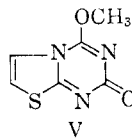
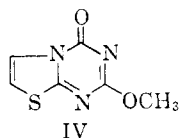


(6) R. H. McKee, *Am. Chem. J.*, **26**, 233 (1901).

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  $1700\text{ cm}^{-1}$  (conjugated ring

carbonyl) and  $1230\text{ cm}^{-1}$  ( $CH_3OC=$ )<sup>7</sup> 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. The former



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.<sup>8</sup> The product melted at  $10^\circ$ .

**Dimethyl 3,3,4,4-Tetrafluoro-1,2-diazetidene-1,2-dicarboxylate.**—The procedure used was a modification of that described by Cramer<sup>9</sup> 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  $150^\circ$  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

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.  $90^\circ$  (28 mm.),  $n_D^{20} 1.3801$ .

*Anal.* Calcd. for  $C_6H_5F_4N_3O_4$ : 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  $25 \times 300$  mm. tube packed with 5-mm. sections of 7-mm. quartz tubing.<sup>10</sup> The internal pressure was 5 mm., and the temperature was maintained at  $600^\circ$ . 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.  $43-44^\circ$ , and a forerun of 6 g. (7%), b.p.  $41-43^\circ$ .

*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.  $240-241^\circ$ .

*Anal.* Calcd. for  $C_6H_5N_3SO_2$ : 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).

WILMINGTON 98, DEL.

(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.

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

## The Hydrolysis of Triisopropanolamine Borate<sup>1</sup>

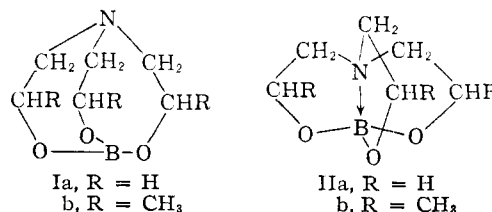
By H. STEINBERG AND D. L. HUNTER

RECEIVED APRIL 18, 1959

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-nitrogen<sup>2</sup> 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 Fletcher<sup>3</sup> 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 DeFord<sup>4</sup> 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.