

would be no reason—except for the somewhat questionable interpretation of acidity function relationships—to believe that the mechanism of decarbonylation of formic and triphenylacetic acids are dissimilar.

Acknowledgments.—The author wishes to thank John D. Roberts, F. A. Long, A. N. Bourns, A. J. Weinberger and Erling Grovenstein, Jr., for helpful discussions during the course of this work.
OAK RIDGE, TENN.

[CONTRIBUTION NO. 556 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

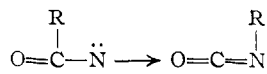
Methoxydifluoromethyl Isocyanate by Thermal Cleavage of a Diazetidine

BY J. C. KAUER AND A. K. SCHNEIDER

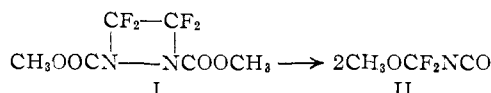
RECEIVED JUNE 25, 1959

Dimethyl 3,3,4,4-tetrafluoro-1,2-diazetidene-1,2-dicarboxylate pyrolyzes with the migration of a methoxyl group to yield methoxydifluoromethyl isocyanate in over 70% yield. Some of the reactions and properties of this material are described.

Rearrangements are involved in a number of well-known syntheses of isocyanates. Thus, in the Hofmann, Lossen and Curtius reactions, alkyl or aryl groups migrate from the carbon atom of a carbonyl group to an adjacent univalent nitrogen atom.¹

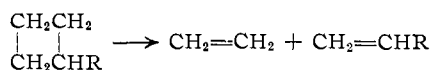


We wish to report the synthesis of an isocyanate by a rearrangement involving the migration of a methoxyl group. Dimethyl 3,3,4,4-tetrafluoro-1,2-diazetidene-1,2-dicarboxylate (I) was prepared in 47% yield by the thermal addition of tetrafluoroethylene to dimethyl azodicarboxylate. Methoxydifluoromethyl isocyanate (boiling point, 44°) (II) was obtained in over 70% yield by the passage of this ester at 5 mm. pressure through a quartz-packed tube heated to 600°.



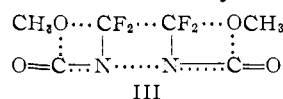
Although the elemental analysis of the product was the same as that of the diazetidine ester I, the molecular weight was just one-half. A strong infrared absorption at 2270 cm^{-1} and the lack of absorption at 1600–1800 cm^{-1} indicated that an isocyanate rather than an ester function was present in the molecule.

Although the thermal cleavage of diazetidines has not previously been reported, the analogous reaction is well known in the cyclobutane series.²

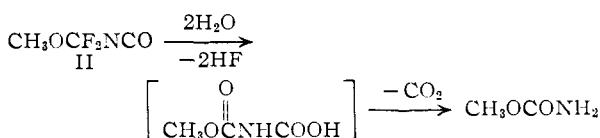


A similar cleavage has been reported for the fluorinated cyclobutanes.³ These homogeneous reactions exhibit first-order kinetics and do not appear to be radical chain reactions.² For the pyrolysis of I a concerted reaction involving a

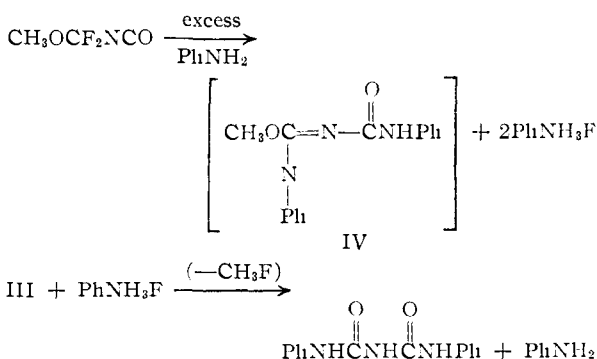
transition state such as III is a reasonable explanation of the formation of the isocyanate.



It is known that the difluoromethylene group adjacent to an isocyanate function is extremely sensitive to nucleophilic attack.^{4,5} Methoxydifluoromethyl isocyanate reacted vigorously with water to form methyl carbamate.



Methyl carbamate was also isolated from the reaction of II with methanol. Aniline reacted with the isocyanate II to form diphenylbiuret, possibly through the intermediate formation of the amidine IV. A similar reaction has been reported for perfluoropropyl isocyanate and ammonium hydroxide.⁶



Acid cleavage of IV to form diphenylbiuret has been reported.⁶

(1) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 497 ff.

(2) (a) C. T. Genaux, F. Kern and W. D. Walters, *THIS JOURNAL*, **75**, 6196 (1953); (b) M. N. Das, F. Kern, T. D. Coyle and W. D. Walters, *ibid.*, **76**, 6271 (1954).

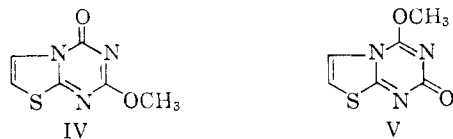
(3) (a) J. L. Anderson, U. S. Patents 2,733,278 (1956); (b) 2,773,089 (1956).

(4) (a) R. L. Dannley and M. Lukin, *J. Org. Chem.*, **21**, 1036 (1956); (b) R. L. Dannley, R. G. Taborsky and M. Lukin, *ibid.*, **21**, 1318 (1956); (c) R. J. Dannley, R. G. Taborsky and M. Lukin, Abstracts of Papers, 130th American Chemical Society Meeting, Atlantic City, N. J., September 16–21, 1956, p. 26-O; (d) R. L. Dannley, D. Yamashiro and R. G. Taborsky, Abstracts of Papers, 134th American Chemical Society Meeting, Chicago, Ill., September 7–12, 1958, p. 38-P.

(5) A. H. Ahlbrecht and D. R. Husted, U. S. Patent 2,617,817 (1952).

(6) R. H. McKee, *Am. Chem. J.*, **26**, 233 (1901).

2-Aminothiazole reacted rapidly with II to form a crystalline product, $C_6H_5N_3SO_2$. The infrared spectrum showed no NH absorption. Strong bands at 1700 cm.^{-1} (conjugated ring carbonyl) and 1230 cm.^{-1} ($\text{CH}_3\text{OC}=\text{N}$)⁷ were present, however. A strong absorption in the ultraviolet ($\lambda_{\text{max}} 2900\text{ \AA.}$, $\epsilon 11,900$) suggested structure IV for this material, although the alternative structure V could not be ruled out.



would be expected if initial attack occurred at the difluoromethylene group of the isocyanate. The latter would result from initial formation of the normal urea derivative followed by ring closure.

Experimental

Dimethyl azodiformate was synthesized by the oxidation of dimethyl hydrazodicarboxylate with fuming nitric acid.⁸ The product melted at 10° .

Dimethyl 3,3,4,4-Tetrafluoro-1,2-diazetidene-1,2-dicarboxylate.—The procedure used was a modification of that described by Cramer⁹ for the diethyl ester. To 100 g. of dimethyl azodiformate in a 400-ml. stainless steel autoclave was added under pressure 80 g. of tetrafluoroethylene. The autoclave was held at 150° for 7 hours and was then cooled. Unreacted tetrafluoroethylene was bled from the autoclave. The viscous yellow product was flash distilled at 3 mm. pressure from a flask heated with the vapor of refluxing cyclohexanol. The volatile material was dissolved in a mixture

(7) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," second edition, John Wiley and Sons, Inc., New York, N. Y., 1958, p. 117.

(8) O. Diels and P. Fritzsche, *Ber.*, **44**, 3026 (1911).

(9) R. D. Cramer, U. S. Patent 2,456,176, December 14, 1948.

of 500 ml. of ether and 50 ml. of ethanol to which 30 ml. of a saturated aqueous solution of sodium bisulfite had been added. The solution was stirred until colorless (5 minutes). The organic layer was separated, washed with water, and dried over magnesium sulfate. The solvent was evaporated, and the product was fractionally distilled to yield 80 g. (47%) of colorless liquid, b.p. 90° (28 mm.), $n_D^{20} 1.3801$.

Anal. Calcd. for $C_6H_8F_4N_2O_4$: C, 29.3; H, 2.5; F, 30.9; N, 11.4; mol. wt., 246. Found: C, 29.9; H, 2.8; F, 30.7; N, 10.9; mol. wt. (freezing point in benzene), 249.

Methoxydifluoromethyl Isocyanate.—The pyrolysis was carried out by dropping 80 g. of dimethyl 3,3,4,4-tetrafluoro-1,2-diazetidene-1,2-dicarboxylate at the rate of 2 ml./minute through a 25×300 mm. tube packed with 5-mm. sections of 7-mm. quartz tubing.¹⁰ The internal pressure was 5 mm., and the temperature was maintained at 600° . Volatile products were condensed in a trap cooled by liquid nitrogen. The contents of the trap were distilled into a second trap at reduced pressure by allowing the first trap to warm to room temperature. The residue (32 g.) was then recycled through the pyrolysis tube. This process was repeated twice. The product in the second trap weighed 67 g. and was fractionally distilled to yield 54 g. (68%), b.p. $43\text{--}44^\circ$, and a forerun of 6 g. (7%), b.p. $41\text{--}43^\circ$.

Anal. Calcd. for $C_3H_3F_2NO_2$: C, 29.3; H, 2.5; F, 30.9; N, 11.4; mol. wt., 123. Found: C, 29.6; H, 2.4; F, 30.9; N, 11.9; mol. wt., 117.

Reaction of Methoxydifluoromethyl Isocyanate with 2-Aminothiazole.—A solution of 7.2 g. of 2-aminothiazole in 20 ml. of tetrahydrofuran was added slowly to a stirred solution of 4.40 g. of methoxydifluoromethyl isocyanate in 20 ml. of tetrahydrofuran. After an hour, a tan solid was removed by filtration and recrystallized from 200 ml. of boiling acetonitrile to yield 4.0 g. (61%) of white crystals, m.p. $240\text{--}241^\circ$.

Anal. Calcd. for $C_6H_8N_3SO_2$: C, 39.3; H, 2.8; N, 22.9; S, 17.5. Found: C, 39.3; H, 2.7; N, 22.9; S, 17.8.

(10) J. C. Kauer, U. S. Patent 2,860,154 (1958).

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[CONTRIBUTION FROM THE U. S. BORAX RESEARCH CORP.]

The Hydrolysis of Triisopropanolamine Borate¹

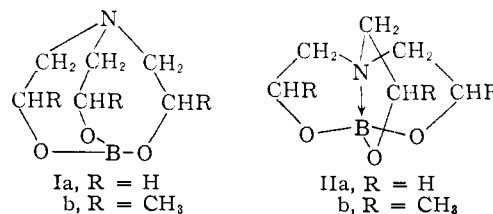
By H. STEINBERG AND D. L. HUNTER

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Commercially available triisopropanolamine has been found by kinetic analysis to consist of a 38.1–61.9% mixture of diastereomers. The less prevalent isomer has been isolated. Triisopropanolamine borates prepared from these isomers are interpreted as diastereomers (IVa and IVb) which differ only in the configuration about one methyl-bearing carbon atom.

The borates equilibrate in water or aqueous dioxane with their products of hydrolysis, triisopropanolamine and boric acid, at widely divergent rates. The equilibrium points are approached by pseudo first-order kinetics with half-lives of 29.5 and 4080 hours in water, 11.0 and 983 hours in 60% dioxane, and 2.74 and 39.0 hours in 91% dioxane. In dilute hydrochloric acid, the hydrolyses proceed to completion at accelerated rates. This unusual hydrolytic stability is attributed to the unavailability of boron for coordination with water due to a transannular interaction of amino-nitrogen² and boron across the eight-membered ring (IIb). The magnitude of the transannular interaction is dependent upon the steric requirements of the isomers.

Brown and Fletcher³ have stated that triethanolamine borate could exist either as structure Ia in which the BO_3 group is planar or the tetrahedral counterpart IIa resulting from a nitrogen-boron transannular interaction. More recently Lucchessi and DeFord⁴ have demonstrated an equi-



(1) Presented in part before the Division of Organic Chemistry, 128th Meeting of the American Chemical Society, Minneapolis, Minn., Sept., 1955.

(2) Transannular interactions of amino-nitrogen and carbonyl groups have been reported for eight and nine-membered rings [N. J. Leonard, *et al.*, *THIS JOURNAL*, **76**, 630, 5708 (1954)].

(3) H. C. Brown and E. A. Fletcher, *ibid.*, **73**, 2808 (1951).

librium between the planar and tetrahedral forms of triethanolamine borate in which water or butanol

(4) C. A. Lucchessi, Doctoral Dissertation Series Publication No. 13, 109; Northwestern Univ. (D. D. Deford), 1955.