4,5-Dihydroxy-4,5-di(*p*-bromophenyl)-2-imidazolidinone.—4,5-Di(*p*-bromophenyl)-2-imidazolone[9] (3.94 g., 0.01 mole) as above gave the glycol which crystallized poorly from acetone–ether, m.p. 305–310° (with slow heating), lit.[10] m.p. 320–325°, yield 3.95 g. (92%).

Periodate Oxidation of the Glycols.—Periodic acid (0.40 g.), water (10 ml.), ethanol (50 ml.), and the appropriate glycol (0.002 mole) were allowed to stand overnight. N,N′-Dibenzoylurea or N,N′-di(*p*-bromobenzoyl)urea separated out; the identity of these compounds was confirmed by mixture melting point.

The Effect of Acid on the Glycols.—The appropriate glycol (0.50 g.), ethanol (15 ml.), and concentrated sulfuric acid (1 ml.) were refluxed for 2 hr., diluted with water, and filtered. In the one case the solid was washed with methanol (75 ml.) to give 3a,6a-diphenylglycoluril,[11] m.p. 354–356°, 0.17 g. (31%). Evaporation of the methanolic filtrate gave benzil, 0.24 g. (62%). In the other case the solid was extracted with boiling benzene to give 3a,6a-di(*p*-bromophenyl)glycoluril,[12] m.p. 360–362°, 0.15 g. (28%). Evaporation of the benzene gave 4,4′-dibromobenzil, 0.25 g. (58%).

Effect of Urea on the Glycols.—The appropriate glycol (0.50 g.), ethanol (15 ml.), urea (0.5 g.), and concentrated hydrochloric acid (1 ml.) were allowed to stand overnight. The corresponding glycolurils were obtained in quantitative yields.

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Reaction of Butyramidine with Epoxides. Preparation of 2-Propyl-2-oxazolines

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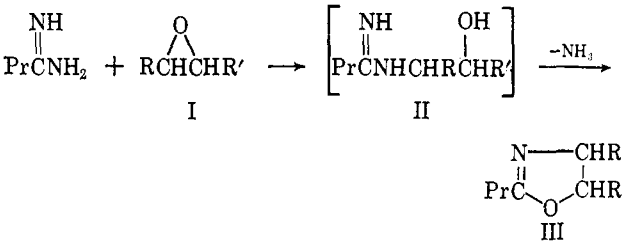
It has been postulated[2] that N-(2-hydroxyethyl)-amidine salts, or closely related structures, are intermediates in the formation of 2-oxazolines from N-alkylamidines and salts of 2-aminoethanol. Likewise, the formation of 2-oxazolines from 2-amino alcohols and imino esters has been shown to involve N-(2-hydroxyalkyl)amidine intermediates.[3]

It therefore might be expected that reaction of amidines with epoxides would also produce 2-oxazolines through the intermediate formation of N-(2-hydroxyalkyl)amidines. This latter method would be advantageous in that epoxides are often more readily available than the amino alcohols required for most other methods of oxazoline preparation. Preparations of 2-oxazolines from epoxides and nitriles[4] and from epoxides and cyanamide[5] apparently are useful only in special cases.

As expected, we have found that 2-propyl-2-oxazolines can be readily obtained from the reaction of butyramidine with various epoxides. Butyramidine reacted at room temperature with each of the first three epoxides listed, Ia–c, to form the corresponding intermediates (IIa–c) which, on heating, evolved ammonia to give the oxazolines (IIIa–c). Reaction of both *cis* and *trans* Id with butyramidine required somewhat higher temperatures. At these higher temperatures, the intermediates were unstable and the oxazolines (*trans* and *cis* IIId) were obtained directly.



a, R = R′ = H
b, R = H, R′ = CH_3
c, R = H; R′ = CH_2CH_3
d, R = R′ = CH_3 (*cis* I → *trans* III, *trans* I → *cis* III)

Both of the unsymmetrical epoxides, Ib and Ic, reacted at the unsubstituted epoxide ring position to give 5-substituted oxazolines. 2-Propyl-5-methyl-2-oxazoline (IIIb) was identified by comparison with an authentic sample,[6] and analysis by gas chromatography showed that it contained no more than a trace of the isomeric 4-methyl compound. 2-Propyl-5-ethyl-2-oxazoline (IIIc) also appeared homogeneous by gas chromatography, although an authentic sample was not available for comparison.

In the n.m.r. spectrum of each of these two oxazolines, the tertiary ring proton appeared at lower τ values than the methylene ring protons. This confirms that the single proton, and thus the ring substituent, is in the 5-position adjacent to O rather than the 4-position adjacent to N. For IIIb and IIIc, the single C-5 protons appeared as complex multiplets at τ 5.35 and 5.52, respectively, and the C-4 methylene protons appeared as complex multiplets at τ 6.35 for both compounds. The multiplets assigned to the C-4 protons correspond to the AB part of ABC spectra, and, in both cases, there is additional fine structure arising from long-range coupling (~2 c.p.s.) with the α-methylene protons of the *n*-propyl substituent.[7]

Intermediates IIa–c were not stable enough for purification but were identified by the infrared spectra of samples taken from the reaction mixtures before heating. IIb and IIc are apparently not completely stable even at room temperature since their spectra before heating showed the presence of some oxazoline.

Inversion occurs during the epoxide ring opening as evidenced by the fact that *cis* Id gives *trans* 2-propyl-4,5-dimethyl-2-oxazoline (*trans* IIId), and *trans* Id gives *cis* IIId. The stereochemical assignments were made on the basis of the n.m.r. spectra. The n.m.r. spectrum of *trans* IIId includes a quartet at τ 5.95 assignable to the C-5 proton and indicating no appreciable coupling with the C-4 proton. This agrees with the expected dihedral angle between these

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protons of near 90°.[8] In contrast, the spectrum of the *cis* compound did show coupling between the C-4 and C-5 protons. The C-5 proton appeared as two overlapping quartets at τ 5.35 ($J \sim 8$ c.p.s.) indicating the dihedral angle is approximately 0° as expected for *cis* IIId. The downfield shift for the C-5 proton from the *trans* to the *cis* compound can be explained in terms of more effective shielding by the methyl groups in the former. This downfield shift also occurs for the C-4 protons. The C-4 proton appears as a multiplet at τ 6.35 in the *trans* oxazoline and at τ 5.95 in the *cis*. Again, in both cases, the C-4 proton couples with the α-methylene protons in the 2-position. Each of the five oxazolines had a strong infrared absorption peak at 1650 cm.$^{-1}$ (C=N) and was transparent in the region 3100–3600 cm.$^{-1}$.

Experimental Section[9]

Butyramidine.[10]—A mixture of 39 g. (1 mole) of sodamide in 250 ml. of *p*-xylene was stirred under N_2 while 69 g. (1 mole) of butyronitrile was added over a 30-min. period. The mixture was then stirred and heated at 105–110° for 3 hr. After cooling, 250 ml. of toluene was added to reduce the freezing point of the solvent, and the reaction flask was fitted with a Dry Ice condenser, and liquid ammonia was added until the mixture became slushy. Ammonium chloride (53 g., 1 mole) was then carefully added to the stirred mixture over a 2-hr. period. The ammonia was allowed to evaporate and the mixture stood for 3 days under N_2 with occasional stirring. The mixture was filtered, the solids were washed with benzene, and the combined filtrate and washings were distilled under reduced pressure. The pressure was periodically adjusted to keep the distillation temperature below 50° until the solvents had been removed. The product was then distilled, b.p. 83–87° (3 mm.). The yield was 60 g. (70%), and the product had a melting point of 26–27°. An analytical sample was obtained by fractionation, b.p. 96° (10 mm.).

Anal. Calcd. for $C_4H_{10}N_2$: C, 55.80; H, 11.71; N, 32.53. Found: C, 55.66; H, 11.74; N, 31.71.

The product formed a hydrochloride[11] with m.p. 107–109° (ethyl acetate–isopropyl alcohol).

Anal. Calcd. for $C_4H_{11}ClN_2$: C, 39.18; H, 9.04; N, 22.86. Found: C, 39.38; H, 9.22; N, 22.57.

Reaction of Butyramidine with Ethylene Oxide (Ia).—A mixture of 8.6 g. (0.1 mole) of butyramidine and 13 g. (0.3 mole) of ethylene oxide was allowed to stand for 3 days at room temperature in a pressure bottle. There was no increase in pressure. Removal of the excess epoxide left a viscous liquid with an infrared spectrum consistent[3a] with the structure IIa, showing peaks at 1610, 1570, and 3340 (broad) cm.$^{-1}$. Attempts to distil this product at reduced pressure resulted in decomposition to form 2-propyl-2-oxazoline (IIIa). The distillation temperature gradually rose from 53 to 165° (0.8 mm.). The distillate was then redistilled at atmospheric pressure to give 4.6 g. (40% yield) of IIIa, b.p. 135–145°. Fractionation gave an analytical sample b.p. 141°.

Anal. Calcd. for $C_6H_{11}NO$: C, 63.69; H, 9.79; N, 12.39. Found: C, 63.70; H, 9.86; N, 12.45.

The product gave 2-(3,5-dinitrobenzamido)ethyl butyrate, m.p. 75–77° (ethanol–water), on reaction with 3,5-dinitrobenzoyl chloride in $NaHCO_3$ solution.[12]

Anal. Calcd. for $C_{13}H_{15}N_3O_7$: C, 48.00; H, 4.65; N, 12.92. Found: C, 48.05; H, 4.83; N, 13.05.

Reaction with Propylene Oxide (Ib).—A mixture of 0.1 mole of butyramidine and 0.2 mole of propylene oxide in a pressure bottle was allowed to stand at room temperature for 3 days. An infrared spectrum of the product corresponded to the intermediate IIb; however, a peak at 1650 cm.$^{-1}$ indicated the presence of some 2-propyl-5-methyl-2-oxazoline (IIIb) also. The material evolved NH_3 on distillation under reduced pressure, and the distillation temperature gradually rose from 30 to 53° (3 mm.). Redistillation at 40 mm. gave 10.6 g. (83% yield) of IIIb, identical with an authentic sample.[6]

Reaction with 1,2-Butylene Oxide (Ic).—A mixture of 0.1 mole of butyramidine and 0.2 mole of 1,2-butylene oxide was heated on an oil bath at 50° for 8 hr. The excess epoxide was then removed, and the product distilled at reduced pressure, b.p. 65–75° (15 mm.). The yield was 11.5 g. (82%) of 2-propyl-5-ethyl-2-oxazoline (IIIc). An analytical sample was obtained by Todd column fractionation, b.p. 76° (20 mm.).

Anal. Calcd. for $C_8H_{15}NO$: C, 68.09; H, 10.71; N, 9.92. Found: C, 67.55; H, 10.35; N, 10.48.

1-(3,5-Dinitrobenzamido)-2-butyl butyrate from the oxazoline and 3,5-dinitrobenzoyl chloride melted at 90–91° (alcohol).

Anal. Calcd. for $C_{15}H_{19}N_3O_7$: C, 51.00; H, 5.42; N, 11.90. Found: C, 51.26; H, 5.57; N, 11.02.

When the reaction was repeated and the reactants allowed to stand 3 days at room temperature, the infrared spectrum indicated a mixture of the oxazoline IIIc and the intermediate IIc.

Reaction with *cis*-2,3-Butylene Oxide (Id).—A mixture of 8.6 g. (0.1 mole) of butyramidine and 14.4 g. (0.2 mole) of *cis*-2,3 butylene oxide underwent no change on standing 3 days at room temperature and was therefore heated on an oil bath at 75° for 20 hr. The excess epoxide was removed and the product was distilled. Six grams (42% yield) of *trans*-2-propyl-4,5-dimethyl-2-oxazoline (IIId) was obtained, b.p. 60–66° (27 mm.). The analytical sample, obtained by fractionation of the product on a Todd column, had a boiling point of 69° (30 mm.), $n^{20}\mathrm{D}$ 1.4262.

Anal. Calcd. for $C_8H_{15}NO$: C, 68.05; H, 10.71; N, 9.92. Found: C, 67.74; H, 10.50; N, 10.42.

The derivative with 3,5-dinitrobenzoyl chloride, *threo*-3-(3,5-dinitrobenzamido)-2-butyl butyrate, melted at 131–132° (alcohol).

Anal. Calcd. for $C_{15}H_{19}N_3O_7$: C, 50.99; H, 5.42; N, 11.89. Found: C, 51.05; H, 5.32; N, 12.03.

Reaction with *trans*-2,3-Butylene Oxide (Id).—A mixture of 0.1 mole of butyramidine and 0.2 mole of *trans*-2,3-butylene oxide remained unchanged after heating 20 hr. on an oil bath at 75°. The mixture was then placed in a pressure bottle and heated at 100° for 5 hr. until there was no more pressure increase. The excess epoxide was removed and the product was distilled. *cis*-2-Propyl-4,5-dimethyl-2-oxazoline (IIId, 9.5 g., 60% yield) was obtained, b.p. 70–75° (30 mm.). Fractionation gave an analytical sample, b.p. 77° (32 mm.), $n^{20}\mathrm{D}$ 1.4362.

Anal. Calcd. for $C_8H_{15}NO$: C, 68.05; H, 10.71; N, 9.92. Found: C, 67.68; H, 10.58; N, 10.27.

Reaction of the oxazoline with 3,5-dinitrobenzoyl chloride in $NaHCO_3$ solution gave an oil which did not crystallize.

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(8) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 79.

(9) Microanalyses were by Huffman Laboratories, Wheatridge, Colo. N.m.r. spectra were run at 60 Mc. in deuteriochloroform with tetramethylsilane as an internal standard. Infrared spectra were on neat material.

(10) This preparation is a modification of that described by E. F. Cornell, *J. Am. Chem. Soc.*, **50**, 3311 (1928).

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Baeyer-Villiger Oxidation of Cyclopropyl Ketones

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Although a great deal of data has been published concerning migratory aptitudes in the Baeyer-Villiger reaction,[2] very little is known about the behavior of

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(2) For a recent review, see P. A. S. Smith in "Molecular Rearrangements," Vol. I. P. DeMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp. 577–591.