and the contents were poured into a polyethylene beaker and hydrogen fluoride was permitted to evaporate partially by standing overnight. The reaction mixture was originally colorless upon discharge from the autoclave but became blue on exposure to the air. The product was made alkaline with 25% sodium hydroxide solution and the mixture was steam distilled until 4 l. of distillate were collected. The latter was saturated with sodium chloride and extracted three times with 200-ml. portions of diethyl ether. The ethereal extracts were combined, dried over magnesium sulfate, concentrated, and distilled. The main distillation fraction (16.0 g.) was assayed by infrared spectroscopy.

Because of the narrow difference in boiling points of aniline (184.3°/762.2 mm.) and *p*-fluoroaniline (187.4°/760.0 mm.), no attempt was made to rectify further the reaction product.[21]

Table I summarizes experiments conducted with platinum oxide and other catalysts, as well as the effect of temperature, molar ratios of reactants, presence of water, aniline *p*-aminophenol, azoxybenzene, or potassium nitrate, use of highly purified hydrogen fluoride, and the use of a stainless steel autoclave in place of the monel pressure autoclave normally employed.

One experiment was conducted to determine what effect the restriction of hydrogen absorption would have on the yield of *p*-fluoroaniline and by-product formation. In a monel microautoclave were placed 0.50 g. of platinum oxide catalyst, 0.41 mole of nitrobenzene, and 7.0 moles of anhydrous hydrogen fluoride. Hydrogen was added to the desired pressure and the contents were heated at 50°. The reaction was stopped after one half of the calculated amount of hydrogen (0.41 mole) was absorbed. After processing the reaction mixture in the manner described earlier, it was found that a 65% conversion of nitrobenzene was achieved, with 32.7 and 19.0% yields of *p*-fluoroaniline and aniline, respectively.

Analytical. The reaction product was scanned in a 0.025-mm. sodium chloride cell from 8.0 μ to 12.25 μ by use of a Perkin-Elmer Model 21 infrared spectrophotometer.

The "base line" was taken as that of carbon tetrachloride. The following analytical reference points were employed: nitrobenzene, 10.70 μ; aniline, 11.39 μ; *p*-fluoroaniline, 8.67 μ.

Attempts were made to employ ultraviolet spectroscopy in order to distinguish between aniline and *p*-fluoroaniline by diazotization and subsequent coupling with β-naphthol or α-naphthylamine. However, identically colored dyes were obtained with both anilines.

Consideration was also given to nonaqueous titration to distinguish between aniline and *p*-fluoroaniline. However, the difference in dissociation constants[22] was so small that they could not be conveniently titrated in aqueous medium or by determination in benzene with perchloric acid.

Attempts were made to isolate and characterize any by-products in the steam-distillation residues. Ultraviolet absorption spectroscopy suggested the presence of hydroquinone and an aminophenol. Separation of the constituents of the steam distillation residues by column chromatography were not successful.

Rearrangement of phenylhydroxylamine to p-fluoroaniline in hydrogen fluoride. In a typical reaction, a total of 0.34 mole of *N*-phenylhydroxylamine,[23] prepared from the reaction of nitrobenzene with zinc and ammonium chloride, was added over a 15-min. period to 8.1 moles of anhydrous hydrogen fluoride in a copper flask at 13° and permitted to stand for 48 hr. at this temperature. The reaction mixture was made alkaline with sodium hydroxide and the aqueous solution steam distilled. The steam distillate was saturated with sodium chloride, extracted with diethyl ether, the extract dried over magnesium sulfate and distilled, b.p. 186 to 187°, n_D^{25} 1.5349, wt. 22 g. (0.20 mole; 58% uncorrected yield of *p*-fluoroaniline). (Reported[21] for *p*-fluoroaniline, b.p. 187.4°; n_D^{20} 1.5395.) The *N*-acetyl derivative of *p*-fluoroaniline, was prepared, and after one recrystallization from hot water, melted at 150.0° (reported[24] for *p*-fluoroacetanilide, 150.5°).

The reaction time can be decreased to 0.5 hr. with a slightly lower yield of *p*-fluoroaniline. From 0.25 mole of *N*-phenylhydroxylamine and 5.0 moles of anhydrous hydrogen fluoride (5° to 18°), a 46% yield of *p*-fluoroaniline, b.p. 185 to 187°, n_D^{25} 1.5337, was obtained.

Acknowledgment. The authors wish to thank D. Robins, W. Harple, C. Guy, and H. Hyer of the Energy Division Analytical Department for the cooperation provided during this investigation.

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(22) G. M. Bennett, G. L. Brooks, and S. Glasstone, *J. Chem. Soc.*, 1821 (1935). pK_b (in 30% ethanol) aniline, 9.90; *p*-fluoroaniline, 9.92.

(23) O. Kamm, *Org. Syntheses*, Coll. Vol. I, 445 (1951).

(24) A. Lapworth and L. K. Pearson, *J. Chem. Soc.*, **119**, 767 (1921).

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

Fluorinated C-Nitroso Compounds. III.[1] The Reaction of Nitrosyl Chloride with Some Fluoroolefins in the Presence of Ferric Chloride or Actinic Light

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Received April 7, 1961

Various fluorinated ethylenes, tetrafluoroethylene, trifluorochloroethylene, and 1,1-difluoro-2,2,dichloroethylene react with nitrosyl chloride in the presence of ferric chloride to give good yields of nitrosoethanes, 1,1,2,2-tetrafluoro-1-chloro-2-nitrosoethane, 1,1,2-trifluoro-1,2-dichloro-2-nitrosoethane, and 1,1-difluoro-1,2,2-trichloro-2-nitrosoethane respectively. This reaction is also accompanied by a corresponding reduction of the ferric ion to the ferrous state.

Nitroso derivatives have also been obtained from hexafluoropropene and 1,1-difluoro-2,2-dichloroethylene with nitrosyl chloride in photochemical reactions.

It has been previously shown[1] that the major products of the reaction of the fluorinated olefins tetrafluoroethylene, trifluorochloroethylene, and 1,1-difluoro-2,2-dichloroethylene, respectively, with

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[1] Paper No. II in this series, *J. Org. Chem.*, 26, 3316 (1961).

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nitric oxide and ferric chloride are the nitrosoethanes which result from the addition of the elements of nitrosyl chloride, derivable from nitric oxide and ferric chloride. The present paper reports on studies of the reaction of nitrosyl chloride with the same olefins. The reaction was studied under the same conditions in which nitric oxide was used in conjunction with ferric chloride. The reaction was also studied in a static system in order to repeat some work which has been reported recently by other workers, because we had reasons to disagree on some points with the results of these workers.[3,4]

Tetrafluoroethylene, trifluorochloroethylene, and 1,1-difluoro-2,2-dichloroethylene each react with nitrosyl chloride in the presence of anhydrous ferric chloride to form the various addition-products given in Table I.

All the compounds[1] obtained in this study were also obtained in the reaction of the parent olefins with nitric oxide and ferric chloride.

The role of ferric chloride in the addition of nitrosyl chloride to the olefins studied has not been determined, but in view of the reported results of other studies[5,6] it is assumed to be catalytic in nature. However, on the basis of the products obtained and of the known chemical behavior of the olefins studied, it can be safely assumed that this reaction proceeds predominantly by a free radical mechanism. Nitrosyl chloride under appropriate conditions ionizes as follows[6]:

$$NOCl \longrightarrow NO^+ + Cl^-$$

This means that if addition to the double bond occurs by an ionic process, either the nitrosonium ion or the chloride ion would have to attack the olefin at a rate controlling step and form an intermediate or transition complex such as $ClCF_2^-CX_2^-$ or $^+CF_2CX_2NO$ ($X = F$ or Cl). An electrophilic addition to the fluoroolefins is extremely difficult and no such addition has been unambiguously demonstrated yet. Electrophilic additions on the other hand are common, but not with chloride ions. Thus, a consistent over-all ionic process can be logically eliminated.

The reaction is thought to proceed purely by a free radical mechanism and, as nitro, nitronitroso, and dinitro compounds are also found in the reaction mixture, the intermediacy of a diazonium nitrate in the reaction must be recognized. The plausibility of this is augmented by known reactions of nitroso compounds with nitric oxide, (reaction 4), in line with the mechanism suggested in one of our papers.[1]

The fact that compounds such as $O_2NCF_2CX_2ONO$, O_2NCF_2COX, and $ClCF_2CX_2NO_2$ have not been observed in these reactions may be rationalized on the basis of the relatively low concentration of nitrogen dioxide with respect to nitric oxide and nitrosyl chloride in the system. Thus, the probability that the radicals $O_2NCF_2\dot{C}X_2$ and $ClCF_2\dot{C}X_2$ would react with nitrogen dioxide to form these compounds would be very small. When the reaction conditions are such—*i.e.*, higher reaction temperatures—that the proportion of nitro compounds with respect to the other products is increased, the probability that $O_2NCF_2CX_2ONO$, O_2NCF_2COX, and $ClCF_2CX_2NO_2$ might be formed should also be increased. The reasons why such compounds were not observed in the case of trifluorochloroethylene and 1,1-difluoro-2,2-dichloroethylene under these conditions are not clear. It may be assumed that with trifluorochloroethylene both 1-nitro-1,1,2-trifluoro-2,2-dichloroethane and 1-nitro-1,2,2-trifluoro-1,2-dichloroethane were formed and could not be separated because of small differences in their boiling points. Another argument in favor of this view is the very low melting point (below −78°C.) of the nitro compound whose structure was assigned as 1-nitro-1,1,2-trifluoro-2,2-dichloroethane as compared to the much higher melting point (−35°) of its pure isomer, 1-nitro-1,2,2-trifluoro-1,2-dichloroethane. It may be argued that the lower melting point of the former is an indication that the compound is actually a mixture of the two isomers. These arguments can be eliminated when the following observations are taken in account.

(a) The substance whose structure is assigned as 1-nitro-1,1,2-trifluoro-2,2-dichloroethane did not react with zinc dust in either pyridine or dibutoxytetraethylene glycol at room temperature or at 50°. The reaction could be brought about only at 75–80°. This resistance to zinc dust is generally indicative of structure $—CF_2CCl_2—$ in the molecule; removal from such structures of ClF by zinc dust is relatively difficult. (b) 1-Nitro-1,2,2-trifluoro-1,2-dichloroethane prepared by the oxidation of 1-nitroso-1,2,2-trifluoro-1,2-dichloroethane reacted instantly and vigorously with zinc dust in the same solvents as above and at room temperature. (c) The probability that 1-nitro-1,2,2-trifluoro-1,2-dichloroethane could be formed by the oxidation of 1-nitroso-1,2,2-trifluoro-1,2-dichloroethane with nitrosyl chloride during the reaction as the nitroso compound is formed is very small because both 1-nitroso-1,2,2-trifluoro-1,2-dichloroethane and 1-nitroso-2,2-difluoro-1,1,2-trichloroethane have been stored in the dark over long periods in the presence of nitrosyl chloride without significant change. Concentrated nitric acid, hydrogen peroxide in ether, neutral permanganate, and chromium tri-

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(3) R. N. Haszeldine, *J. Chem. Soc.*, 2075 (1953); 1151 (1960).

(4) A. Ya. Yakubovich, V. A. Shpanskii, and A. L. Lemke, *Chem. Abstr.*, **50**, 206 (1956).

(5) L. J. Beckham, U. S. Patent **2,417,675** (1947).

(6) *Recent Aspects of the Inorganic Chemistry of Nitrogen*, Special publication No. **10**, p. 12, The Chemical Society, London, 1957.

oxide in glacial acetic acid acted very slowly upon 1-nitroso-1,2,2-trifluoro-1,2-dichloroethane.

The latter reagent brought about fast oxidation only in the presence of concentrated sulfuric acid (d) NMR studies on 1-nitro-1,1,2-trifluoro-2,2-dichloroethane would have detected any appreciable amounts of the isomeric 1-nitro-1,2,2-trifluoro-1,2-dichloroethane.

The above considerations make it clear that there can be no question concerning the identity and purity of the nitro compound 1-nitro-1,1,2-trifluoro-2,2-dichloroethane. This compound was obtained from trifluorochloroethylene in all its reactions with either nitric oxide or nitrosyl chloride under photochemical conditions, catalytic conditions (carbon or ferric chloride), and in reactions under pressure. Other workers[3,4] reported that nitrosyl chloride and trifluorochloroethylene in a sealed tube yielded as one of the products a nitro compound whose structure was assigned as 1-nitro-1,2,2-trifluoro-1,2-dichloroethane. As was pointed out above this reaction was reinvestigated in this study and the results obtained for the structure of this nitro compound are not in agreement with that reported by these workers. The nitro compound from this reaction was found to be identical to 1-nitro-1,1,2-trifluoro-2,2-dichloroethane whose characteristics have been summarized above and in the Experimental section.

The thermal stability of the nitroso compounds 1 - nitroso - 1,1,2,2 - tetrafluoro - 2 - chloroethane (I), 1-nitroso-1,2,2-trifluoro-1,2-dichloroethane (II), 1-nitroso-2,2-difluoro-1,1,2-trichloroethane (III), 1-nitroso-1,1,2,2,-tetrafluoro-2-nitroethane (IV), 1-nitroso-1,2,2-trifluoro-1-chloro-2-nitroethane (V), 1-nitroso-2,2-difluoro-1,1-dichloro-2-nitroethane (VI) follows the order I > II $\cong$IV > III $\cong$ V > VI which is the order of their boiling points in the opposite direction. The same order of thermal stability appears to be followed when the nitroso groups of these compounds are converted to nitro groups. Compound VI was not isolated, nor was its corresponding dinitro derivative, but their presence in the reaction mixture is assumed on the basis of the analogous compounds observed with the similar reaction of the other olefins. These nitroso compounds when heated undergo decomposition with the elimination of the elements of nitrosyl chloride or nitryl chloride. Both of these were isolated during the distillation of the products from trifluorochloroethylene and 1,1-difluoro-2,2-dichloroethylene. Because of this difficulty (decomposition) no values in actual yield could be determined for the products from the latter olefin.

When II was heated in a sealed tube, it was changed to 1-nitro-1,1,2-trifluoro-2,2-dichloroethane (VII), 1,1,2-trifluoro-1,2,2-trichloroethane (VIII), and other products. Here, along with oxidation, a rearrangement occurred. Thermal data concerning the carbon-nitrogen bond in nitroso compounds of this type are not available, but it would not be unreasonable to assume that this bond is the weakest in the molecule, and that a homolytic dissociation of this bond would be the first event in the reaction.

$$\mathrm{ClCF_2CFClNO} \longrightarrow \mathrm{ClCF_2CFCl\cdot} + \mathrm{NO} \qquad (1)$$

$$\mathrm{ClCF_2CFCl\cdot} \longrightarrow \mathrm{CF_2{=}CFCl} + \mathrm{Cl\cdot} \qquad (2)$$

$$\mathrm{ClCF_2CFCl\cdot} + \mathrm{Cl\cdot} \longrightarrow \mathrm{ClCF_2CFCl_2} \qquad (3)$$

$$\mathrm{ClCF_2CFClNO} + 2\mathrm{NO} \longrightarrow \mathrm{ClCF_2CFClN_2NO_3} \qquad (4)$$

$$\mathrm{ClCF_2CFClN_2NO_3} \longrightarrow \mathrm{ClCF_2CFCl\cdot} + \mathrm{N_2} + \mathrm{NO_3} \xrightarrow{\mathrm{NO}} 2\mathrm{NO_2} \qquad (5)$$

$$\mathrm{CF_2{=}CFCl} + \mathrm{NO_2} \longrightarrow \mathrm{O_2NCF_2CFCl\cdot} \qquad (6)$$

$$\mathrm{O_2NCF_2CFCl\cdot} + \mathrm{Cl\cdot} \longrightarrow \mathrm{O_2NCF_2CFCl_2} \qquad (7)$$

The infrared spectra of the two isomers 1-nitro-1,1,2-trifluoro-2,2-dichloroethane (VII) and 1-nitro-1,2,2-trifluoro-1,2-dichloroethane (IX) are similar except for a very sharp band at 8.8 μ which is absent in IX. The spectra of these compounds will be discussed in later papers.

In contrast to the reaction of nitrosyl chloride with trifluorochloroethylene in a sealed tube, in which no nitroso derivative was isolated, 1,1-difluoro-2,2-dichloroethylene and hexafluoropropene both yielded the corresponding nitroso adducts 1-nitroso-2,2-difluoro-1,1,2-trichloroethane (III) and a compound having the formula $\mathrm{C_3F_6ClNO}$ (X). III was identical to that formed in the reactions of 1,1-difluoro-2,2-dichloroethylene with either nitric oxide and ferric chloride or with nitrosyl chloride and ferric chloride. The structure of X has not been established but most likely it is 2-nitroso-1,1,1,2,3,3-hexafluoro-3-chloropropane.

When a mixture of trifluorochloroethylene and nitric oxide is passed through a tube packed with activated carbon (cocoanut shell), a reaction again takes place in which the same array of compounds is formed as that obtained with this olefin in its reactions with nitric oxide or nitrosyl chloride and ferric chloride. This reaction is not surprising in view of the reported chemical behavior of nitric oxide absorbed on carbon.[7] Addison and Barrer[7] have shown that nitric oxide adsorbed on charcoal disproportionated to nitrogen and nitrogen dioxide. The formation in this reaction of II, V, VII, VIII, and 1,2-dinitro-1,1,2-trifluoro-2-chloroethane (XI) can easily be accounted for by the reaction paths proposed in this and previous papers.[1]

EXPERIMENTAL

Reaction of nitrosyl chloride and fluoroolefins over ferric chloride at 45° for 24 hr. A reactor tube similar to that previously described was used and the results tabulated in Table I. 1. Tetrafluoroethylene (1.05 moles) and nitrosyl

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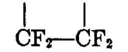
[7] W. E. Addison and R. M. Barrer, *J. Chem. Soc.*, 755 (1955).

TABLE I

SUMMARY OF THE REACTION PRODUCTS[8] OBTAINED FROM THE REACTION OF FLUOROOLEFINS WITH NITROSYL CHLORIDE OVER FERRIC CHLORIDE AT 45°

From CF_2=CF_2		From CF_2=CFCl	
Compound	%	Compound	%
$CF_2Cl—CF_2NO$	79.6	$CF_2Cl—CFCl(NO)$	82
$CF_2Cl—CF_2Cl$	3.2	$CF_2Cl—CFCl_2$	3.3
$CF_2(NO_2)—CF_2NO$	1	$CF_2(NO_2)—CFCl(NO)$	Trace
$CF_2Cl—CF_2NO_2$	4	$CF_2(NO_2)—CFCl_2$	7.5
$CF_2—(NO_2)—CF_2(NO_2)$	1	$CF_2(NO_2)—CFCl(NO_2)$	<1
	1.6		
$CF_2Cl—COF$	Trace		

chloride (1 mole). 2. Trifluorochloroethylene (1.12 moles) and nitrosyl chloride (1 mole).

Photochemical reaction of trifluorochloroethylene with nitrosyl chloride. Exactly 30 g. (0.256 mole) of trifluorochloroethylene and 16.8 g. (0.256 mole) of nitrosyl chloride were placed in an evacuated heavy wall Pyrex tube. The tube was sealed and then exposed to an ultraviolet radiation for 2.5 hr. The reaction started in about 15 min. and was very exothermic. At the end of 2.5 hr. the tube was cooled to −75° with Dry Ice and was opened. Even at this low temperature some gaseous material escaped from the tube when the seal was broken. The contents (40 g.) were washed with water and dried with calcium chloride, which upon distillation yielded 7 g. of unchanged olefin, 10 g. (28.6%) of 1,1,2-trifluoro-1,2,2-trichloroethane, b.p. 41–42°/630 mm. 21 g. (60%) of *1,1,2-trifluoro-2,2-dichloro-1-nitroethane*, b.p. 70.5–72/630 mm. and 4 g. of a higher boiling material, and nondistillable residue.

Photochemical reaction of 1,1-difluoro-2,2-dichloroethylene with nitrosyl chloride. One hundred and thirty two grams (1 mole) of 1,1-difluoro-2,2-dichloroethylene and 65 g. (1 mole) of nitrosyl chloride were placed in an evacuated heavy wall Pyrex tube of approximately 300-ml. capacity, which was provided with a pressure gauge. The tube was irradiated with an ultraviolet lamp for about 1 hr. The reaction started in 15–20 min. and was extremely exothermic. The color of the contents changed progressively from red-brown to blue. At the end of 1 hr. the tube was cooled with Dry Ice and upon opening a small quantity of gas escaped. The crude blue product was washed with water and dried over calcium chloride. The product (162.5 g.) was distilled at atmospheric pressure (630 mm.) and gave the following fractions: (a) 9 g. of 1,1-difluoro-2,2-dichloroethylene. (b) 14.5 g. (9.3%) of 1-nitroso-2,2-difluoro-1,1,2-trichloroethane. (c) 55 g. (36%) of 1,1,1,2-tetrachloro-2,2-difluoroethane. (d) 30 g. (19.6%) of a compound having the formula $C_2F_2Cl_3NO_2$. (e) 25 g. (16.3 %) higher boiling material, and nondistillable residue. (f) 29 g. (18.8%) of a low boiling green liquid collected in a Dry Ice-cooled trap which was attached to the condenser of the distillation apparatus. Most of this liquid was soluble in water; nitrosyl chloride and nitryl chloride were isolated from it.

In another similar experiment in which distillation was carried out at reduced pressures, 63 g. of 1,1-difluoro-1,2,2-trichloro-2-nitrosoethane, b.p. 14–16°/200 mm. was obtained. This compound as well as the compound having a formula of $C_2F_2Cl_3NO_2$ are thermally unstable and decompose when distilled at normal pressure (630 mm.).

When the period of irradiation with ultraviolet light is more than 1 hr. the yield of the nitroso adduct is considerably diminished while the yields of 1,1,1,2-tetrachloro-2,2-difluoroethane, the compound with formula $C_2F_2Cl_3NO_2$ and of the higher boiling materials are increased.

Note: A violent explosion took place in one of these reactions in which 132 g. of 1,1-difluoro-2,2-dichloroethylene and 66 g. of nitrosyl chloride were treated in a 300-ml. heavy wall Pyrex tube under the influence of two ultraviolet lamps.

Photochemical reaction of hexafluoropropene with nitrosyl chloride. Hexafluoropropene, 50 g. (0.333 mole), and nitrosyl chloride, 22 g. (0.33 mole), were placed in an evacuated 22-l. flask. The flask was exposed to sunlight for 8 hr. during which period a blue-green liquid condensed at the bottom and a solid thin white film was deposited on the walls of the flask. At the end of this period the contents of the flask were slowly pumped into a liquid air trap in which it solidified. After about 5 hr. the white solid (nitrogen tetroxide) started subliming and filled the evacuated flask with a brown gas which was nitrogen dioxide.

The product collected in the trap was washed with water and dried with calcium chloride. Distillation gave the following fractions: (a) 25 g. of hexafluoropropene. (b) 12 g. of a blue liquid, b.p. 20.5°/630 mm. n_D 1.3003. d_4 1.5729, mol. wt. 212. No consistent analytical results could be obtained for this compound. Its empirical formula is C_3F_6ClNO: this was established by conversion to a compound having the formula $C_3F_6ClNO_2$ for which a good analysis was obtained. On the basis of the results of previous experiments, its structure is tentatively assigned at 2-nitroso-1,1,1,2,3,3-hexafluoro-3-chloropropane. (c) 5 g. of a colorless liquid, b.p. 30°/630 mm., n_D 1.3110, d_4 1.5977. This compound was shown by its infrared spectra to be 1,1,1,2,3,3-hexafluoro-2,3-dichloropropane. Mol. wt. calcd. for $C_3Cl_2F_6$: 221; found, 220. (d) 14 g. of a colorless liquid, b.p. 51.5–52°/630 mm., n_D^{25} 1.3145, d_D^{25} 1.6313. Mol. wt. calcd. for $C_3ClF_6NO_2$: 231.4; found 236.

Anal. Calcd. for $C_3F_6ClNO_2$; C, 15.52; N, 6.03; Cl, 15.3; F, 49.14. Found: C, 15.81; N, 5.82; Cl, 15.11; F, 48.97.

Reaction of trifluorochloroethylene with nitric oxide over activated carbon. About 117 g. (1 mole) of trifluorochloroethylene and nitric oxide in a ratio of 1:2 by volume were passed during a period of 20 hr. at room temperature through a 90 cm. × 20 mm. Pyrex glass tube packed tightly with coarse cocoanut shell carbon. The experimental setup was similar to that in which ferric chloride was employed as the reactor packing.[1] During the reaction, appreciable quantities of a gas which was not condensable in the Dry Ice-cooled trap was continuously escaping. Much of this gas was unchanged nitric oxide and perhaps some unchanged olefin and difluoroacetyl fluoride. There was a vigorous exothermic reaction on the surface of the carbon packing as the gaseous mixture of the reactants were coming into contact with the former, and the temperature at this spot was about 100°. The hot spot traveled along the length of the packing as the gaseous mixture was passed through, and when it reached the other end of the packing the reaction practically ceased. During the reaction extensive carbon-fluorine bond cleavage must have occurred because the reactor glass tubing was badly etched. A glass vessel in which the carbon packing was subsequently stored also was badly etched. The blue-green

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(8) All the physical properties of the compounds given in the Experimental (unless otherwise given) are in agreement with the data presented in one of our previous works.[1]

product which weighed 152 g. was washed with water and dried over calcium chloride. Twenty-one grams of the product was lost in the wash water. The latter gave a test for chloride ion and for fluoride ion, and was strongly acidic, perhaps because of difluoronitroacetic acid and chlorodifluoroacetyl fluoride.

Distillation of the remaining 131 g. of product gave the following fractions:

(a) 51 g. of trifluorochloroethylene. (b) 12 g. (15%) of 1-nitroso-1,2,2-trifluoro-1,2-dichloroethane. (c) 14.5 g. (18.1%) $ClCF_2CFCl_2$ (d) 19 g. (23.8%) of 1-nitoso-1,2,2-trifluoro-1-chloro-2-nitroethane. (e) 20 g. (25%) of 1-nitro-1,1,2-trifluoro-2,2-dichloroethane. (f) 7 g. (8.75%) of 1,2-dinitro-1,1,2-trifluoro-2-chloroethane. (g) 7.5 g. (9.35%) of residue.

Acknowledgment. We wish to acknowledge support of this work by the U. S. Army Quartermaster Corps under Dr. Juan C. Montermoso as scientific officer.

BOULDER, COLO.

[CONTRIBUTION FROM THE RESEARCH DIVISION, JACKSON LABORATORY, E. I. DU PONT DE NEMOURS AND CO.]

Nucleophilic Substitution in Fluoroalkyl Sulfates, Sulfonates, and Related Compounds

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Received February 3, 1961

New chemistry based on highly fluorinated alcohols is described. The difficult nucleophilic substitution at the carbon-oxygen bond of polyfluoroalkoxy compounds takes place at appreciably lower temperatures in the chlorosulfate and sulfate esters than in the tosyl esters. Fluoroalkylamines have been prepared from the corresponding alcohols going through one intermediate step.

Fluorinated alcohols containing the grouping $—CF_2—CH_2OH$ are much more acidic than ordinary alkyl alcohols being almost as acidic as phenol.[1] Like the phenols, the fluoro alcohols are cleaved only with difficulty at the carbon-oxygen bond, so that direct exchange of the hydroxy function for halide, amino, or anilino groups has been reported only in isolated cases.[2]

Halide substitution at the carbon-oxygen bond of *p*-toluenesulfonate esters of fluorinated alcohols has been accomplished[3–5] by reaction of these esters with sodium iodide, lithium chloride, and lithium bromide in diethylene glycol at elevated temperatures, usually in excess of 200°. This method has been extended to methane-, ethane-, and benzenesulfonate esters[6] of fluoro alcohols and has given satisfactory results in the formation of 1*H*,1*H*,ω*H*-perfluoroalkyl halides.[7]

It is rather surprising that the attempted reactions of ammonia, methylamine and diethylamine at the fluoroalkyl-oxygen bond of tosyl esters have, heretofore, been unsuccessful,[8,9] while piperidine and aniline under similar conditions have been fluoroalkylated on the nitrogen atom without apparent difficulty.[8]

Formation of fluoroalkyl halides. Selected fluoroalkyl sulfates, sulfites, chlorosulfates, methanesulfonates, and *p*-toluenesulfonates have been prepared. The properties of some of these esters are given in Tables I and II. The sulfate and chlorosulfate esters proved to be useful as fluoroalkylating agents. Thus, 1*H*,1*H*,3*H*-tetrafluoropropyl chlorosulfate (I) was converted to the chloride (II) with lithium chloride in diethylene glycol at 125°, a temperature which is unexpectedly low for the scission of the fluoroalkyl-oxygen bond. The same chloride made from the tosyl ester required a minimum temperature of 165°.

$$\underset{\text{I}}{HCF_2CF_2CH_2OSO_2Cl} \xrightarrow[125^\circ]{LiCl} \underset{\text{II}}{HCF_2CF_2CH_2Cl} \quad (61.2\%)$$

$$\underset{\text{III}}{H(CF_2CF_2)_2CH_2OSO_2Cl} \xrightarrow{KF} \underset{\text{IV}}{H(CF_2CF_2)_2CH_2F} \quad (17.1\%)$$

Similarly, the chlorosulfate ester of 1*H*,1*H*,5*H*-octafluoropentanol (III) was converted to the fluoride (IV) below 145°. The tosyl esters of this alcohol and of 1*H*,1*H*,7*H*-dodecafluoroheptanol could not be made to react with potassium fluoride in diethylene glycol at temperatures up to 245°, so that neither of the fluoroalkyl fluorides was formed. The shorter chain 1*H*,1*H*,3*H*-tetrafluoropropyl tosylate (V), however, was suitable for fluoride formation reacting readily at 170°–210° (76%). It appears that

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(1) R. N. Haszeldine, *J. Chem. Soc.*, 1953, 1757; A. L. Henne and W. C. Francis, *J. Am. Chem. Soc.*, **75**, 991 (1953).

(2) A. M. Lovelace, W. Postelnek, and D. A. Rausch, *Aliphatic Fluorine Compounds*, Monograph -138, Reinhold, p. 46.

(3) G. V. D. Tiers, H. A. Brown, and T. S. Reid, *J. Am. Chem. Soc.*, **75**, 5978 (1953).

(4) W. F. Edgell and L. Parts, *J. Am. Chem. Soc.*, **77**, 4899 (1955).

(5) E. T. McBee, D. H. Campbell, C. W. Roberts, *J. Am. Chem. Soc.*, **77**, 3149 (1955).

(6) P. D. Faurote and J. G. O'Rear, *Ind. & Eng. Chem.*, **49**, 189 (1957).

(7) P. D. Faurote and J. G. O'Rear, *J. Am. Chem. Soc.*, **78**, 4999 (1956).

(8) H. A. Brown and G. V. D. Tiers, *J. Org. Chem.*, **22**, 454 (1957).

(9) B. S. Marks and G. S. Schweiker, *J. Am. Chem. Soc.*, **80**, 5789 (1958).