formation of $ROCF$=CF_2. Such a compound was not isolated under our reaction conditions. If the addition of alcohols to chlorotrifluoroethylene leads to the thermodynamically most stable product, then considerably more heat must be liberated when the isomer containing the —$CHFCl$ group is formed, in which case tables of bonding energies will not be sufficiently precise to determine the course of the reaction.

(1) F. Swartz, *Bull. acad. roy. Belg.*, [3] **37**, 357-383 (1899).

(2) F. Swartz, *ibid.*, 563-589 (1911).

(3) F. Swartz, *Mem. Courones Acad. roy. Belg.*, **61**, 94 (1901); *Chem. Zentr.*, **74**, I, 12-14 (1903).

(4) T. B. Gowland (to Imperial Chem. Ind.), Brit. Patent 523,449 (July 15, 1940).

(5) E. T. McBee and R. O. Bolt, *Ind. Eng. Chem.*, **39**, 412 (1947).

(6) W. E. Hanford and G. W. Rigby (to du Pont), U. S. Patent, 2,409,274 (Oct. 15, 1946).

(7) E. G. Locke, W. R. Brode and A. L. Henne, THIS JOURNAL, **56**, 1726 (1934).

(8) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1944.

(9) J. G. Aston, *Ind. Eng. Chem.*, **34**, 514 (1942).

(10) G. R. Cuthbertson and G. B. Kistiakowsky, *J. Chem. Phys.*, **3**, 631 (1935).

(11) K. K. Kelley, Bureau of Mines, Bulletin 434.

(12) H. A. Smith and W. E. Vaughan, *J. Chem. Phys.*, **3**, 341 (1935).

TABLE I

PHYSICAL PROPERTIES OF POLYFLUORO ALKYL ETHERS

Formula	B. p., °C. 630 mm.	d^{20}_4	$n^{20}_D{}^a$	MR^b	$AR_F{}^c$	Fluorine analyses, %	
						Calcd.	Found
$CH_3OCF_2CHFCl^d$	64.4	1.3632	1.33381	22.460	1.063	38.4	38.2
$C_2H_5OCF_2CHFCl$	82.0	1.2726	1.34787	27.163	1.094	35.0	34.8
$n\text{-}C_3H_7OCF_2CHFCl$	102.3	1.2173	1.35751	31.814	1.105	32.3	32.1
$Iso\text{-}C_3H_7OCF_2CHFCl$	94.0	1.2010	1.35211	31.800	1.100	..	..
$n\text{-}C_4H_9OCF_2CHFCl$	124.5	1.1779	1.36796	36.448	1.100	29.9	29.8

[a] Determinations made with a Pulfrich refractometer. [b] MR denotes molecular refraction calculated by the Lorentz–Lorenz formula. [c] AR_F denotes the atomic refraction for fluorine obtained from MR by subtracting the customary increments for C, H, Cl, O, and the ether linkage. [d] This compound has also been prepared by Miller, et al., THIS JOURNAL, **70**, 432 (1948).

The fact that the ethers were obtained in yields between 70 and 85% indicates that the heat of reaction is greater than that calculated.

Physical Properties.—Some physical properties of the ethers are listed in Table I. The boiling points, densities, and refractive indices are in line with what one might expect for an homologous series. The atomic refraction for fluorine is reasonable for compounds of this type.

The absorption spectra of the ethers were measured using a Beckman quartz spectrophotometer model DU. Pure cyclohexane was used as a reference liquid and the experiments were carried out in a 10-mm. quartz cell. The ethers were transparent from 9000 to about 3600 Å. Below this wave length they absorb strongly. The curves in the ultraviolet region are given in Figs. 1 and 2. In order to bring out the details of the curves, the logarithm of the extinction coefficient, log E, is given as a function of wave length in Ångstrom units.

the methyl compound the peaks occur at 2420, 2480, 2540 and 2600 Å. giving separations between them of 1000, 950 and 900 cm.$^{-1}$, respectively. The isopropyl ether shows peaks of 2535, 2605, and 2685 Å. with separations of 1050 and 1150 cm.$^{-1}$. These frequencies may be reliable to $\pm 10\%$ and could correspond either to a C–F or C–C stretching vibration.[13] It is also possible for a bending motion in the molecule to have a frequency in this range.

The isopropyl compound shows a slight shoulder between 2800 and 2900 Å., which, in case of the n-propyl derivative, is a distinct broad band. The n-butyl ether gives only a shoulder. Absorption in this region may be due to unresolvable fine structure or to the presence of small amounts of the isomer formed by the reverse addition of the alcohol to chlorotrifluoroethylene. We plan to extend absorption studies to longer wave lengths using our infrared spectrometer.
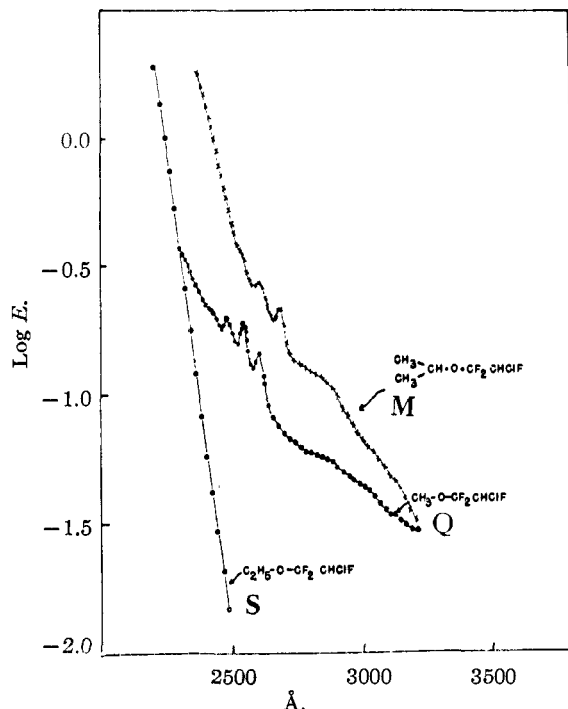

Fig. 1.—Ultraviolet absorption spectra of some alkyl fluoroethers. Logarithm of the extinction coefficient against wave length in Ångström units.
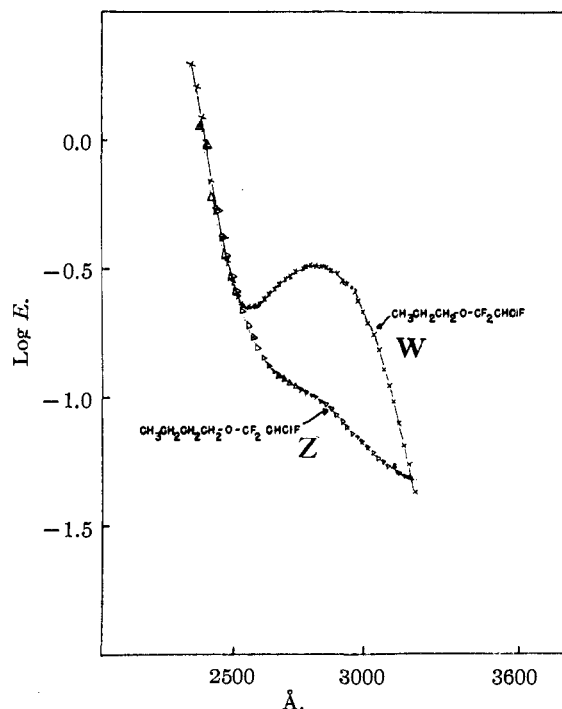

Fig. 2.—Ultraviolet absorption spectra of some alkyl fluoroethers. Logarithm of the extinction coefficient plotted against wave length in Ångström units.

In case of the ethyl ether, absorption sets in sharply below 2500 Å. The logarithm of the extinction coefficient as a function of the wave length is a straight line and no structure is evident. Both the methyl and isopropyl ethers show vibrational fine structure. In case of

Summary

This paper reports the base-catalyzed addition

(13) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., New York, N. Y., 1945.

of alcohols to chlorotrifluoroethylene resulting in the formation of ethers of the type $ROCF_2CFClH$, which in general are quite stable. The reaction is carried out at room temperature and atmospheric pressure. Some of the physical properties of the ethers, along with their ultraviolet absorption spectra are discussed.

Alkylation of Thiophene with Olefins[1]

BY W. G. APPLEBY, A. F. SARTOR, S. H. LEE, JR.,[2] AND S. W. KAPRANOS[3]

In connection with other work in these laboratories, it was necessary to prepare several alkyl thiophenes. When the experimental work was started in 1943, no method of preparation of the desired compounds which would meet our needs was found in the literature. It seemed worthwhile, consequently, to investigate the possibility of the direct alkylation of thiophene with appropriate olefins. This paper presents the results of our investigation of the alkylation of thiophene with propylene and isobutylene.

In the intervening time, the direct alkylation of thiophene by olefins and alcohols was reported by Kutz and Corson.[4] These authors reported the results of two experiments on the direct alkylation of thiophene with propylene and isobutylene under conditions considerably removed from those to be presented here. It is remarkable that in these experiments no evidence was presented for the formation of 3-isopropyl- and 3-t-butylthiophene, whereas in the experiments described below a considerable reaction to the 3-isomer was observed with each olefin. An explanation of the discrepancy will be presented in following sections of this paper.

Experimental

Purity of Chemicals.—The catalyst was phosphoric acid on kieselguhr (50–60%) manufactured by Universal Oil Products Company. The commercial 1/4-inch pellets were cut into 1/8-inch pellets. A fresh sample of catalyst was used for each experiment.

Synthetic thiophene was obtained from the Eastman Kodak Company. Satisfactory purity of the sample was indicated by a comparison of its properties with those reported in the literature: our sample, $n^{20}D$ 1.5287, d^{20}_4 1.0646; literature,[5] $n^{20}D$ 1.5286, d^{20}_4 1.0642.

Technical isobutylene from the Phillips Petroleum Corporation and propylene from the Ohio Chemical Company were used. The propylene had a purity of 98%, and the isobutylene contained a maximum of 4% isobutane as the only impurity.

Apparatus.—The alkylation reactions were carried out under continuous flow conditions in an 18–8 stainless steel reactor with a one-inch diameter. The unit was pressured with nitrogen prior to the introduction of thiophene and the olefin. For experiments in which 1:1 thiophene to

olefin mole ratios were used, the liquids were charged from separate cylinders of a dual displacement pump. Higher thiophene to olefin ratios were obtained by dissolving the liquid olefin in the thiophene and maintaining the mixture at a low temperature until it was charged to the pump.

Alkylation of Thiophene with Propylene.—The alkylation of thiophene with propylene was carried out at 288°, 21.5 atmospheres, 1.1 thiophene to propylene mole ratio, and a flow rate of 3.6 g. of liquid charge per gram of catalyst per hour (WHSV). Under these conditions 70% of the thiophene and 50% of the propylene reacted to give an 80% by weight yield of liquid product which contained 40% mono-isopropylthiophene and significant amounts of di-isopropylthiophenes. This was equivalent to 30–35% conversion of propylene to the mono-isopropylthiophene. The amount of mono-isopropylthiophene recovered in in each experiment was too small for analysis. The combined monoalkylate fractions from several experiments were therefore distilled and then hydrogenated over a catalyst of mixed tungsten and nickel sulfides[6] at 288°, 33 atmospheres pressure, 0.1 WHSV and a hydrogen/-alkylate molal ratio of 15. The resulting paraffin hydrocarbons, as determined by physical properties and infrared spectra, consisted by weight of 38% 2,3-dimethylpentane, 54% 2-methylhexane and 8% of lower boiling hydrocarbons (perhaps from the propylene polymerization reaction). These values correspond to a relative distribution by weight of the mono-isopropylthiophenes in the liquid product of 41% 3-isopropylthiophene and 59% 2-isopropylthiophene.

Although the isopropylthiophenes were not purified as efficiently as the t-butylthiophenes (see below), the physical properties of selected distillation cuts were as follows: 2-isopropylthiophene,[7] b. p. 152.0°, $n^{20}D$ 1.5037, d^{20}_4 0.9673; 3-isopropylthiophene,[7] b. p. 155.5°, $n^{20}D$ 1.5060, d^{20}_4 0.9722.

Infrared analysis of the C_{10} hydrocarbons resulting from the hydrogenation of the di-isopropylthiophenes showed that the principal product was 2,7-dimethyloctane (from 2,5-di-isopropylthiophene). The presence of the other three possible decanes (2,3,4,5-tetramethylhexane, 2,3,6-trimethylheptane, and 2,5-dimethyl, 3-ethylhexane) was also indicated.

Alkylation of Thiophene with Isobutylene.—No physical properties were available in the literature for t-butylthiophene. Consequently, in order to have this information for identification of the products in later experiments, it was necessary to prepare pure samples of these compounds for such determinations. The liquid product for this purpose was prepared by alkylating thiophene with isobutylene (1:1 mole ratio) at 21.5 atmospheres, 270°, and a WHSV of 4.3.

The liquid product from this experiment was distilled in a column having nine theoretical plates at total reflux. This distillation separated the product roughly into three fractions: (1) unreacted thiophene, (2) mono-alkylthio-

(1) Presented before the Organic Division at the September, 1947, meeting of the American Chemical Society at New York City.

(2) Present address: Department of Chemistry, University of Texas, Austin, Texas.

(3) Present address: Corn Products Company, Chicago, Illinois.

(4) Kutz and Corson, THIS JOURNAL, **68**, 1477 (1946).

(5) Haines, Wanger, Helm and Ball, U. S. Bur. Mines, R. I. 4060 (1946).

(6) Appleby, Lovell and Love, U. S. Patent 2,429,575 (1947).

(7) Haines, et al., ref. 5, reported for the 2-isomer, b. p. 153°, $n^{20}D$ 1.503, d^{20}_4 0.967; for the 3-isomer, b. p. 157°, $n^{20}D$ 1.505, d^{20}_4 0.973.