Di-(γ-aminopropyl) Ether

BY PAUL F. WILEY

The hydrogenation of di-(β-cyanoethyl) ether to give di-(γ-aminopropyl) ether has been reported[1,2,3] but various workers have disagreed as to the properties of the compound. Di-(γ-aminopropyl) ether has also been reported in patents[4,5] without mention of properties or method of preparation. In view of the uncertainty as to the properties of this amine it appeared worth while to report the results of a study of di-(γ-aminopropyl) ether conducted in these laboratories.

Di-(γ-aminopropyl) ether was synthesized as above from di-(β-cyanoethyl) ether.

Procedure.—Ten grams of Raney nickel was added to a solution of 86.9 g. (0.7 mole) of di-(β-cyanoethyl) ether dissolved in 340 cc. of methanol containing 95.7 g. (5.65 moles) of anhydrous ammonia, and the nitrile was hydrogenated at a pressure of 1500 lb. per sq. in., and a temperature of 100–110°. The reduction was quite rapid, requiring about one-half hour. The reaction mixture was filtered, and the methanol and ammonia were removed by distillation at atmospheric pressure. The residue was distilled under reduced pressure. The first fraction consisted of 8.2 g. of a basic liquid boiling at 35–40° at 50 mm. The second fraction distilling at 72–76° at 3 mm. was retained as di-(γ-aminopropyl) ether. The yield of the desired product was 71.2 g. (77.3%). There remained 8.3 g. of residue in the distilling flask.

Several runs such as the above were combined and fractionated using a 30-cm. Fenske column. Eighty-five per cent. of the crude product was di-(γ-aminopropyl) ether boiling at 81–82° at 4 mm. Two more fractionations gave a product boiling at 59° at 1.5 mm., $n^{20}\text{D}$ 1.4605, $d^{20°}$ 0.9429.[6]

Anal. Calcd. for $C_6H_{16}N_2O$: C, 54.50; H, 12.20; N, 21.19; mol. wt., 132.2; *MR*, 38.395; neut. eq., 66.1. Found: C, 54.51; H, 11.68; N, 21.05; mol. wt., 141, 144; *MR*, 38.379; neut. eq., 68.8.

The picrate of di-(γ-aminopropyl) ether was prepared by adding 1 g. of amine to 20 cc. of a saturated solution of picric acid in alcohol and heating to boiling. The cooled solution deposited golden-yellow crystals which, after several recrystallizations from alcohol, melted at 151–152°.

Anal. Calcd. for $C_{18}H_{22}O_{15}N_8$: C, 36.6; H, 3.7; N, 19.0. Found: C, 36.5, 36.5; H, 3.6, 3.5; N, 19.2.

Di-(γ-aminopropyl) ether was also synthesized by the action of ammonia on γ,γ′-dichloropropyl ether. A mixture of 26.6 g. (0.15 mole) of γ,γ′-dichloropropyl ether and 200 cc. of 28% ammonia solution was shaken at 100–120° for twenty hours. The cooled reaction mixture was filtered, boiled with activated charcoal and refiltered. The water and the ammonia were removed from the filtrate by distillation. The residual sirup was mixed into a paste with 20 g. (0.5 mole) of finely-ground sodium hydroxide and distilled. There was obtained 6.7 g. (34.1% yield) of di-(γ-aminopropyl) ether boiling at 70–74° at 3 mm. Redistillation gave a colorless liquid boiling at 64–65° at 2 mm., $n^{20}\text{D}$ 1.4609.

The picrate of this product melted at 150–151°, and there was no depression in melting point when it was mixed with the picrate (m. p. 151–152°) of the amine prepared by reduction.

The closely similar properties of the products of the two methods of synthesis and the unaltered melting point of a mixture of them show that they are identical.

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(1) Wiedeman and Montgomery, THIS JOURNAL, **67**, 1994 (1945).

(2) Whitmore, Mosher, Adams, Taylor, Chapin, Weisel and Yanko, *ibid.*, **66**, 725 (1944).

(3) The article by Wiedeman and Montgomery states that this reaction was reported in French Patent 879,788.

(4) Carothers, U. S. Patent 2,191,556 (February 27, 1940).

(5) Martin, U. S. Patent 2,359,867 (October 10, 1944).

(6) We learn in a private communication from Messrs. W. H. Montgomery and O. F. Wiedeman that, following the above procedure, they have obtained di-(γ-aminopropyl) ether with the physical properties described, b. p. 73° at 3 mm. An equal weight of γ-aminopropanol was also obtained, with nearly the same refractive index and boiling point, 60° at 3 mm. The ratio of γ-aminopropanol formed varied with different samples of Raney nickel and with increased heating periods, so that three hours at 110° yielded almost entirely γ-aminopropanol and little amino ether.

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NEW COMPOUNDS

2-Tosyl-D-galactosan<1,5>β<1,6>[1]

A suspension of 3.9 g. of 2-tosyl-3,4-isopropylidene-D-galactosan<1,5>β<1,6> in 50 ml. of 20% acetic acid was refluxed for thirty minutes, at which time solution was complete. The crystalline 2-tosyl-D-galactosan<1,5>β<1,6> (2.9 g., 89%) which deposited from the cooled solution was recrystallized from 12 parts of 20% acetic acid as clusters of long, slender needles which melted at 114–115° and rotated $[\alpha]^{20}\text{D}$ −20.7° in chloroform (*c*, 0.7). The compound is soluble in hot water and ethyl alcohol, cold chloroform, benzene and ethyl acetate and nearly insoluble in cold water.

Anal. Calcd. for $C_{13}H_{16}O_7S$: C, 49.36; H, 5.10; S, 10.14. Found: C, 49.49; H, 5.20; S, 10.02.

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(1) *Cf.* Hann and Hudson, THIS JOURNAL, **64**, 2436 (1942).

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p-Chlorophenyl Phenacyl Sulfide[1]

The procedure of Delisle[2] was used. *p*-Chlorothiophenol (35 g., 0.24 mole) and 5.6 g. (0.24 g. atom) of finely sliced sodium metal were allowed to react in 300 ml. of anhydrous ether for sixteen hours. The suspension was cooled to −5° and the mixture was stirred and cooled while 48 g. (0.24 mole) of phenacyl bromide was added during forty-five minutes. The temperature was held at 0° throughout the addition, then the mixture was allowed to warm to room temperature during a further two-and-one-half hour period. Dry ether (1500 ml.) was added, the sodium bromide filtered, and the product crystallized from alcohol after removal of the ether; yield, 43.1 g. (68%) of *p*-chlorophenyl phenacyl sulfide, m. p. 77–80°. A second recrystallization gave colorless plates, m. p. 81–82°, unchanged by further recrystallization.

Anal. Calcd. for $C_{14}H_{11}ClOS$: C, 63.99; H, 4.22; S,

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(1) This work was carried out under a contract, recommended by the Committee on Medical Research, between the University of Pennsylvania and the Office of Scientific Research and Development. The compound was tested for antimalarial activity as SN 14,007.

(2) Delisle, *Ber.*, **22**, 309 (1889).