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The Addition of Alkanols to 1,1,2-Trichloro-3,3,3-trifluoropropene—Some Corrective Data

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We[1] had previously reported the addition of alkanols to $CF_3CCl=CCl_2$ in the presence of a base. The principal product was identified as an unsaturated fluorochloroether. However, an examination of the infrared spectrogram taken of these vinyl ethers revealed the presence of an impurity having a characteristic carbonyl absorption peak.

base and ethers of the structure of $CF_3CCl=CClOR$ were isolated, R being the methyl, ethyl, n-propyl, or n-butyl group.

Infrared spectrograms of these compounds were quite similar and showed them to be practically free of carbonyl-containing impurities.

As a further proof, the dibromide $CF_3CClBrCCl-BrOCH_3$ was prepared by the addition of bromine to $CF_3CCl=CClOCH_3$. This compound was a solid and easily purified by sublimation at near room temperatures under reduced pressure. The carbon, hydrogen, chlorine, and bromine analyses compared closely with the theoretical values calculated for the above structure.

The dibromides of the higher members of this series of ethers were liquids. No attempts were made to purify and identify them.

As a further proof, these vinyl ethers were hydrolyzed according to the method of Tarrant and Young[2,3] to the corresponding saturated esters by treatment with 90 per cent sulfuric acid. This method is similar to the acid hydrolysis[4] of $CHCl=CClOC_2H_5$ to $CH_2ClCO_2C_2H_5$.

The methyl, ethyl, n-propyl, and n-butyl esters of $CF_3CHClCO_2H$, are new compounds and were identified by analyses and by the conversion of the methyl and ethyl members of the series to the amide, $CF_3CHClCONH_2$ by the usual method.

The carbonyl-containing compounds which were present as impurities in the previous chlorofluorovinyl alkyl ethers[1] were isolated by careful fractionation on a modified Todd precision column with a platinum spiral. These compounds had exactly the same physical and chemical properties as the series of esters prepared by the hydrolysis of the ethers, $CF_3CCl=CClOR$ to the corresponding

TABLE I

PHYSICAL PROPERTIES OF SUBSTITUTED TRIFLUOROPROPENE DERIVATIVES

Compound	B.p., °C.	Mm.	d_4^{20}	n_D^{20}	M.R. Exptl.	M.R. Calc'd	AF_f	Magnetic Susceptibility[a] Calc'd	Magnetic Susceptibility[a] Obsd.
$CF_3CHClCO_2CH_3$	104.0	628	1.4170	1.3588	27.42	27.19	1.18	− 95.2	− 83.4
$CF_3CHClCO_2C_2H_5$	119.0	620	1.3215	1.3634	32.06	31.81	1.18	−107.1	− 98.2
$CF_3CHClCO_2C_3H_7$	135.0	629	1.2678	1.3733	36.74	36.43	1.20	−118.9	−108.9
$CF_3CHClCO_2C_4H_9$	156.0	627	1.2275	1.3803	41.26	41.03	1.18	−130.8	−118.0
$CF_3CHCl(OCH_3)_3$	150.0	626	1.3311	1.3842	39.09	39.70	0.92	—	—
$CF_3CCl=CClOCH_3$	115.0	626	1.4981	1.4070	32.06	31.57	1.26	−100.4	− 93.5
$CF_3CCl=CClOC_2H_5$	130.0	612	1.3945	1.4058	36.98	36.19	1.36	−112.3	−106.7
$CF_3CCl=CClOC_3H_7$	74.5	43	1.3330	1.4123	41.64	40.81	1.38	−124.1	−121.6
$CF_3CCl=CClOC_4H_9$	81.0	29	1.2581	1.4180	47.24	45.70	1.70	−136.0	−138.6

[a] Determined by the Quincke method.

This work was repeated in order to obtain pure samples of these vinyl fluorochloroethers and to isolate and identify this carbonyl-containing compound and any other by-products.

Methyl, ethyl, n-propyl, and n-butyl alcohols were added to $CF_3CCl=CCl_2$ in the presence of a

esters CF_3CHCO_2R where R is the methyl, ethyl, n-propyl, and n-butyl group. One other by-product proved to be $CF_3CHClC(OCH_3)_3$.

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(2) Young and Tarrant, *J. Am. Chem. Soc.*, **72**, 1860 (1950).

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Acid-catalyzed hydrolysis of this *ortho* ester produced the ester $CF_3CHClCO_2CH_3$, a compound previously prepared by the hydrolysis of $CF_3CCl = CClOCH_3$. The amide $CF_3CHClCONH_2$, also prepared from this hydrolysis product, melted at the same temperature as that prepared above.

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The Reaction of Perfluoroalkyl Isocyanates with Alcohols

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Perfluoroalkyl isocyanates have been reported[2] to react in the conventional way with alcohols to form N-perfluoroalkylurethans. This represents the only available synthetic route to these unusual carbamates since the corresponding perfluoroalkylamines are not known.

In the present work, however, initial attempts to use this route as a preparative method led to very low yields of the desired products. A unique reaction of excess alcohol with the perfluoroalkylurethan has been found responsible for these low yields. By treating the isocyanates with a stoichiometric quantity of alcohol, yields of the desired carbamates have been increased to 83–90%.

Proof was readily obtained that alcoholysis of the urethans occurred. Refluxing ethyl N-*n*-perfluoropropylcarbamate with excess alcohol produced 85 mole-% of ethyl carbamate and 52 mole-% of ethyl perfluoropropionate. During the course of the reaction hydrogen fluoride was liberated, for the glass reaction vessel became etched, the odor of hydrogen fluoride was evident, and an inorganic residue containing fluoride and ammonium ions was obtained.

Rigid proof of the mechanism of the reaction with excess alcohol may be difficult to secure. The perfluorourethan can be converted to N-perfluoro-

propionylurethan by a somewhat analogous mild alkaline hydrolysis.[3] This suggests that reaction with the *alpha* fluorine atoms should precede cleavage of the carbon to nitrogen bond. In fact, perfluoroacylurethans may be produced as intermediates in the present alcoholysis reaction for it has been shown[3] that N-*n*-perfluoropropionylurethan is readily cleaved by ethanol to produce ethyl carbamate and ethyl perfluoropropionate.

In the present system it must be recognized that the fluorine atoms may undergo reaction with either alcohol or water. The water may be produced by reaction of the liberated hydrogen fluoride with alcohol[4] or with the glass flask. Differentiation between these two possible mechanisms of reaction was not considered essential to the synthetic problem involved, and additional experiments are not planned.

EXPERIMENTAL

Ethyl N-n-perfluoropropylcarbamate. To 50 g. (0.236 mole) of *n*-perfluoropropyl isocyanate kept below 5° was slowly added 11.5 g. (0.249 mole, 5% excess) of anhydrous ethanol. After completion of the addition, vigorous stirring was continued for one-half hour after which the mixture was stored in a refrigerator overnight. Distillation *in vacuo* gave 50.7 g. (83% yield) of ethyl N-perfluoropropylcarbamate, b.p. 66–69° (16.5 mm.), n_D^{20} 1.3403, d_{25}^{25} 1.458.

Anal. Calc'd for $C_6H_6F_7NO_2$: C, 28.02; H, 2.33; F, 51.75; N, 5.45. Found: C, 28.19; H, 2.45; F, 51.4; N, 5.50.

Ethyl N-n-perfluoroheptylcarbamate. By an identical procedure, 8.7 g. (0.0212 mole) of *n*-perfluoroheptyl isocyanate[5] and 1.10 g. (0.0240 mole) of anhydrous ethanol gave 8.7 g. (89.8% yield) of ethyl N-perfluoroheptylcarbamate, b.p. 71–74° (1.5 mm.), n_D^{20} 1.3291.

Anal. Calc'd for $C_{10}H_6F_{15}NO_2$: C, 26.27; H, 1.33. Found: C, 26.14; H, 1.20.

Alcoholysis of ethyl N-n-perfluoropropylcarbamate. A solution of 10 g. (0.039 mole) of the urethan in 9 g. (0.20 mole) of anhydrous ethanol was refluxed for 20 hours. At the end of this time the reaction vessel had become etched, but nothing had condensed in a Dry Ice trap attached to the reflux condenser. Distillation at atmospheric pressure gave Fraction I (8.7 g.), b.p. 62–78°. and ethanol (4.5 g.). Continued distillation *in vacuo* of the residual material gave 2.97 g. (85% yield) of quite pure ethyl carbamate, m.p. 48–51°, and 0.58 g. of an inorganic residue. Recrystallization of the distilled ethyl carbamate from carbon tetrachloride gave a pure product, m.p. 50–51°, which did not depress the m.p. of an authentic sample. The inorganic material liberated ammonia upon the addition of alkali and gave a test for fluoride ion. It consisted of more than one substance, however, for sublimation left a substantial residue.

Redistillation of Fraction I through a metal-spiral Todd column gave 7.5 g. of a white liquid, b.p. 63–65°. The infrared absorption curve of the distillate gave the peaks characteristic of ethyl perfluoropropionate. Upon washing the material with 8 ml. of 5% sodium carbonate and 5 ml. of water, followed by distillation from phosphoric anhydride, 3.68 g. (52% yield) of pure ethyl perfluoropropionate, b.p. 74–76° (lit. b.p. 76.5°), was obtained. Treatment with anhydrous ammonia converted the ester to perfluoropropionamide, m.p. 96–97° (lit. m.p. 95–95.5°).[6] The origi-

(1) This paper is based on a portion of the thesis to be submitted by Marvin Lukin in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Western Reserve University. This material was presented in part at the American Chemical Society Meeting, Atlantic City, N. J., September 16–21, 1956.

(2) Reid and Smith, *Abstracts of Papers, 116th Meeting of the American Chemical Society,* Atlantic City, N. J., September 18, 1949, page 9K.

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(6) Haszeldine, *Nature,* 166, 192 (1950).