(VI) and 1-(*o*-nitrophenoxy)-2-acetoxy-3-phthalimidopropane (VII). A solution of yellow fuming nitric acid (sp. gr. 1.5) in glacial acetic acid was added to a solution of IV in 4 parts of glacial acetic acid to 1 part of acetic anhydride at 80°, and the resulting red solution was kept at 80° for another hour before it was poured into ice-water. Filtration and washing with 5% sodium bicarbonate and water, followed by trituration with boiling ethanol produced a crystalline mixture of VI and VII which was recrystallized from benzene. The pale yellow mixture was obtained in 81.6% yield, m.p. 140–146°.

Separation of the ortho and para isomers at this stage seemed inadvisable because of the great loss of material during recrystallizations of an analytical sample. The results of a nitrogen analysis on this sample, m.p. 158–160°, were in keeping with the composition of either VI or VII or a mixture of the two.

Anal. Calcd. for $C_{19}H_{16}O_7N_2$: N, 7.29. Found: N, 7.48.

1-(*p*-**Nitroanilino**)-**2,3-propanediol (VIII)**. **A.**—The mixture of VI and VII (m.p. 140–146°) was hydrolyzed in the manner[4] used to hydrolyze II, except that the refluxing time with hydrazine (2 moles in this case) was lengthened to 6 hours, and refluxing with 1 to 1 hydrochloric acid was lengthened to 8 hours. The dark oil so produced yielded only 5.4% of orange-yellow crystalline material, m.p. 112–114°, after many extractions and fractional crystallizations with various solvents.

Anal. Calcd. for $C_9H_{12}O_4N_2$: C, 50.94; H, 5.70; N, 13.20. Found: C, 50.74; H, 5.70; N, 13.15.

It was found later that this constant melting material was still a mixture of the ortho and para isomers.

B.—Sixty grams (0.156 mole) of the mixture of VI and VII (m.p. 140–146°) was mixed with 20 g. of sodium hydroxide (0.50 mole) in 160 ml. of water and refluxed for 1 hour. As reflux temperature was approached, the two phase system changed into a deep red solution after approximately 5 minutes of heating. After cooling, orange crystals were filtered off and recrystallized from water and ethyl acetate. (Acidification of the filtrate produced phthalic acid.) The product was extracted with three small portions of chloroform, and the material which did not dissolve was extracted with an alcohol–chloroform mixture. The yellow crystals (VIII) still remaining undissolved were recrystallized from alcohol–acetone and alcohol–chloroform; m.p. 126–127°. From many fractional crystallizations of the chloroform extracts, two separate piles of material were collected and recrystallized separately from ethyl acetate. The yield of yellow VIII was 2 g., m.p. 126–127°; the yield of the orange-yellow mixture of VIII and its ortho isomer (IX) was 18 g., m.p. 106–112°.

C.—VIII was made in 6% yield, m.p. 126–127°, in a fashion analogous to that described by Karrer,[6] *et al.*, for the preparation of its ortho isomer (IX), using 1-amino-2,3-propanediol[12] and *p*-nitrochlorobenzene.

Anal. Calcd. for $C_9H_{12}O_4N_2$: N, 13.20. Found: N, 13.06.

A mixed m.p. determination of VIII prepared as described in B and C gave no depression.

1-(*o*-**Nitroanilino**)-**2,3-propanediol (IX)**. **A.**—Recrystallizations of the mixture of VIII and IX, as prepared in B above (m.p. 106–112°), from chloroform gave a constant melting mixture, m.p. 112–114°, and the yield decreased to 4 g. However, orange-yellow IX, m.p. 117–118°, was isolated from this constant melting mixture by chromatographic adsorption. The mixture was deposited upon alumina from chloroform solutions, developed with 10% absolute ethanol in chloroform, and eluted with methanol.

B.—IX was made in 14% yield as described by Karrer,[6] *et al.*, m.p. 117–118°.

A mixed m.p. determination of IX prepared as described in A and B gave no depression.

1-(*o*-**Nitroanilino**)-**2,3-propanediol hydrochloride** could not be isolated from an aqueous hydrochloric acid solution of IX by evaporation of the solvent in a vacuum desiccator. However, the white salt was obtained by passing hydrogen chloride gas through an ether solution of IX, containing a small amount of methanol. The salt turned pale yellow during filtering and washing with ether, and a portion in moist air very quickly decomposed into the original orange-yellow IX.

(12) L. and E. Knorr, *Chem. Ber.*, **32**, 750 (1899).

PHILADELPHIA 22, PENNA.

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES, BROWN UNIVERSITY]

2-Propyl-4-ethyl-3-nitrosoöxazolidine, a Novel Product from the Nitrous Acid Deamination of 2-Amino-1-butanol

BY HAROLD R. NACE AND MORTON H. GOLLIS[1]

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The nitrous acid deamination of 2-amino-1-butanol in acetic acid yields 2-propyl-4-ethyl-3-nitrosoöxazolidine (49–52%), 1,2-butanediol (4%) and crotyl alcohol (4%). When the reaction is carried out in hydrochloric acid, 2-chloro-1-butanol (2%) is also obtained. The nitrosoöxazolidine is cleaved by acid to *n*-butyraldehyde and the starting amino alcohol. The nitrosoöxazolidine was synthesized by nitrosation of the oxazolidine, formed by the condensation of *n*-butyraldehyde with 2-amino-1-butanol.

Many examples of the reaction of β-amino alcohols with nitrous acid have been reported.[2] In the majority of the cases studied products with rearranged carbon skeletons have resulted, the products being analogous to those of the pinacol rearrangement. However, the reaction has been complicated by one or more factors: (a) The presence of one or more aryl groups on the substituent-bearing carbon atoms has superimposed migratory aptitude and steric effects on the course of the rearrangement.[3] (b) The substituents were attached to carbon atoms incorporated in alicyclic structures, thus bringing into play the effect of polar and equatorial bonds on the ease and direction of the rearrangement.[4] Simple aliphatic amino alcohols would be free of these complicating factors, and a study of them should facilitate the understanding of the more involved cases.

A search of the literature revealed only a few examples of the reaction of simple aliphatic amino alcohols with nitrous acid. Krassusky and Duda[5] obtained in unstated yields pinacol and pinacolone from the reaction of 2,3-dimethyl-3-amino-2-butanol with nitrous acid. Neuberg and Rewald[6]

(1) Research Corporation Fellow, 1951–1952.

(2) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, Chap. 12.

(3) For further discussion and references see P. I. Pollak and D. Y. Curtin, THIS JOURNAL, **72**, 961 (1950).

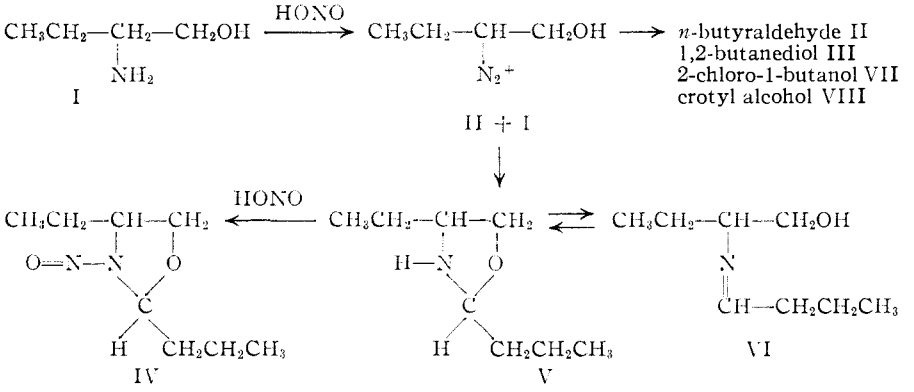
(4) G. E. McCasland, *ibid.*, **73**, 2293 (1951).

(5) K. Krassusky and L. Duda, *J. prakt. Chem.*, [2] **77**, 96 (1908).

(6) C. Neuberg and B. Rewald, *Biochem. Z.*, **67**, 132 (1914).

reported a 30% yield of acetaldehyde from the nitrous acid deamination of ethanolamine. Karrer and Klarer[7] and Levene and co-workers[8,9] obtained in unstated yields levo-1,2-propanediol from the reaction of levo-1-amino-2-propanol with nitrous acid. In view of the limited number of previous studies further investigation seemed desirable.

2-Amino-1-butanol (I) was chosen because of its availability and because the products expected, *n*-butyraldehyde (II) and 1,2-butanediol (III), would be readily identifiable.



When the butanolamine was treated with nitrous acid in either dilute hydrochloric or acetic acid, the expected aldehyde was not isolated, and the glycol was obtained in small amounts (3–4%). The major product was a yellow liquid, insoluble in the reaction mixture and distillable only under reduced pressure. It contained nitrogen and readily formed under acidic conditions the 2,4-dinitrophenylhydrazone of *n*-butyraldehyde, accompanied by the evolution of a gas. The presence of an easily oxidizable group was indicated by a positive Tollens test. Common functional groups such as carbonyl, hydroxyl, olefinic or carbon–nitrogen double bonds, and nitrogen–hydrogen bonds were absent in the infrared spectrum. Cleavage with acid yielded with gas evolution *n*-butyraldehyde and 2-amino-1-butanol. The elemental analysis and molar refraction were in agreement with the structure 2-propyl-4-ethyl-3-nitroso-oxazolidine (IV).

If the reaction of 2-amino-1-butanol with nitrous acid follows a path involving the formation of *n*-butyraldehyde and condensation of this with unreacted amino alcohol to yield an equilibrium mixture of oxazolidine (V) and Schiff base (VI), nitrosation of the oxazolidine would shift the equilibrium and hence remove any of the Schiff base present. Evidence for this route was obtained by nitrosation of the oxazolidine (V), prepared by the method of Cope and Hancock,[10] to give a product identical with the deamination product. The synthesis of the oxazolidine also yielded a higher boiling fraction, which was probably the isomeric Schiff base, 2-butylideneamino-1-butanol (VI).

Although numerous examples of the reaction of β-amino alcohols with nitrous acid have been reported, no instances of the isolation of N-nitroso-oxazolidines could be found. Also no reports were found of N-nitroso derivatives of oxazolidines from other sources. The nitrosoöxazolidine is a yellow liquid, stable when pure, but decomposing slowly in acids. Under the conditions studied, consistently lower yields (35–43%) were obtained from the hydrochloric acid reaction than from the deamination run in acetic acid (49–53%). Increasing concentrations of acid decreased the yield. For example, when the amounts of hydrochloric acid and sodium nitrite used were increased to 1.5 molar equivalents, a 29% yield of the nitroso-oxazolidine was obtained. When the amounts of hydrochloric acid and sodium nitrite were increased to 2.5 and 2.1 molar equivalents, respectively, the compound could not be isolated. Also, when the amounts of acetic acid and sodium nitrite used were increased to 5.5 and 5.0 molar equivalents, respectively, the yield dropped to 27%.

In addition to the nitrosoöxazolidine and glycol there were isolated from the reaction carried out in hydrochloric acid 2-chloro-1-butanol (VII) (2%) and crotyl alcohol (VIII) (4%). The reaction carried out in acetic acid yielded only crotyl alcohol as an additional product (4%). The fact that only 70–75% of the starting organic material could be accounted for is attributed to the difficulty in recovering from aqueous solution the glycol and unreacted amino alcohol.

The deamination of 2-amino-1-butanol appears to be similar to the reaction of aliphatic primary amines with nitrous acid. For example, the diazotization of *n*-butylamine[11] was reported to give *n*- and *s*-butyl alcohol and chlorides, traces of nitrites and 1- and 2-butene.

The infrared spectra of the nitrosoöxazolidine, oxazolidine and Schiff base were taken for possible use in identification and structure determination. The infrared spectrum of the nitrosoöxazolidine (Fig. 1A) did not show any distinguishing absorption in the functional group region. The broad moderate band at 3.00 μ in the spectrum of the Schiff base (Fig. 1B) was assigned to hydrogen-bonded O–H and the strong band at 6.17 μ to the C=N grouping.[12] The oxazolidine spectrum (Fig. 1C) exhibited a broad absorption band of moderate intensity at 3.06 μ, which was assigned to hydrogen-bonded N–H. The weak band (6.03 μ) in the double bond region could not be assigned to any grouping in the oxazolidine structure since the two spectra of oxazolidines reported by Daasch[13] did not show any absorption in the 6–6.5 μ region. This band may be due to an impurity, and the fact

(7) P. Karrer and W. Klarer, *Helv. Chim. Acta*, **8**, 393 (1925).
(8) P. A. Levene and H. L. Haller, *J. Biol. Chem.*, **65**, 53 (1925).
(9) P. A. Levene and A. Walti, *ibid.*, **68**, 423 (1926).
(10) A. C. Cope and E. M. Hancock, THIS JOURNAL, **64**, 1503 (1942).
(11) F. C. Whitmore and D. P. Langlois, *ibid.*, **54**, 3441 (1932).
(12) L. W. Daasch and U. E. Hanninen, *ibid.*, **72**, 3673 (1950).
(13) L. W. Daasch, *ibid.*, **73**, 4523 (1951).

that the oxazolidine did not analyze satisfactorily supports this reasoning (see Experimental section).

Acknowledgment.—We are grateful to Dr. A. C. Cope for helpful discussions and to the Research Corporation for financial assistance.

Experimental[14]

Reaction of 2-Amino-1-butanol with Sodium Nitrite and Hydrochloric Acid.—A solution of 40.0 g. (0.45 mole) of freshly distilled 2-amino-1-butanol (Commercial Solvents Corp.) in 150 ml. of water and 48 ml. (0.56 mole) of concentrated hydrochloric acid was cooled to 0–5° in a three-necked 500-ml. round-bottomed flask, equipped with a stirrer, dropping funnel and a reflux condenser. A solution of 33.2 g. (0.48 mole) of sodium nitrite in 100 ml. of water was added dropwise with stirring over a period of about one hour while the temperature was maintained at 0–5°. The mixture was stirred an additional hour at this temperature and then overnight (13–16 hours) at room temperature. A yellow oil was present on the surface. The mixture was extracted with six 50-ml. portions of ether and the aqueous layer saved. The ether extract was washed with 100 ml. of aqueous saturated sodium bicarbonate solution (no organic acids present on acidification), 100 ml. of aqueous saturated sodium chloride solution, and was then dried over anhydrous sodium sulfate.

The ether was removed from the yellow ether layer by distillation through an 18-cm. Vigreux column, and the residue was distilled through the same column under reduced pressure to yield a low boiling fraction, collected in a Dry Ice trap; 16.13 g. (41.7%) of 2-propyl-4-ethyl-3-nitrosoöxazolidine (IV), b.p. 83–84° (4 mm.); and 1.84 g. of tarry residue. (In several runs yields of the nitrosoöxazolidine ranging from 35–43% were obtained.) The nitrosoöxazolidine was refractionated to constant refractive index by distillation through a semi-micro column.[15] The analytical sample had b.p. 54.5–55.5° (2 mm.), $n^{20}D$ 1.4617, $n^{25}D$ 1.4596, d^{25}_4 1.0159, MD 46.39, calcd. 46.46.

Anal. Calcd. for $C_8H_{16}N_2O_2$: C, 55.79; H, 9.37; N, 16.27; mol. wt., 172. Found: C, 55.53; H, 9.33; N, 16.51; mol. wt., 191, 183, 193 (Rast method in borneol).

The low boiling fraction, which had been collected in the Dry Ice trap, was refractionated through a 10-cm. Vigreux column to yield two products, the first of which was crotyl alcohol (1.42 g., 4.4%), b.p. 65–67° (72 mm.), $n^{25}D$ 1.4253, $n^{17}D$ 1.4291, reported[16] $n^{17}D$ 1.4290. The α-naphthylurethan had m.p. 93.5–95°, mixed m.p. with an authentic sample 94.5–96°. The second fraction was 2-chloro-1-butanol (0.95 g., 1.9%), b.p. 83–88° (72 mm.), $n^{25}D$ 1.4368. The α-naphthylurethan had m.p. 77.5–79°, mixed m.p. with an authentic sample 78–79°.

The deamination aqueous layer was diluted to 500 ml. The water was removed from 250 ml. by distillation under reduced pressure (water-pump). The residue was triturated with ether and saved. After drying over anhydrous potassium carbonate the ether was removed from the ether extract to yield an amber liquid residue, which was distilled through a 10-cm. Vigreux column to yield 0.65 g. (3.2%) of 1,2-butanediol, b.p. 56–58° (2 mm.), $n^{20}D$ 1.4382. The bisphenylurethan had m.p. 118°, mixed m.p. with an authentic sample 118–119°.

To the aqueous layer residue, from which the glycol was extracted, was added approximately 50 g. of potassium hydroxide pellets and 50 ml. of ether. The mixture was allowed to stand for one hour with chilling and occasional shaking. The resulting amber ether layer was decanted, and the residue was extracted again with ether. The combined ether extracts were dried and the ether removed by distillation to yield a viscous orange residue which could not be distilled. Treatment with benzenesulfonyl chloride in aqueous sodium hydroxide yielded 1.35 g. of crude 2-amino-1-butanol benzenesulfonamide, which melted at 82–82.5° after six recrystallizations from benzene–hexane, mixed m.p. with an authentic sample 82.5–84.5°.[17]

The amount of amino alcohol present in the deamination aqueous layer was estimated to be 8.6 g. (21.5% unreacted) from Kjeldahl nitrogen analyses; ammonia found: 97 meq., 97 meq. per total aqueous layer.

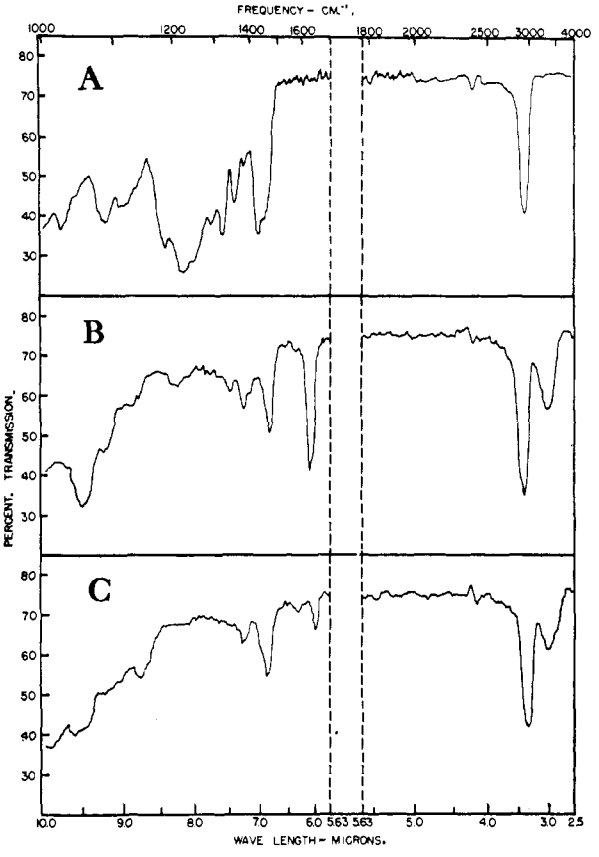


Fig. 1.—A, 2-Propyl-4-ethyl-3-nitrosoöxazolidine; B, 2-butylideneamino-1-butanol; C, 2-propyl-4-ethyloxazolidine.

Reaction of 2-Amino-1-butanol with Sodium Nitrite and Acetic Acid.—The quantities of reactants and solvent (0.45 mole of the butanolamine in 150 ml. of water, 0.56 mole of acetic acid and 0.48 mole of sodium nitrite in 100 ml. of water) and the deamination procedure were the same as described above for the reaction in hydrochloric acid. The reaction mixture was worked up in a like manner.

Distillation of the ether layer gave two fractions, the first of which was crotyl alcohol (1.2 g., 4%); b.p. 62–64° (72 mm.), $n^{17}D$ 1.4293. The α-naphthylurethan had m.p. 94–94.5°, mixed m.p. with an authentic sample 94–95°. The second fraction was 2-propyl-4-ethyl-3-nitrosoöxazolidine (IV) (20.03 g., 51.7%), b.p. 83–86° (3–4 mm.). (In several runs yields ranging from 49–52% were obtained.) There was also obtained 1.55 g. of tarry residue.

The diluted aqueous layer (250 ml.) yielded two products, the first of which was 1,2-butanediol (0.80 g., 3.9%), b.p. 67–69° (4 mm.), $n^{20}D$ 1.4388. The bisphenylurethan had m.p. 117.5–118.5°, mixed m.p. with an authentic sample 117.5–118.5°. The second product was 2-amino-1-butanol, which was isolated as the benzene-sulfonamide, m.p. 80.5–82.5°; mixed m.p. with an authentic sample 83.5–84.5°.

The total amount of unreacted amino alcohol present in the aqueous layer was estimated to be 3.9 g. (9.8% unre-

(14) Melting points are corrected; boiling points are uncorrected. Microanalyses were performed by Mr. S. M. Nagy and associates, Microchemical Laboratory, Mass. Institute of Technology, Cambridge, Mass. The infrared spectra were obtained with a rocksalt prism on a double-beam spectrophotometer described by D. F. Hornig, G. E. Hyde and W. A. Adcock, *J. Optical Soc. Am.*, **40**, 497 (1950). Samples were prepared by pressing the liquids between two polished calcium fluoride plates.

(15) C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

(16) L. N. Owen, *J. Chem. Soc.*, 463 (1943).

(17) The benzenesulfonamide of 2-amino-1-butanol was prepared by the Hinsberg method and recrystallized to constant m.p. 82.5–83.5°. *Anal.* Calcd. for $C_{10}H_{15}NO_2S$: C, 52.38; H, 6.59; N, 6.11. Found: C, 52.17; H, 6.57; N, 6.16.

acted) from Kjeldahl nitrogen analyses; ammonia found: 44 meq., 43 meq. per total aqueous layer.

Acid Cleavage of 2-Propyl-4-ethyl-3-nitrosoöxazolidine (IV).—When a sample of the nitrosoöxazolidine was treated with 2,4-dinitrophenylhydrazine reagent[18] and the solution allowed to stand at room temperature, orange needles formed slowly, accompanied by the evolution of a gas. Two recrystallizations from ethanol-water gave m.p. 120.5–121.5°; mixed m.p. with the 2,4-dinitrophenylhydrazone of *n*-butyraldehyde 120.5–121.5°.

A solution of 5 g. of the nitrosoöxazolidine in 30 ml. of 95% ethanol was acidified with 20 ml. of 10% sulfuric acid. Immediate gas evolution took place. The mixture was refluxed for four hours, during which period an additional 10 ml. of 10% sulfuric acid was added. After overnight refrigeration the mixture was extracted with ether, the ether extract washed with aqueous saturated sodium bicarbonate solution and aqueous saturated sodium chloride solution, and then dried over anhydrous sodium sulfate. The ether was removed from a portion of the ether extract to yield an almost colorless liquid, which gave a positive fuchsin aldehyde test. Treatment of this liquid with 2,4-dinitrophenylhydrazine reagent yielded, without gas evolution, orange needles, m.p. after four recrystallizations from dilute ethanol 117–121°, mixed m.p. with the 2,4-dinitrophenylhydrazone of *n*-butyraldehyde 118–121°. Treatment of the aldehydic liquid with methone[19] yielded a white solid which had m.p. 133–134° after two recrystallizations from methanol–water, mixed m.p. with the methone derivative of *n*-butyraldehyde 133–134°. The yield of *n*-butyraldehyde, based on the 2,4-dinitrophenylhydrazone, was 62%.

Evaporation of the acidic aqueous layer on a steam-bath was accompanied by much charring, and attempts to isolate 2-amino-1-butanol failed. The hydrolysis was repeated using dilute hydrochloric acid in the above procedure. One-half of the aqueous layer remaining after ether extraction was made basic with sodium hydroxide pellets and shaken with 4 ml. of benzenesulfonyl chloride for ten minutes. The reaction mixture was filtered, and the filtrate was acidified dropwise with concentrated hydrochloric acid to turbidity. Overnight refrigeration caused the separation of an oil, which was extracted with ether. The ether was removed and the oil taken up in hot benzene. Chilling and scratching precipitated a white solid, which had m.p. 82.5–83.5° after three recrystallizations from benzene–hexane, mixed m.p. with the benzenesulfonamide of 2-amino-1-butanol 83–85°.

The remaining half of the acidic aqueous layer was evaporated to dryness on a steam-bath to yield a brown viscous oil, which was taken up in hot absolute ethanol. Chilling, dilution with ether and seeding with 2-amino-1-butanol hydrochloride precipitated a white solid, which had m.p. 87.5–89° after several recrystallizations from ethanol–ether, mixed m.p. with an authentic sample of 2-amino-1-butanol hydrochloride 87.5–89°. The yield of 2-amino-1-butanol, based on the hydrochloride, was 41%.

2-Propyl-4-ethyloxazolidine (V).—A solution of 10.3 g. (0.14 mole) of freshly distilled *n*-butyraldehyde and 8.9 g. (0.10 mole) of 2-amino-1-butanol in 100 ml. of dry benzene was heated under reflux under a constant water separator until no further water was collected. The benzene was removed by distillation, and the residue was fractionated from a modified Claisen flask. The first fraction collected was 2-propyl-4-ethyloxazolidine (6.27 g., 43.8%); b.p. 41–50° (mostly 45–49°) (3–4 mm.), $n^{20}D$ 1.4549. A sample refractionated to constant refractive index had b.p. 38–40° (2 mm.), $n^{20}D$ 1.4430, $n^{25}D$ 1.4428, d^{25}_4 0.9039, MD 42.09, calcd. 42.19.

Anal. Calcd. for $C_8H_{17}NO$: C, 67.08; H, 11.96; N, 9.78. Found: C, 65.79; H, 12.08; N, 11.01.[20]

The benzenesulfonamide, prepared by the Hinsberg method, had constant m.p. 61.5–62.5°.

Anal. Calcd. for $C_{14}H_{21}NO_3S$: C, 59.33; H, 7.47; N, 4.94. Found: C, 59.73; H, 7.38; N, 4.93.

The *p*-toluenesulfonamide had constant m.p. 67.5–68° after several recrystallizations from ethanol-water.

Anal. Calcd. for $C_{15}H_{23}NO_3S$: C, 60.57; H, 7.80; N, 4.71. Found: C, 60.45; H, 7.79; N, 5.11.

The second fraction from the distillation of the benzene residue was probably the Schiff base, 2-butylideneamino-1-butanol (VI); yield of pale yellow liquid 3.16 g. (22.1%), b.p. 79–104° (mostly 101.5–103.5°) (3–4 mm.), $n^{20}D$ 1.4841. A sample refractionated to constant refractive index was almost colorless and had b.p. 78.5–80° (1 mm.) and $n^{25}D$ 1.4828. No attempt was made to characterize this fraction other than by its infrared spectrum.

2-Propyl-4-ethyl-3-nitrosoöxazolidine (IV).—To a suspension of 5.29 g. (0.037 mole) of 2-propyl-4-ethyloxazolidine in 15 ml. of water was added 3.9 ml. (0.046 mole) of concentrated hydrochloric acid. The mixture was cooled to 0–5° and a solution of 2.73 g. (0.040 mole) of sodium nitrite in 15 ml. of water was added dropwise with stirring. The mixture was stirred for one hour at 0–5° and then overnight at room temperature (13 hours). A yellow oil was observed approximately two hours after the addition of the sodium nitrite solution. The reaction mixture was extracted with ether and the ether extract dried over anhydrous magnesium sulfate. Removal of the ether left a yellow liquid, which was fractionated through a semimicro column[15] to yield 2.4 g. (38%) of 2-propyl-4-ethyl-3-nitrosoöxazolidine; b.p. 58–58.2° (2–3 mm.), $n^{20}D$ 1.4614, $n^{25}D$ 1.4597; d^{25}_4 1.0130; MD 46.54, calcd. 46.46.

Anal. Calcd. for $C_8H_{16}N_2O_2$: C, 55.79; H, 9.37; N, 16.27. Found: C, 55.44; H, 9.28; N, 16.47.

2-Chloro-1-butanol (VII).—α-Chlorination of *n*-butyryl chloride was carried out in 31% yield with sulfuryl chloride in the presence of iodine according to the method of Kharasch and Brown.[21] The α-chloro acid chloride had b.p. 63–65° (70 mm.), reported b.p. 62–63° (70 mm.).[22] Reduction of the chloro acid chloride with lithium aluminum hydride according to the method of Sroog and co-workers[23] gave the chlorohydrin in 50% yield; b.p. 74–77° (62 mm.), $n^{25}D$ 1.4441. The α-naphthylurethan, prepared by heating the chlorohydrin overnight with α-naphthyl isocyanate in a few ml. of heptane, had constant m.p. 79–79.5°.

Anal. Calcd. for $C_{15}H_{16}NO_2Cl$: C, 64.86; H, 5.81; Cl, 12.77. Found: C, 64.89, 64.92; H, 6.10, 6.04; Cl, 12.74.

1,2-Butanediol (III).—The glycol was prepared in 21% over-all yield from butadiene monoxide according to the method of Clendenning and co-workers,[24] using platinum at low pressure instead of Raney nickel at high pressure to reduce the intermediate unsaturated glycol. The bisphenylurethan melted at 117–118° after several recrystallizations from ethanol–water.

Anal. Calcd. for $C_{18}H_{20}N_2O_4$: C, 65.84; H, 6.14; N, 8.53. Found: C, 66.19; H, 6.24; N, 8.33.

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(18) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

(19) Reference 18, p. 172.

(20) Repeated fractionation failed to give a sample which analyzed satisfactorily.

(21) M. S. Kharasch and H. C. Brown, THIS JOURNAL, **62**, 925 (1940).

(22) E. E. Blaise, *Bull. soc. chim. France*, [4] **15**, 668 (1914).

(23) C. E. Sroog, C. M. Chili, F. A. Short and H. M. Woodburn, THIS JOURNAL, **71**, 1710 (1949).

(24) K. A. Clendenning, F. J. MacDonald and D. E. Wright, *Can. J. Research*, **28B**, 608 (1950).