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-perfluoropropionylurethan 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-

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(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.

(3) Dannley and Lukin, unpublished work.

(4) Meslans, *Compt. rend.,* **111,** 882 (1890).

(5) Haszeldine and Leedham, *J. Chem. Soc.,* 50–51 (1953).

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

nal fraction, b.p. 63–65°, probably consisted of an azeotrope. The yield of pure ester represents the minimum value for large mechanical losses were sustained in handling the small sample.

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Triazines. XVI. A New Synthesis for 1,2,4-Triazoles

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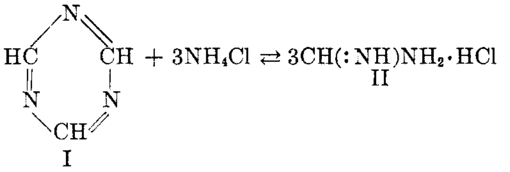
In our previous work on *s*-triazines it has been found that *s*-triazine (I) reacts with ammonia to form dark intractable resins.[3] However, with ammonium chloride in boiling ethanol a nearly quantitative reaction was observed which leads, with complete ring cleavage, to formamidine hydrochloride (II):[4]

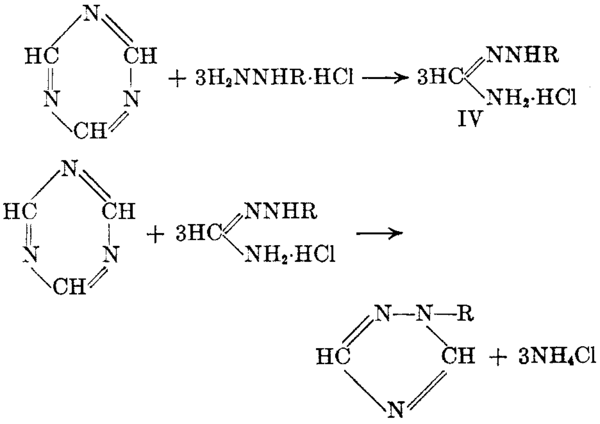


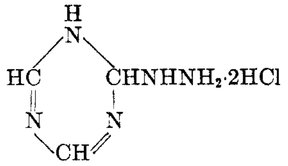
This reaction is essentially the reverse of the previously described formation of *s*-triazine by thermal decomposition of formamidine hydrochloride.[5] In contrast to its formation from *s*-triazine, the reconversion of the formamidine hydrochloride into I is far from being quantitative even in the presence of scavengers for hydrogen chloride.

The above described findings prompted us to attempt the reaction of I with hydrazine monohydrochloride (III) anticipating the formation of the yet unknown formamidrazone hydrochloride (IV, R = H). In boiling absolute ethanol I and III reacted promptly, but instead of IV, 1,2,4-triazole (V) and ammonium chloride were obtained in almost theoretical yields, according to the equation:

$$2C_3H_3N_3 + 3N_2H_4\cdot HCl \longrightarrow 3NH_4Cl + 3C_2H_3N_3$$

This reaction can be explained by a two-step process. First, one molecule of I undergoes the expected ring cleavage to IV. The formamidrazone then will react immediately with another molecule of *s*-triazine, in the same manner as recently described for *ortho*-diamines,[3] to yield 1,2,4-triazole and ammonia. This cyclization reaction seems to be favored since even with an excess of hydrazine monohydrochloride 1,2,4-triazole is the only isolable product.





VIII

V R = H
VI R = CH_3
VII R = C_6H_5

It seems that this reaction can be generalized in that use of mono-substituted hydrazine monohydrochlorides leads to 1-substituted 1,2,4-triazoles. Thus from methyl hydrazine monohydrochloride, 1-methyl-1,2,4-triazole (VI) is recovered and from phenylhydrazine monohydrochloride, 1-phenyl-1,2,4-triazole (VII) has been obtained. Good yields result in both cases.

Hydrazine dihydrochloride reacts in quite a different manner with I, since the only product isolated was an adduct, $C_3H_3N_3\cdot N_2H_4\cdot 2HCl$ which may tentatively be formulated as the dihydrochloride of 1,2-dihydro-2-hydrazino-1,3,5-triazine (VIII).

EXPERIMENTAL[6]

Formamidine hydrochloride from s-triazine. A mixture of 2.8 g. of *s*-triazine and 3.55 g. of ammonium chloride in 25 ml. of absolute alcohol was gently refluxed. After six hours, all of the NH_4Cl had gone into solution and the formamidine salt could be isolated by addition of an excess of ether. In

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[1] This article is based on work performed under Project 116-B of The Ohio State University Research Foundation sponsored by the Olin Mathieson Chemical Corporation, New York, N. Y.

[2] Preceding communication: Grundmann and Kober, *J. Org. Chem.*, 21, 641 (1956).

[3] Grundmann and Kreutzberger, *J. Am. Chem. Soc.*, **77**, 6559 (1955).

[4] This reaction has been found independently in the laboratories of the American Cyanamid Co. (private communication by I. Hechenbleikner at the 127th A.C.S. meeting in Cincinnati, March–April 1955).

[5] Grundmann, Schroeder, and Ruske, *Chem. Ber.*, **87**, 1865 (1954).

[6] All melting points are determined with the Fisher-Johns apparatus. Microanalyses are by Galbraith Laboratories, Knoxville, Tenn., and Spang Microanalytical Laboratory, Ann Arbor, Michigan.