[Contribution from the Organic Chemistry Laboratories of the University of Florida]

MONOALKYLATION OF ETHYLENEDIAMINE WITH ALKENE OXIDES[1]

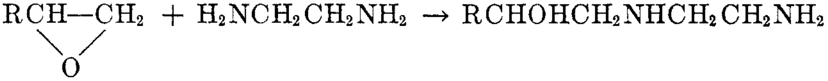
LELAND J. KITCHEN[2] AND C. B. POLLARD

Received May 17, 1943

Knorr and Brownsden (1) have prepared N-(β-hydroxyethyl)ethylenediamine by the reaction of ethylene oxide with an excess of ethylenediamine. When an excess of ethylene oxide was used, the reaction product was the completely alkylated amine, N,N,N′,N′-tetrakis-(β-hydroxyethyl)ethylenediamine (1, 2). N,N′-bis-(β-hydroxyethyl)ethylenediamine also has been obtained from an ethylenediamine-ethylene oxide reaction mixture (3).

In this investigation the corresponding mono-β-hydroxyalkyl ethylenediamines were synthesized by alkylation of ethylenediamine with the oxides of propene, 2-methylpropene, and styrene. The reaction (I) of a substituted ethylene oxide proceeds according to the rule of Krasuskii (4), the oxygen atom remaining attached to the carbon atom which, in the original compound, was associated with the least number of hydrogen atoms.

I.



$$RCH{-}CH_2(O) + H_2NCH_2CH_2NH_2 \rightarrow RCHOHCH_2NHCH_2CH_2NH_2$$

From our experimental data it appears that in general the yield of the monoalkylated product varies with the amount of ethylenediamine used in excess. When the ratio of ethylenediamine to propene oxide was one to one, the yield was 45%. Styrene oxide with a two-fold excess of diamine gave a 60% yield while a seven-fold excess of diamine with 2-methyl propene oxide gave a 90% yield. Likewise a seven-fold excess of diamine with propene oxide gave a 90% yield.

EXPERIMENTAL

The picrates and hydrochlorides were recrystallized from alcohol or aqueous alcohol. All melting points are corrected.

N-(β-Hydroxypropyl)ethylenediamine. Three hundred forty-two grams (5.9 moles) of propene oxide was slowly added through a separatory funnel to 544 g. of 60.5% aq. ethylenediamine (5.48 moles) dissolved in 2 liters of methanol and contained in a 5-liter, 3-necked flask fitted with a stirrer and a reflux condenser. The temperature was kept at 40–50° by a water-bath. A period of three hours was required for the addition of the propene oxide. The product, a water-white slightly viscous liquid with a mild ammoniacal odor, was obtained by fractional distillation. Two hundred eighty-four grams was obtained, a yield of 41%; b.p. 94°/3 mm., 112°/10 mm.; d_4^{25} 0.9837; $d_4^{28.5}$ 0.9810; n_D^{20} 1.4758; n_D^{25} 1.4738; $n_D^{28.5}$ 1.4725.

Molecular refraction: Calc'd for $C_5H_{14}N_2O$: 33.84. Found: 33.79.

Anal. Calc'd for $C_5H_{14}N_2O$: N, 23.69. Found: N, 23.64.

---

[1] The material in this paper is abstracted from part of a dissertation submitted by L. J. Kitchen to the Graduate Council of the University of Florida in partial fulfillment of the requirements for the Ph.D. degree.

[2] Present address: Firestone Tire and Rubber Co., Akron, Ohio.

Dihydrochloride: m.p. 184.7–185.0°.

Anal. Calc'd for $C_5H_{16}Cl_2N_2O$: Cl, 37.09. Found: Cl, 37.18.

Picrate: m.p. 191.0–192.5°.

Phenylthiourea. The amino alcohol was mixed with two moles of phenylisothiocyanate, and the mixture was warmed for several minutes. The amorphous product was crystallized and recrystallized from alcohol; m.p. 149.8–150.0°.

N-(β-Hydroxy-β-methylpropyl)ethylenediamine. Two thousand seven hundred nineteen grams of 70% ethylenediamine (31.7 moles) without any added diluent was treated at 70° to 80° with 365 g. (5 moles) of 2-methylpropene oxide in the manner described above during the course of two hours. After removal of the excess ethylenediamine by fractional distillation at atmospheric pressure and then under vacuum, the product was collected. The yield of pure amino alcohol, a water-white slightly viscous liquid with a mild amine odor, was 572 g. (87%), b.p. 91.2°/5 mm.; 103.7°/10 mm.; d_4^{25} 0.9556; n_D^{25} 1.4672; n_D^{28} 1.4655.

Molecular refraction: Calc'd for $C_6H_{16}N_2O$: 38.45. Found: 38.40.

Anal. Calc'd for $C_6H_{16}N_2O$: N, 21.19. Found: N, 21.06.

Dihydrochloride: m.p. 195.7–196.4°.

Anal. Calc'd for $C_6H_{18}Cl_2N_2O$: Cl, 34.57. Found: Cl, 34.62.

Picrate: m.p. 198.5–200.5° (dec.).

N-(β-Hydroxy-β-phenylethyl)ethylenediamine. Two hundred seventy grams (2.25 moles) of styrene oxide dissolved in 500 ml. of methanol was added during a ten minute period to a solution of 440 g. of ethylenediamine (60.5%, 4.5 moles) in 500 ml. of methanol. The mixture was allowed to stand. The temperature gradually rose to the boiling point of the methanol, and some white solid precipitated after about an hour. Two hundred forty-six grams of monoalkylation product was obtained by fractional distillation after the mixture had stood overnight. The viscous yellow oil, b.p. 184.8°/10 mm., solidified in the receiver while still hot. After recrystallization from hexane-absolute alcohol, the m.p. was 76–80°.

Dihydrochloride: m.p., 196.7–200.8°.

Anal. Calc'd for $C_{10}H_{18}N_2O_2$: N, 28.01. Found: N, 28.01.

N-(β -Hydroxyethyl)ethylenediamine. The Carbide and Carbon product was purified by fractional distillation; b.p. 115.3°/6.2 mm.; b.p. 123°/10 mm.; d_4^{25} 1.0254; n_D^{25} 1.4851.

Molecular refraction: Calc'd for $C_4H_{12}N_2O$: 29.22. Found: 29.12.

Picrate: m.p. 224° (dec.).

Dihydrochloride: m.p. 114.3–115.2°.

SUMMARY

The 1,2-amino alcohols obtained by monalkylation of ethylenediamine with the oxides of propene, 2-methylpropene, and styrene are described and characterized. Properties of N-(β-hydroxyethyl)ethylenediamine are given. Good yields of monalkylation product are obtainable by using large excesses of ethylenediamine.

GAINESVILLE, FLA.

REFERENCES

(1) KNORR AND BROWNSDEN, *Ber.*, **35**, 4470 (1902).
(2) SHERLIN, BERLIN, AND RABINOVITCH, *J. Gen. Chem.* (U.S.S.R.), **11**, 305 (1941).
(3) MACDOWELL, Dissertation, Univ. of Fla., **1936**, p. 11.
(4) KRASUSKII, *Compt. rend.*, **146**, 236 (1908).