point, 101.5–102.5°, refractive index and infrared absorption.

Materials.—Eastman Kodak Co. benzotrichloride, Practical, was fractionated through a 33-plate column, and the fraction boiling at 101° at 17 mm. was used.

When possible, commercial fluorides were used directly. Potassium fluoride hydrate was dehydrated by heating[7a] and copper and aluminum fluoride hydrates by treatment with hydrogen fluoride.[7b] Insoluble bismuth,[7c] cadmium[7d] and lead[7a] fluorides were prepared by precipitation and manganese fluoride by the method of Nuka.[7d]

Results

The fluorides of lithium, potassium, calcium, magnesium, aluminum and manganese gave no benzotrifluoride. With the other fluorides the yields were: NaF, 15; ZnF_2, 70; CdF_2, 15; CoF_2, 18; PbF_2, 45; SbF_3, 60-65[8]; BiF_3, 29; CuF_2, 44%.

The results show that the reactive fluorides are those of metals (except sodium) with oxidation–reduction potentials below that of manganese. Within this group there is no parallelism between yield and potential.

There also appears to be no correlation of the activities of these fluorides with crystal structures of the fluorides or chlorides, nor with their solubilities in organic solvents.

Summary

Bismuth, cadmium, cobalt, copper, lead, sodium and zinc fluorides are effective in the fluorination of benzotrichloride.

There is a qualitative relationship between the reactivity of various metal fluorides with benzotrichloride and the oxidation–reduction potential of the metal–metal ion couple.

DURHAM, N. H. RECEIVED FEBRUARY 8, 1949

[7] (a) Fremy, *Ann. chim. phys.*, [3] **47**, 27 (1856); (b) Poulenc, *ibid.*, [7] **2**, 58 (1894); (c) Hassel and Nilssen, *Z. anorg. Chem.*, **181**, 172 (1929); (d) Nuka, *ibid.*, **180**, 235 (1929).

[8] For liquid phase reaction: Henne, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1944, Vol. II, p. 62.

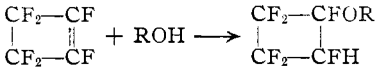
[CONTRIBUTION FROM THE UNIVERSITY OF COLORADO]

Action of an Alcohol on Perfluorocyclobutene[1,2]

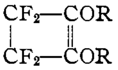
BY J. D. PARK, M. L. SHARRAH[3] AND J. R. LACHER

A review of the art on the preparation of fluorinated ethers has been previously covered.[4]

The present study involves the reaction of alcohols with hexafluorocyclobutene in the presence of a base. By analogy with previous evidence[5,6,7] this reaction was expected to follow the equation



Instead, there was obtained a compound of the general formula



Starting Materials.—Perfluorocyclobutene was made by the procedure of Henne[8] from $CF_2{=}CFCl$, a gift of the du Pont Company. The cyclobutene boiled at 0.0 to 0.6° at 630 mm. The alcohols were of technical grade. The reaction with methanol serves as an example for ethyl, *n*-propyl and *n*-butyl alcohols.

Procedure.—A six-foot section of 20-mm. tubing was mounted in a vertical position and fitted with a sintered glass dispersion disk at the bottom and an upright, water-cooled reflux condenser at the top. The outlet end of the condenser was connected by means of rubber tubing to a secondary bubbler. Both the main reaction tube and the secondary bubbler were roughly half-filled with 10% potassium hydroxide–methanol solution. Exactly 279 g. of pure hexafluorocyclobutene from a cylinder was bubbled into the methanolic alkali over a period of four hours. The flow of the olefin through the disk was adjusted so that practically all the reaction occurred in the main reaction tube. The reaction was quite slow at first. However, as the reaction proceeded, the rate increased rapidly with resultant warming of the solution and rise in liquid level. The spent methanolic alkali solution was removed and replaced with new solution several times during the course of the reaction. This was presumably due to the formation of alkali fluoride, which effectively removed the basic catalyst. Upon completion of the reaction, the reaction mixture was poured into water and the product separated as a lower layer. The product was washed several times with water and dried over calcium oxide. The ether was fractionated under reduced pressure; yield 71.6% (based on olefin used).

Any attempt to store the ethers over calcium chloride, calcium sulfate or with no drying agent over long periods of time was unsuccessful. Decomposition quite frequently took place.

The yields of the various 1,2-dialkoxy-3,3,4,4-tetrafluorocyclobutenes were: methoxy-, 71.6%; ethoxy-, 75%; *n*-propoxy-, 58.3%; and *n*-butoxy-, 56%.

Proof of Structure

All of the ethers showed unsaturation with potassium permanganate and gave no test for the presence of the hydroxyl group when treated with metallic sodium. The infrared spectra displayed absorption bands near 1750 cm.$^{-1}$ (in the vicinity of the carbon-to-carbon double bond stretching band in hydrocarbons).

[1] Presented before the Division of Inorganic and Physical Chemistry, 114th meeting of the American Chemical Society, Portland, Oregon, September 13-17, 1948.

[2] This paper represents part of a thesis submitted by M. L. Sharrah to the Graduate School, University of Colorado, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1948. This work was supported in part by Contract N6-onr-231, Task Order 6, with the Office of Naval Research, United States Navy.

[3] Present address: Continental Oil Company, Ponca City, Oklahoma.

[4] J. D. Park, J. R. Lacher, *et al.*, THIS JOURNAL, **70**, 1550 (1948).

[5] W. E. Hanford and G. W. Rigby, U. S. Patent 2,409,274.

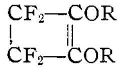
[6] W. T. Miller, Jr., E. W. Fager and P. H. Griswold, THIS JOURNAL, **70**, 431 (1948).

[7] J. D. Park, D. K. Vail, K. R. Lea and J. R. Lacher, *ibid.*, **70**, 1550 (1948).

[8] A. L. Henne and R. P. Ruh, *ibid.*, **69**, 279 (1947).

Table I

Physical Properties of 1,2-Dialkoxy-3,3,4,4-tetrafluorocyclobutenes,



$$\begin{array}{l}CF_2—COR\\ |\qquad\ \ \|\\ CF_2—COR\end{array}$$

R	F. p., °C.	B. p., °C.	Mm.	d^{25}_4	n^{25}_D	$M_R{}^a$	$M_R{}^b$	$AR_F{}^c$		Fluorine,[d] % Calcd.	Fluorine,[d] % Found	Mol. wt. Calcd.	Mol. wt. Found
$-CH_3$	− 5.3	36.8	11.3	1.3409	1.3690	31.3	30.73	1.17	$C_6H_6O_2F_4$	40.8	39.28	186	...
$-C_2H_5$	−50.9	52.8	10.3	1.2123	1.3790	40.8	39.96	1.24	$C_8H_{10}O_2F_4$	35.5	36.1	214	216
$-C_3H_7$		82.0	17.0	1.1501	1.3915	50.0	49.20	1.23	$C_{10}H_{14}O_2F_4$	31.4	...	242	...
$-C_4H_9$	−49.2	132–133	37.6	1.0965	1.4019	59.7	58.43	1.35	$C_{12}H_{18}O_2F_4$	28.1	27.6	270	274.5

[a] M_R denotes the molecular refraction calculated by Lorentz–Lorenz formula. [b] M_R denotes the molecular refraction calculated by adding the customary increments for C, H, O, F and double bond (F = 1.03). [c] AR_F is the atomic refraction for fluorine, obtained from $M_R{}^a$ by subtracting the customary increments for C, H, O and double bonds. [d] Fluorine analysis carried out by the lead chlorofluoride method after fusion. Molecular weights determined by the freezing point depression method.

The structure of the unsaturated diethyl ether, for example, was proved by the formation of diethyl tetrafluorosuccinate (80% yield) by alkaline oxidation with potassium permanganate of the ether. The properties of the ester checked those listed by Henne, *et al.*,[9] for the compound prepared by esterification of tetrafluorosuccinic acid with ethanol. As a further structural proof, the ester was hydrolyzed to the acid, m. p. 86–87° (literature[9] 86.4 to 87.4°).

Substitution of a vinylic fluorine atom by an OR group is postulated, with a mechanism similar to the formation of an anisole from a phenyl halide.

The fact that hexafluorocyclobutene undergoes a substitution reaction with alcoholic caustic while tetrafluoroethylene and trifluorochloroethylene undergo an addition reaction[5,6,7] is consistent with existing thermochemical data on these olefins.[10] The vapor phase heats of chlorination of tetrafluoroethylene and trichlorofluoroethylene are 13.7 and 5.2 kcal. greater than that of ethylene.[11] On the other hand, the heat of chlorination of hexafluorocyclobutene is 6.2 kcal. *less* than that of ethylene. If one extrapolates these results to the addition of alcohols to these olefins, it follows that the reaction is thermodynamically impossible in case of the cyclic olefin at ordinary conditions of temperature and pressure. Under these conditions, substitution reactions may still take place as has been pointed out by Conant and Kistiakowsky.[12]

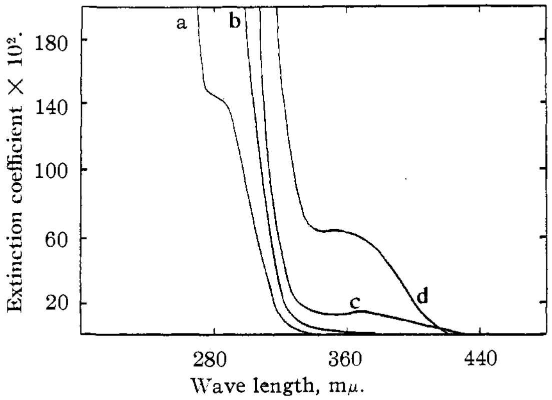


Fig. 1.—The ultraviolet absorption spectra of: (a) 1,2-dimethoxy-3,3,4,4-tetrafluorocyclobutene; (b) 1,2-diethoxy-3,3,4,4-tetrafluorocyclobutene; (c) 1,2-dibutoxy-3,3,4,4-tetrafluorocyclobutene and (d) 1,2-dipropoxy-3,3,4,4-tetrafluorocyclobutene.

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 ultraviolet absorption spectra of the ethers were measured with a Beckman quartz spectrophotometer. Water was used as the reference liquid and the experiments were carried out on the pure liquid ethers in a 10-mm. quartz cell. The extinction coefficient, E, defined by $\log I/I_0 = -El$ was measured; l is the length of the cell in

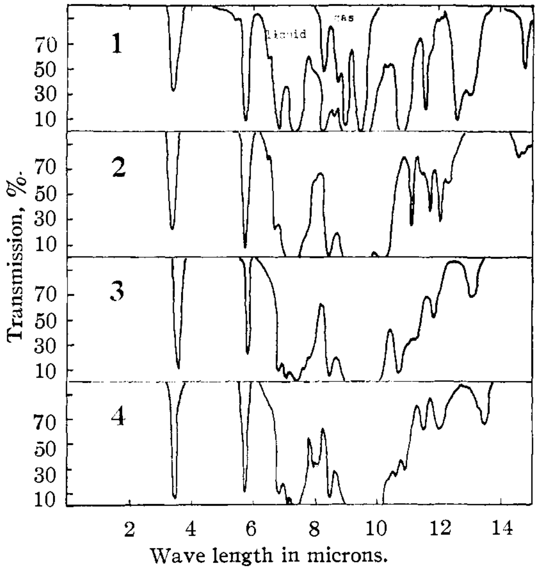


Fig. 2.—The infrared absorption spectra of tetrafluorocyclobutenes: (1) 1,2-dimethoxy-3,3,4,4-; (2) 1,2-diethoxy-3,3,4,4-; (3) 1,2-dipropoxy-3,3,4,4-; (4) 1,2-dibutoxy-3,3,4,4-.

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[9] A. L. Henne and W. J. Zimmerschied, This Journal, **69**, 283 (1947).

[10] J. R. Lacher, J. D. Park, *et al.*, *ibid.*, **71**, 1330 (1949); **71**, 1334 (1949).

[11] G. B. Kistiakowsky, *et al.*, *Ibid.*, **60**, 2764 (1938).

[12] J. B. Conant and G. B. Kistiakowsky, *Chem. Revs.*, **20**, 181 (1937).

cm. which is unity in the present case. Readings were made at approximately every 10 Å. in the regions where absorption took place. The results are given in Fig. 1. The inflections or humps in the curves are probably due to the presence of unresolved vibrational fine structure in the electronically excited state. Some of the ethers made from trifluorochloroethylene[7] do show resolvable vibrational fine structure. Whether or not the fine structure appears depends on the mean life of the electronically excited state.

The infrared absorption spectra of the ethers were measured using an automatic recording Perkin–Elmer Infrared Spectrometer, model 12B. All of the samples were run in the liquid phase in a 0.025-mm. cell. In case of the methyl ether, the region between 8 and 10 microns was studied using a vapor sample (10 mm. pressure in a 10 cm. cell). The results obtained are given in Fig. 2. The spectra of these compounds are strikingly similar and confirm their homologous nature. It is possible to refer certain regions of absorption back to functional groups in the molecule.[13] The strong absorption at 3.38–3.48 which appears in all compounds is due to the C–H stretching vibration in the alkyl groups. The band at 5.70–5.77 μ is in the region of a double bond stretching vibration. The parent olefin also shows absorption in this region, though somewhat weaker.[10] This band disappears in case of the chlorine addition product. These absorption spectra confirm nicely the chemical evidence for the presence of a double bond in these compounds. All of the compounds show very intense absorption between 8.8 and 10μ. This region, in case of the methyl ether, was studied in the vapor phase at low pressure and two strong bands found at 8.88 and 9.73μ. They are probably due to C–O stretching vibrations.

Summary

The reaction of alcohols with hexafluorocyclobutene in the presence of a base, resulting in the formation of 1,2-dialkoxy-3,3,4,4-tetrafluorocyclobutenes has been reported. Some of the physical properties of the ethers, along with their ultraviolet and infrared absorption spectra, are presented.

BOULDER, COLORADO RECEIVED OCTOBER 25, 1948

[13] R. B. Barnes, R. C. Gore, R. W. Stafford and V. Z. Williams, *Anal. Chem.*, **20**, 402 (1948).

[CONTRIBUTION FROM THE UNIVERSITY OF COLORADO]

The Addition of Hydrogen Bromide to Fluorinated Olefins[1,2]

BY J. D. PARK, M. L. SHARRAH AND J. R. LACHER

The heat of addition of hydrogen bromide to fluorinated olefins is under study in our laboratory[3]; we are describing here qualitative results obtained in pilot plant runs under conditions practical for calorimetric measurements. The only literature citation is that of $CF_2{=}CFCl$[4] and no statement is made whether the adduct is $CF_2H{-}CFClBr$, $CF_2Br{-}CHClF$, or a mixture of both.

Starting Materials.—$CF_2{=}CCl_2$, $CF_2{=}CFCl$, $CF_2{=}CF_2$ and $CF_3CF{=}CF_2$ were obtained from the Jackson Laboratory, du Pont and Co.; $CF_2{-}CF_2{-}CF{=}CF$ and $CF_2{-}CF_2{-}CCl{=}CCl$ were made by the procedures of Henne.[5,6]

Apparatus.—The olefin was passed from a reducing valve through a sulfuric acid scrubber, then through a 10% solution of potassium hydroxide followed by drying in a phosphorus pentoxide train. The olefin, thus removed of its polymerization inhibitor, was then metered through a flowmeter into the top of the catalyst chamber. Hydrogen bromide was passed through a series of needle valves, a flowmeter, and into the top of the catalyst chamber. The catalyst chamber of 50-cc. capacity was heated by means of an electric furnace. The exit lines were electrically-heated to prevent product condensation in the lines. The receiver was cooled by means of a Dry Ice–acetone-bath and a manometer served merely as a back-pressure indicator.

Various catalysts were tried, including 90% asbestos–10% carbon, calcium sulfate, chromium trifluoride on "Teflon" (tetrafluoroethylene polymer), silica gel, and reduced iron in silica gel, and found to be inactive. With activated carbon of the gas-carbon type (Columbia Activated Carbon) as a catalyst, the reaction proceeded smoothly, but five hours were required for the system to attain equilibrium (adsorption and desorption on the catalyst surface). With a catalyst composed of 40% carbon and 60% calcium sulfate approximately three hours were required to attain equilibrium. With a catalyst of 75% carbon and 25% calcium sulfate, three and one-half hours were required. The last-mentioned catalyst proved to be the most satisfactory. The carbon and calcium sulfate used were sixteen mesh. After thorough mixing, the catalyst was placed in the catalyst chamber and activated by heating at 200° for three hours *in vacuo*.

Procedure.—The olefin and hydrogen bromide were passed over the catalyst at rates of 20 and 10 cc. per minute, respectively. The contact time was approximately forty-eight seconds, based on the combined flow rates. The catalyst temperature was maintained at about 90°, but was raised to 100° for $CF_2{=}CCl_2$. The gases entering

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[1] Presented before the Division of Inorganic and Physical Chemistry, 114th meeting of the American Chemical Society, Portland, Oregon, September 13–17, 1948.

[2] This paper represents part of a thesis submitted by M. L. Sharrah to the Graduate School, University of Colorado, in partial fulfillment of the requirements for the degree of Doctor of Philosophy August, 1948. This work was supported in part by a grant from the Research Corporation, New York, and under Contract N6onr-231, Task Order #6, from the Office of Naval Research, United States Navy.

[3] J. R. Lacher, J. D. Park, *et al.*, unpublished works.

[4] A. F. Benning, F. B. Downing and R. J. Plunkett, U. S. Patent 2,365,516.

[5] A. L. Henne and R. R. Ruh, THIS JOURNAL, **69**, 279 (1947).

[6] A. L. Henne and W. J. Zimmerschied, *ibid.*, **69**, 281 (1947).