In the absence of a second carboxylic acid, polyvinyl alcohol is quite readily esterified with anhydrous trifluoroacetic acid, yielding trifluoroacetyl esters soluble in many common organic solvents. These esters have been found to lack hydrolytic stability, but form tough, flexible, transparent films, which are slightly plasticized by water and which have low flammability. The hydrolytic instability probably results from the catalytic effect of traces of trifluoroacetic acid. Polyvinyl trifluoroacetate has been made previously by Howk and Jacobson by vinyl polymerization[4] and, except for the hydrolytic instability encountered here, the reported properties were quite similar.

Experimental

Esterification with Acetic Acid Plus Trifluoroacetic Acid.—High viscosity polyvinyl alcohol (Elvanol 91A–65 which was pretreated with dilute alkali to assure complete deacetylation; 5 g.) was heated at 90–100° for 2 hours in a mixture of 18 ml. of glacial acetic acid and 1 ml. of trifluoroacetic acid. At one hour a clear viscous solution was obtained. The viscosity dropped some during the second hour. The product was isolated by diluting the solution with acetone and casting a film. The plastic film was soluble in numerous organic solvents and was highly softened by water. The polymer contained no fluorine and was 74.3% substituted by acetyl groups. Trifluoroacetic anhydride, used in place of the trifluoroacetic acid, produced the same product in a somewhat shorter time.

In a similar reaction with glacial acetic acid alone polyvinyl alcohol remained as a white swollen mass and was still easily water soluble.

Esterification with Trifluoroacetic Acid or Anhydride.—Polyvinyl alcohol (5 g.) was mixed with 45 ml. of trifluoroacetic acid and heated under reflux by an oil-bath at 85° with only initial stirring. The powder dissolved in a very few minutes and esterifications were continued for the periods of time given in the table. The products were isolated by diluting the mixture with acetone, casting a film and washing the film with water. The films were freed of excess water and dried at 85°. They softened somewhat in air at 80° and were limp at 100°.

TABLE I

ANALYSIS FOR CF_3CO– GROUPS

Reacn. time, hours	Fluorine,[5] %	Substn. from F analysis, %	Substn. by sapon., %
0.5	36.6	58.3	58.3
1.5	39.9	70.0	69.5
4.0	44.1	89.7	90.2

Esterification of polyvinyl alcohol with trifluoroacetic anhydride or mixtures of anhydride and acid were more rapid than with the acid alone but the final products were similar in properties.

Tests for Interaction of Trifluoroacetic Anhydride and Acetic Acid.—Glacial acetic acid (10 g.) and trifluoroacetic anhydride (19 g., b.p. 40°) were mixed. Considerable heat was evolved but similar heats of mixing were noted for trifluoroacetic acid with acetic acid or acetic anhydride. The mixture was distilled slowly and distillation started at 73°, the boiling point of trifluoroacetic acid. The boiling point rose slowly to 115° and no definite fractions were obtained, although several cuts were made. The higher fractions had the odor characteristic of acetic anhydride. Titration of the fractions gave no indication of a definite composition. Distillation of mixtures of trifluoroacetic and acetic acids and of trifluoroacetic acid and acetic anhydride gave similar results with no indication of constant boiling fractions. Of course with the acids alone, no odor of anhydride was noted.

As a means of distinguishing between no reaction at all and those represented by equations 1 and 2, freezing point depressions in glacial acetic acid were determined, using a Beckmann thermometer and about 30 g. of additive per 1000 g. of acetic acid. A molal depression of 3.90° was used in the calculations.

TABLE II

MOLECULAR WEIGHTS DETERMINED IN GLACIAL ACETIC ACID

Additive	Molal depression	Mol. wt. Calcd.	Mol. wt. Obsd.
Acetic anhydride	3.68	102	108
Trifluoroacetic acid	3.74	114	119
	3.85		115
Trifluoroacetic anhydride	7.93	210	103
	7.34		112

Since the molal depression of trifluoroacetic anhydride is twice that expected from no reaction, equation 1 must represent the reaction. If equation 2 were correct, the freezing point depression would be three times the normal value.

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[4] B. W. Howk and R. A. Jacobson, U. S. Patent 2,436,144 (1948).

[5] Qualitative test: J. H. Simons and E. O. Ramler, THIS JOURNAL, 65, 391 (1943). Quantitative analysis: M. L. Nichols and J. S. Olsen, *Ind. Eng. Chem., Anal. Ed.*, 15, 342 (1943), and N. H. Furman, "Scott's Standard Methods of Chemical Analysis," 5th ed., Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1939, p. 405.

Physical Properties of Some 1,1-Difluoro-2,2-dichloroethyl Alkyl Ethers[1,2]

BY J. D. PARK, CURTIS M. SNOW AND J. R. LACHER

We have previously reported on the base-catalyzed action of alkanols on $CF_2{=}CFCl$,[3] $\underline{CF_2—CF_2—CF{=}CF}$[4] and $\underline{CF_2—CF_2—CCl{=}CCl}$.[5]

The present study reports on some of the properties of some 1,1-difluoro-2,2-dichloroethyl alkyl ethers obtained by the reaction of $CF_2{=}CCl_2$ and some alkanols described above.[3,4,5] The

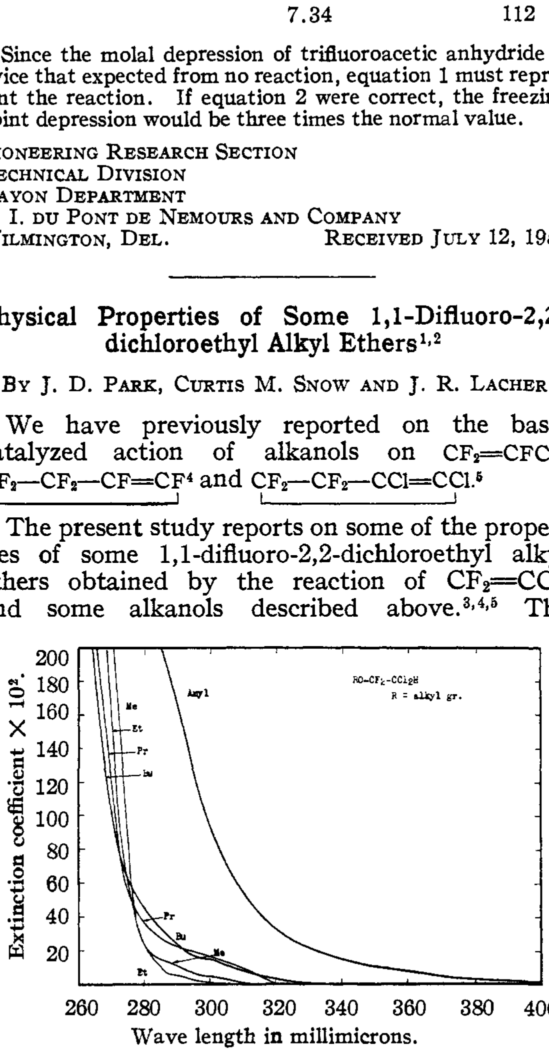

Fig. 1.—Ultraviolet absorption spectra of $ROCF_2–CCl_2H$, R is alkyl group.

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[1] This paper represents part of a thesis submitted by Curtis M. Snow to the Graduate School, University of Colorado, in partial fulfillment of the requirements for the degree Doctor of Philosophy, February, 1950.

[2] This work was supported in part by a grant from the Office of Naval Research, contract N6-onr-231, Task Order 6, project No. NR-056-105.

[3] J. D. Park, D. K. Vail, K. R. Lea and J. R. Lacher, THIS JOURNAL, 70, 1550 (1948).

[4] J. D. Park, M. L. Sharrah and J. R. Lacher, *ibid.*, 71, 2337 (1949).

[5] J. D. Park, C. M. Snow and J. R. Lacher, Abstract of Papers, 118th Meeting of the American Chemical Society, Division of Ind. and Eng. Chemistry, p. 22L.

starting olefin was obtained by dehydrochlorination of $CF_2Cl-CHCl_2$ using a previously described pyrolysis method,[6a,b,c] which consisted of passing $CF_2Cl-CHCl_2$ through a Pyrex tube (65 cm. × 9 mm. i.d.) heated to 650° to give yields of 60–75% of $CF_2{=}CCl_2$ per pass at a contact time of 8–10 seconds.

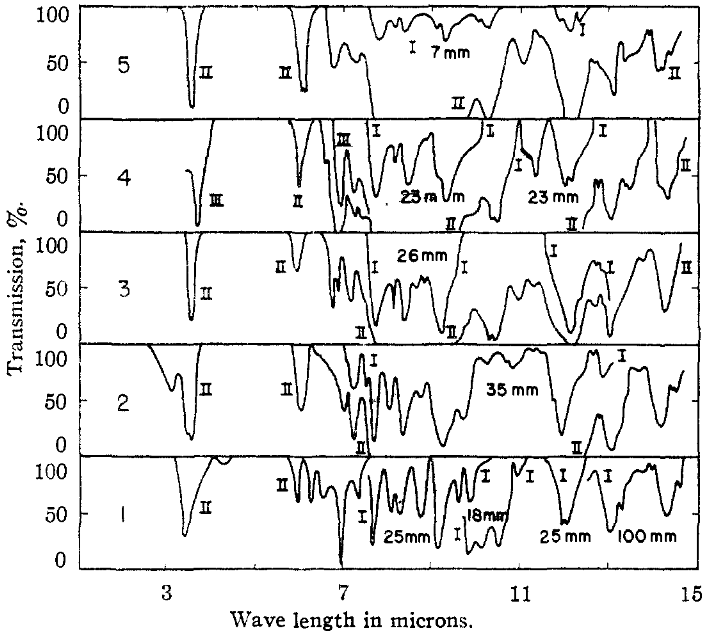

Fig. 2.—The infrared absorption spectrograms at room temperature: I in a 10-cm. gas cell at ind., press., II in a 0.025 mm. liquid cell, and III in a 0.1 mm. liquid cell of (1) $CH_3-O-CF_2CHCl_2$, (2) $C_2H_5-O-CF_2CHCl_2$, (3) $C_3H_7-O-CF_2CHCl_2$, (4) n-$C_4H_9-O-CF_2CHCl_2$, and (5) n-$C_5H_{11}-O-CF_2CHCl_2$.

Some of the physical properties of the ethers are listed in Table I.

TABLE I

PHYSICAL PROPERTIES OF 1,1-DIFLUORO-2,2-DICHLOROETHYLALKYL ETHERS, $R-O-CF_2-CHCl_2$.

R	F.p.	B.p., °C.	B.p., Mm.	$d^{20}{}_4$	$n^{25}d$	$M_r{}^a$	$M_r{}^b$	A_rF^c
$-CH_3{}^d$		104	760	1.4226	1.3864	27.26	27.29	1.01
$-C_2H_5{}^e$	Glass	120	760	1.3461	1.3895	31.51	31.91	0.83
$-C_3H_7$	Glass	136.5	760	1.2636	1.3968	36.79	36.53	1.16
$-C_4H_9$	Glass	153	760	1.2184	1.4029	41.79	41.15	1.19
$-C_5H_{11}$	Glass	172.5	760	1.1817	1.4157	49.51	48.74	1.41

R	Chlorine, % Calcd.	Chlorine, % Found	Molecular weight Calcd.	Molar susceptibility × 10^6 Calcd.	Molar susceptibility × 10^6 Found
$-CH_3$	42.99	42.76	164.99	− 97.53	− 80.68
$-C_2H_5$	39.61	39.61	179.02	−109.39	− 96.13
$-C_3H_7$	36.73	36.48	193.05	−121.25	−107.19
$-C_4H_9$	34.24	34.28	207.08	−133.11	−119.48
$-C_5H_{11}$	32.07	31.88	221.11	−144.97	−129.84

[a] M_r denotes the molecular refraction calculated by the 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] A_rF is the atomic refraction of fluorine, obtained from M_ra by subtracting the customary increments for C, H, O and the double bond. [d] W. T. Miller, E. W. Fager and P. H. Griswold, THIS JOURNAL, 70, 431 (1948). [e] T. B. Gowland, British Patent 523,449; *C.A.*, 35, 6265 (1941).

The ultraviolet absorption spectra of the ethers were measured with a Beckman quartz spectrophotometer model DU. The measurements were made on the pure liquids with an empty reference cell. The quartz cells were 1 cm. long. The extinction coefficient, E, defined by $\log I/I_0 = -El$ was measured; l is the length of the cell in cm. (unity in the present case). The results are given in Fig. 1.

The infrared absorption spectra were measured using an automatic recording Perkin–Elmer infrared spectrometer, model 12B with beam chopper attached. The samples were run in a 0.1 mm. liquid cell, a 0.025 mm. liquid cell or in a 10 cm. gas cell. The results are given in Fig. 2 where per cent. transmission is plotted against wave length in microns. Some qualitative assignments of the peaks are possible using the data of Barnes, *et al.*[7] The strong absorption appearing at 3.37–3.68 microns is due to C–H stretching in alkyl groups. A C–H bending absorption appears at 6.78–6.93. The absorption due to C–O stretching in a saturated ether is strong in the region 9.22–9.32 and is characteristic. The molar diamagnetic susceptibilities measured by the Quincke tube method[8] show a fairly constant deviation from the additive values obtained using Pascal's constants. This deviation is probably due to interaction forces between non-bonded atoms directed along the edges of a tetrahedron.[8,9]

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[6] (a) P. Torkington and H. W. Thompson, *Trans. Faraday Soc.*, **41**, 236 (1945); (b) F. B. Downing, A. F. Benning and R. C. McHarness, U. S. Patent 2,387,247; (c) A. F. Benning, F. B. Downing and J. D. Park, U. S. Patent 2,406,794.

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

[8] J. R. Lacher, R. E. Scruby and J. D. Park, THIS JOURNAL, **71**, 1797 (1949).

[9] J. R. Lacher, *ibid.*, **69**, 2067 (1947).

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Aromatization of Cyclic Compounds by Solid Potassium Perchlorate

BY SAUL PATAI AND LEON RAJBENBACH

In the course of a study of heterogeneous oxidation processes by solid inorganic oxidants[1] we have investigated the reaction of solid potassium perchlorate with aromatic hydrocarbons such as toluene, naphthalene and phenanthrene. Such compounds are generally oxidized without difficulty to the corresponding acids or quinones by various oxidants. Although potassium perchlorate is a powerful oxidizing agent, heating at 370–440° left the mixtures practically unchanged apart from the production of small amounts of potassium chloride and some carbonaceous material. At higher temperatures, approaching the decomposition temperature of potassium perchlorate (510°[2]), very rapid reaction takes place resulting in the explosion of the glass ampoules used.

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[1] Patai and Hoffmann, THIS JOURNAL, **72**, 5098 (1950).

[2] Marvin and Woolaver, *Ind. Eng. Chem.*, *Anal. Ed.*, **17**, 474 (1945).