terminate in the usual manner by chain transfer, cyclization or reaction with the solvent. We believe, however, that the polymerization does not take place through a radical mechanism but rather through an ionic mechanism. This conclusion is based upon the consideration that the catalyst and solvent are promoters of ionic reactions. Indeed, in the large excess of ether, one might expect a radical mechanism to lead to low molecular weight polymer chains terminated by $\underset{|}{CH_3CH}\text{-}OC_2H_5$ groups.

In the following discussion, we present what we believe to be a reasonable ionic mechanism. It has been conveniently divided into initiation, propagation and termination steps.

(A). **Initiation.**—The initiation step of the ionic mechanism involves a resonance form of diazomethane which makes it a potential carbanion (electron donor).

$$BF_3 + :\overset{(-)}{C}H_2-\overset{(+)}{N}\equiv N \longrightarrow F_3\overset{(-)}{B}-CH_2-\overset{(+)}{N}\equiv N$$

$$F_3\overset{(-)}{B}-CH_2-\overset{(+)}{N}\equiv N \longrightarrow F_3\overset{(-)}{B}-\overset{(+)}{C}H_2 + N_2$$

On the other hand, coördination of BF_3 with the terminal nitrogen of diazomethane would give $F_3\overset{(-)}{B}-N=N-\overset{(+)}{C}H_2$, which would lead to a polymer containing nitrogen.

(B). **Propagation.**—The boron trifluoride–methylene complex has a carbonium ion end which can grow by adding diazomethane in the manner:

$$F_3\overset{(-)}{B}-\overset{(+)}{C}H_2 + :\overset{(-)}{C}H_2-\overset{(+)}{N}\equiv N \longrightarrow F_3\overset{(-)}{B}-CH_2-CH_2-\overset{(+)}{N}\equiv N$$

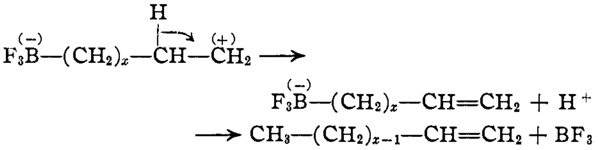
$$F_3\overset{(-)}{B}-CH_2-CH_2-\overset{(+)}{N}\equiv N \longrightarrow F_3\overset{(-)}{B}-CH_2-\overset{(+)}{C}H_2 + N_2$$

Alternatively, attack of the terminal nitrogen of diazomethane on the growing carbonium ion would give an ion of the type

$$F_2\overset{(-)}{B}-CH_2-N=N-\overset{(+)}{C}H_2$$

which would again result in a polymer containing nitrogen.

(C). **Termination.**—There are several possible ways in which the chain might terminate. It could, for example, lose a β-hydrogen and BF_3 to give an olefin thus



$$F_3\overset{(-)}{B}-(CH_2)_x-\overset{H}{C}H-\overset{(+)}{C}H_2 \longrightarrow F_3\overset{(-)}{B}-(CH_2)_x-CH=CH_2 + H^+ \longrightarrow CH_3-(CH_2)_{x-1}-CH=CH_2 + BF_3$$

Acknowledgment.—The authors are indebted to Dr. John D. Hoffman who carried out the thermal analyses and to Dr. Walter L. Roth who obtained the X-ray diffraction patterns.

SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF FLORIDA]

Some Reactions of Fluoroethanes with Sodium Ethoxide[1]

BY PAUL TARRANT AND JOHN A. YOUNG

RECEIVED JUNE 9, 1952

Evidence is offered that the formation of fluoroethers by the reaction of a saturated fluorohalo compound with sodium ethoxide is not due to a simple displacement reaction of the Williamson type in most instances. The products formed in a number of reactions can be accounted for only by assuming that the saturated compounds are converted to fluoroölefins which then add alcohol to give the fluoroether.

The two most common procedures in use today for the preparation of fluoroethers involve the base-catalyzed addition of alcohols to fluoroölefins[2–4] and reaction of a saturated fluorohalo compound with alkoxide or aryloxide.[5,6] The latter method seems to be the common Williamson method for preparing ethers. Representative equations for the two methods, both of which give good yields of ethers, are

$$\text{(I)}\quad CCl_2=CF_2 + HOR \xrightarrow{^-OR} CHCl_2CF_2OR$$

$$\text{(II)}\quad CHCl_2CF_2Cl + {}^-OR \xrightarrow{HOR} CHCl_2CF_2OR + Cl^-$$

McBee and Bolt[5] made a study of the reaction of 1,2,2-trichloro-1,1-difluoroethane with several aryloxides in which compounds of the type $CHCl_2$-CF_2OAr were formed, and concluded that the chlorine atom of the $-CF_2Cl$ group possessed unusual activity since it was the apparent point of attack by the aryloxide. It has been suggested[7] that the $-OAr$ removes a proton from the saturated fluorochloro compound to yield an olefin which then adds a molecule of ArOH to give the aryl ether.

In reactions with a number of saturated compounds such as 1,2,2-trichloro-1,1-difluoroethane, 1,2-dichloro-1,1-difluoroethane, etc., it is not possible to draw conclusions as to the mechanism by which the fluoroethers are formed since both the displacement and the olefin-alcohol addition method yield the same product. However, by judicious choice of other starting materials, the two routes can be made to give different results and the predominance of one mechanism over the other determined by the nature of the products.

A study of the reactions of the isomeric chloro-1,1-difluoroethanes with sodium ethoxide in ethanol would offer some indication of the course of the

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[1] Presented at the Diamond Jubilee Meeting of the American Chemical Society, New York City, September, 1951.

[2] W. E. Hanford and G. W. Rigby, U. S. Patent 2,409,274 (1946).

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

[4] Paul Tarrant and H. C. Brown, *ibid.*, **73**, 1781 (1951).

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

[6] F. Swarts, *Bull. acad. roy. Belg.*, 383 (1901); *Mem. ocur. acad. roy. Belg.*, 61 (1901).

[7] Paul Tarrant and H. C. Brown, THIS JOURNAL, **73**, 5831 (1951).

reaction. If the formation of the fluoroether proceeds through dehydrohalogenation and subsequent addition of alcohol, both ethanes will give the same fluoroether; if the reaction is a simple displacement of the chlorine atom by the ethoxide group, two different products will be obtained.

$$\left.\begin{array}{l}\text{(III)}\ CH_3CF_2Cl \xrightarrow{^-OC_2H_5} \\ \text{(IV)}\ CH_2ClCHF_2 \xrightarrow{^-OC_2H_5}\end{array}\right] \longrightarrow CH_2{=}CF_2 \xrightarrow{HOC_2H_5} CH_3CF_2OC_2H_5$$

$$\text{(V)}\ CH_3CF_2Cl \xrightarrow{^-OC_2H_5} CH_3CF_2OC_2H_5$$

$$\text{(VI)}\ CH_2ClCHF_2 \xrightarrow{^-OC_2H_5} CHF_2CH_2OC_2H_5$$

It has now been found that both difluorochloroethanes give the same end-product; this is ethyl acetate, however, and not the expected 1-ethoxy-1,1-difluoroethane.

In a number of cases, α,α-difluoroethers are reactive and this property seems to be associated with the atoms on the adjacent carbon atom. For example, while perfluorodibutyl ether is inert under a variety of conditions, 1-ethoxy-1,1,2,2-tetrafluoroethane and 2-chloro-1-ethoxy-1,1,2-trifluoroethane are readily converted to ethyl difluoroacetate and ethyl chlorofluoroacetate, respectively, by treatment with sulfuric acid,[8] and 2-chloro-1-ethoxy-1,1-difluoroethane formed ethyl chloroacetate upon remaining in contact with water several hours at room temperature.[4] It then seems plausible that 1-ethoxy-1,1-difluoroethane might be so reactive under the conditions employed here that it is completely converted to ethyl acetate. It does not seem likely that ethyl acetate could have originated from any source but the postulated 1-ethoxy-1,1-difluoroethane and the formation of identical end-products from the isomeric chlorodifluoroethanes is considered to be evidence for the olefin-addition mechanism.

A small amount of a second compound, $CH_2ClCH(OC_2H_5)_2$, has been isolated from the reaction of 2-chloro-1,1-difluoroethane with sodium ethoxide. The presence of this compound can be accounted for by assuming the loss of HF rather than HCl followed by addition of alcohol to the 1-chloro-2-fluoroethylene thus formed to yield 2-chloro-1-ethoxy-1-fluoroethane which gives, finally, the acetal by further dehydrohalogenation and addition.

Interesting results were obtained from the reaction of sodium ethoxide, ethanol and 2-bromo-1,1,1-trifluoroethane. The activity of a halogen on a carbon atom adjacent to a cluster of fluorine atoms is known to be considerably diminished. This fact is confirmed in the case of 2-bromo-1,1,1-trifluoroethane, which was unreactive toward ethoxide under moderate conditions, and, at 150° in an autoclave, gave only products in which bromine was present. The formation of these products, 2-bromo-1-ethoxy-1,1-difluoroethane and 2-bromo-1,1,1-triethoxyethane, indicate the extreme reluctance of the bromine to take part in a displacement reaction of the Williamson type under the experimental conditions employed here. It must be mentioned, however, the patent literature[9] claims that 2-ethoxy-1,1,1-trifluoroethane can be made in small yield by the reaction of 2-chloro-1,1,1-trifluoroethane at elevated temperatures.

A study of the reaction of a number of compounds containing the CHF_2^- group with sodium ethoxide offers additional proof that the olefin-addition mechanism is the preferred route for ether formation.

$$\text{(VII)}\ CHF_2CF_2Cl \longrightarrow CHF_2CF_2OC_2H_5$$

$$\text{(VIII)}\ CHF_2CHCl_2 \longrightarrow CH_2ClCF_2OC_2H_5 + CCl_2{=}CHOC_2H_5$$

$$\text{(IX)}\ CHF_2CHFCl \longrightarrow CH_2ClCF_2OC_2H_5$$

$$\text{(X)}\ CHF_2CH_2Cl \longrightarrow CH_3CO_2C_2H_5 + CH_2ClCH(OC_2H_5)_2$$

In all of these reactions, the products can be accounted for on the assumption of olefin intermediates which add alcohol in such a manner that the ethoxide group becomes attached to the carbon containing the greater number of fluorine atoms.[10]

In reactions VIII and IX, it would be difficult to account for the isolated ethers by any mechanism other than that of olefin-addition since the Williamson type reaction would give entirely different products.

Evidently, in reaction VIII either hydrogen chloride or hydrogen fluoride can be eliminated to give different olefins capable of further reaction.

$$CHF_2CHCl_2 \begin{cases} \longrightarrow CHCl{=}CF_2 \longrightarrow CH_2ClCF_2OC_2H_5 \\ \longrightarrow CCl_2{=}CHF \longrightarrow \\ \qquad [CHCl_2CHFOC_2H_5] \longrightarrow CCl_2{=}CHOC_2H_5 \end{cases}$$

It should be noted that the ethoxy group, in reacting with $CHF{=}CCl_2$, apparently adds to the carbon containing the fluorine atom to give a compound which loses hydrogen fluoride readily to form the stable vinyl ether.

Reaction IX gave unexpected results since the fluorine of the $-CHFCl$ group rather than the chlorine was removed. Apparently 2-chloro-1,1-difluoroethylene, $CHCl{=}CF_2$, resulted, since the direct displacement of the fluorine atom would give rise to 1-chloro-1-ethoxy-2,2-difluoroethane, which was not isolated.

On the basis of the results of this investigation it seems probable that the formation of ethers by the reaction of a saturated chlorofluorohydrocompound with alcohol in the presence of a base proceeds *via* an olefin intermediate.

Experimental

Reaction of 1-Chloro-1,1-difluoroethane.—A solution of 12 g. of sodium (0.5 mole) in 80 ml. of absolute ethanol was placed in a 300-ml. pressure vessel cooled in Dry Ice–acetone. Fifty grams (0.5 mole) of 1-chloro-1,1-difluoroethane was added and the vessel sealed and rocked for 48 hours at 105°. The bomb was then cooled, vented and the products washed with water, dried and distilled. There was obtained 9 g. (21%) of ethyl acetate with the following properties: b.p. 70–77°, $n^{25}\text{D}$ 1.370, $d^{25}{}_{4}$ 0.909.

Reaction of 2-Chloro-1,1-difluoroethane.—This reaction was run a number of times as outlined above. The tem-

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(8) J. A. Young and Paul Tarrant, THIS JOURNAL, **71**, 2432 (1949); **72**, 1860 (1950).

(9) A. F. Benning and J. D. Park, U. S. Patent 2,336,921 (1943).

(10) W. T. Miller, E. W. Fager and P. H. Griswold, THIS JOURNAL, **70**, 431 (1948).

perature was varied from 10 to 100°. Ethyl acetate was identified in the distillate, although in smaller yield; in addition there usually appeared a small fraction of $CH_2ClC(OC_2H_5)_3$, b.p. 147°, $n^{25}D$ 1.4132, d^{25} 1.031. *Anal.* Calcd. for $C_8H_{17}ClO_3$: Cl, 23.1. Found: Cl, 22.8.

Reaction of 2-Bromo-1,1,1-trifluoroethane.—This compound was unreactive and drastic conditions were necessary for the formation of ethers. When shaken at 100° for 48 hours with a 1:1:1.5 molar ratio of halide:base:solvent, two products were obtained. The lower boiling had the following properties: b.p. 114.6°, $n^{25}D$ 1.397, $d^{25}{}_4$ 1.513, *MR*D 30.6. *Anal.* Calcd. for $C_4H_7BrF_2O$: Br, 42.38. Found: Br, 42.32. These data compare well with 2-bromo-1-ethoxy-1,1-difluoroethane, $CH_2BrCF_2OC_2H_5$, prepared from 2-bromo-1-chloro-1,1-difluoroethane. The higher boiling material had properties identical with those of $CH_2BrC(OC_2H_5)_3$.[11]

Reaction of 1,1-Dichloro-2,2-difluoroethane.—This compound was considerably more reactive toward sodium ethoxide than those compounds previously considered and the complexity of the crude reaction product made the identification of individual compounds difficult. The reaction temperature varied from 25 to 100°; at the latter temperature the autoclave was used. In some experiments, potassium hydroxide dissolved in 95% alcohol was used rather than sodium ethoxide in absolute ethanol.

The principal product obtained was always 1,1-dichloro-2-fluoroethylene.[12] At higher temperatures dichlorovinyl ethyl ether[13]; $CCl_2{=}CHOC_2H_5$, b.p. 146°, $n^{25}D$ 1.4575, $d^{25}{}_4$ 1.203, derived from the olefin $CCl_2{=}CHF$ was obtained while the series of compounds related to $CF_2{=}CHCl$ were also present in smaller amounts. The presence of $CH_2ClCF_2OC_2H_5$ was shown by its hydrolysis to ethyl chloroacetate. The dichlorovinyl ether, $CCl_2{=}CHOC_2H_5$, was made in 59% yield by the reaction of $CHCl_2CHF_2$ with alcoholic potassium at the reflux temperature; the addition of ethanol to $CCl_2{=}CHF$ gave a 75% yield of the same ether.

Reaction of 1-Chloro-1,2,2-trifluoroethane.—This compound, when treated with sodium ethoxide and ethanol for 3 hours at 120°, gave a 53% yield of 2-chloro-1-ethoxy-1,1-difluoroethane,[2] b.p. 89–93°, $n^{25}D$ 1.368, $d^{25}{}_4$ 1.168. This ether gave a 72% yield of ethyl chloroacetate upon hydrolysis. In addition, a higher boiling fraction was obtained whose physical properties were reasonably close to the chloroörthoacetate, but it was present in insufficient amount for positive identification.

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[11] F. Beyerstedt and S. M. McElvain, THIS JOURNAL, **59**, 1273 (1937).

[12] A. L. Henne and E. C. Ladd, *ibid.*, **58**, 402 (1936).

[13] F. Neher and W. Foster, *ibid.*, **31**, 412 (1909).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF VANDERBILT UNIVERSITY]

Symmetrical 1,3-Bis-(alkane- and arylsulfonyl)-ureas

BY LAMAR FIELD AND FREDERICK A. GRUNWALD[1]

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A number of bis-sulfonylureas of the general formula $(RSO_2NH)_2CO$ have been prepared by a new method involving condensation of the metal salt of the corresponding sulfonamide with phenyl carbonate. Variables affecting the condensation and certain limitations of the rather general method are discussed. Chemical and pharmacological properties of the products are reported together with evidence for the structure of typical products.

Bis-sulfonylureas, in contrast to monosulfonylureas, have received but little consideration.[2] Both the paucity of information regarding the series of bis-sulfonylureas and the possibility of useful pharmacological activity in some members of this series motivated this investigation. The better known acylureas have several pharmacologically desirable characteristics which are said to make them preferable in several respects to the barbiturates.[3] Inasmuch as diacylureas are known to possess hypnotic activity,[4] it seemed of interest to determine the extent to which bis-sulfonylureas might also possess such activity.

The direct synthesis of bis-sulfonylureas from sulfonyl chlorides and urea apparently is unsuccessful,[2] except possibly in a few special instances. The eight bis-sulfonylureas described in this paper, of which seven are new compounds, were prepared by conversion of the appropriate sulfonamide with an alkali–metal alkoxide to the corresponding sulfonamide salt. The dry salt was then condensed with phenyl carbonate in phenyl ether at 175°. Similar reactions with ethyl carbonate or with magnesium salts did not occur under these conditions.

This previously unreported reaction is probably similar to such base-catalyzed condensations as the Claisen acetoacetic ester condensation.[5] The overall result may be shown by the abbreviated equations, from which anion equilibria and reversibility of steps have been omitted for simplification.

$$2RSO_2NH_2 + 2OR'^- \longrightarrow 2[RSO_2NH]^- + 2R'OH$$

$$\downarrow (C_6H_5O)_2CO$$

$$(RSO_2NH)_2CO \xleftarrow{2H^+} [(RSO_2N)_2CO]^- + 2C_6H_5OH$$

The presumed similarity in mechanism to the Claisen condensation permits rationalization of the failure of ethyl carbonate to function in the condensation, since an intermediate ion formed by the attack of the sulfonamide anion on the ester would presumably release a resonance-stabilized phenoxide ion more readily than an ethoxide ion. The failure of the reaction with the magnesium salt of benzenesulfonamide might be ascribed to decreased anion activity of the less polar magnesium salt.

The general procedure as outlined above was used for the preparation of the 1,3-bis-(arylsulfonyl)-ureas (procedure A). Preparation of the 1,3-bis-(alkanesulfonyl)-ureas required a considerable reduction in the time of heating in order to obviate decomposition (procedure B); the greater solubility of the alkane-sulfonylureas in both water and organic solvents required usually that pro-

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[1] Milbank Memorial Fellow, 1950–1951. Abstracted from the Ph.D. dissertation of Frederick A. Grunwald, September, 1952.

[2] For a review of sulfonylureas see F. Kurzer, *Chem. Revs.*, **50**, 1 (1952).

[3] F. G. Hobart, "Open-chain Ureide Sedatives," Leonard Hill, Ltd., London, 1951, p. 6 ff.

[4] R. W. Stoughton, *J. Org. Chem.*, **2**, 514 (1938); R. W. Stoughton, H. L. Dickison and O. G. Fitzhugh, THIS JOURNAL, **61**, 408 (1939).

[5] C. R. Hauser and B. E. Hudson, Jr., "Organic Reactions," Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 266.