2-Amino-2-oxazolin-4-ones. III. Spectral Studies

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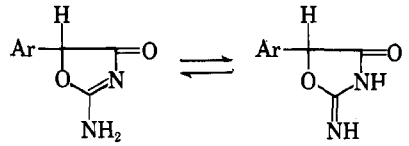
2-Dimethylamino-5-phenyl-2-oxazolin-4-one (II) exhibits n.m.r. signals for two different N-methyl groups which collapse at 70–80° to a single resonance. These signals are attributed to delocalization of the nonbonded electrons throughout the π-system which results in restricted rotation. Solutions of 2-methylamino-5-phenyl-2-oxazolin-4-one (VI) exhibit two unequal n.m.r. signals for each type of proton present. Concentration dependence of n.m.r. and infrared spectra indicate that a dimerization equilibrium (k_2 = 0.3) occurs. 2-Amino-5-(2,3-dimethoxyphenyl)-2-oxazolin-4-one (VIIIa) was shown to exist as the conjugated tautomer similar to other members of the series and unlike previous formulations as the 2-imino tautomer (Ib).

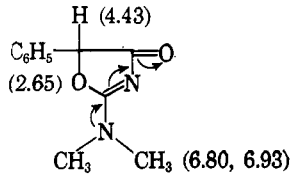
Recently we presented evidence[1] that 2-amino-2-oxazolin-4-ones (Ia) exist, at least in polar solvents, in this form rather than as the tautomers Ib previously formulated.[2,3] These conclusions were based largely



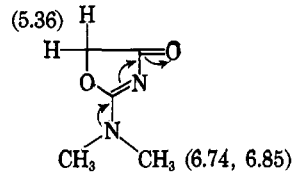
Ia Ib

upon the ultraviolet spectra of I and the methylated derivatives II–VI, and upon their chemical transformations.[1,4] Ionization constants are difficult to obtain in this series because of the limited solubility of these substances and because the pH-dependent changes in the ultraviolet spectra are apparently small and occur at 200–230 mμ. Difficulties in the interpretation of the infrared spectra have already been described.[1,3]

To obtain another type of evidence regarding tautomerism in this series,[5] the n.m.r. spectra of typical N-methyl derivatives (II–VI) were determined in deuteriochloroform. The positions of the n.m.r. peaks in τ units are appended to appropriate groups in the structures given.



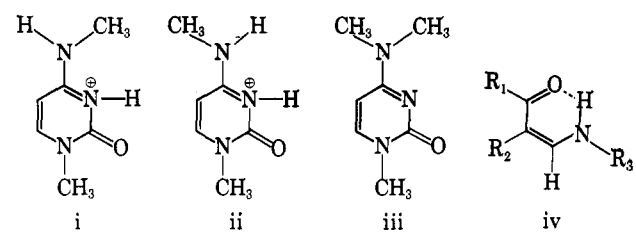
II



III

The presence of two separate N-methyl resonances (each due to 3 protons) in the spectrum of 2-dimethylamino-5-phenyl-2-oxazolin-4-one (II) had not been anticipated. This behavior could not result from coupling since the structure of II apparently does not permit this[6] and, particularly, since the signals at τ 2.65 and 4.43 are singlets. The integrated intensities (5:1:3:3) eliminate the possibility that enolization at C-5 could be involved, and, moreover, there is no hydroxyl signal. The unsymmetrical substitution at C-5 is not responsible for the two N-methyl signals of II, since the symmetrical derivative III behaves similarly. The two N-methyl resonances of II broaden and merge as the temperature is raised from 28° to 67° and collapse to a single broad peak at 84°. This becomes a single sharp signal at higher temperature. Compound III behaves similarly with the temperature of coalescence (T_c) at about 70–75°. This behavior is entirely analogous to that of dimethylformamide[7a,b] (T_c = 148.5° at 60 Mc.),[7c] dimethylacetamide (T_c = 87.2°), other dimethylamides[7c] and alkyl nitrites, nitrosamines, etc.[7d,e] Our spectra are similar to these published examples. The energy of activation (E_a) for this rotation about the partial C–N double bond of dimethylformamide has been variously determined as 7 ± 3,[7a] 9.6 ± 1.5,[7b] or 18.3 ± 0.7 kcal./mole.[7c] Determination of this activation energy for II requires more precise control of temperature and usually larger chemical shifts (8 and 3 c.p.s. for the peak separation and half-band width, respectively, at 25° and 56.4 Mc.) than were available to us. Relatively few N,N-disubstituted vinylogous amides have been investigated by n.m.r. techniques,[8] and hindered rotation apparently has not been reported in such systems.[8-10]

The twin peaks for the N-methyl resonances in II and III result from delocalization of the free pair of electrons of the dimethylamino moiety throughout the vinylogous amides. Since our work was completed two N-methyl signals have been observed (ref. 5b) for iii which may be attributed to restricted rotation. Many vinylogous amides exist as chelated ketamines (iv) (ref. 9) wherein one configuration is stabilized by strong hydrogen bonding.



i ii iii iv

(1) C. F. Howell, N. Q. Quinones, and R. A. Hardy, Jr., *J. Org. Chem.*, **27**, 1679, 1686 (1962).

(2) W. Traube and R. Ascher, *Ber.*, **46**, 2077 (1913).

(3) (a) H. Najer, R. Giudicelli, E. Joannic-Voisinet, and M. Joannic, *Bull. soc. chim. France*, 1226 (1961); (b) H. Najer and R. Giudicelli, *ibid.*, 1231 (1961).

(4) (a) H. Najer, R. Giudicelli, J. Menin, and J. Loiseau, *Compt. rend.*, **254**, 2173, 2591 (1962); (b) *Bull. soc. chim., France*, 1186 (1962); (c) 328 (1963).

(5) (a) See A. R. Katritzky, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **23**, 223 (1962), for a review of some applications of n.m.r. to problems in heterocyclic chemistry; (b) A. R. Katritzky and A. J. Waring, *J. Chem. Soc.*, 3046 (1963).

(6) However, M. A. Weinberger and R. Greenhalgh [*Can. J. Chem.*, **41**, 1038 (1963)] have described the coupling of the methyl group of 2-methyl-2-oxazoline with the 4-methylene moiety (J = 1.3 c.p.s.).

(7) (a) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956); (b) G. Fraenkel and C. Franconi, *J. Am. Chem. Soc.*, **82**, 4478 (1960); (c) M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962); (d) W. D. Phillips, *Ann. N. Y. Acad. Sci.*, **70**, 817 (1958); (e) W. D. Phillips, "Determination of Organic Structures by Physical Methods," Vol. II, F. C. Nachod and W. D. Phillips, Ed., Academic Press, New York, N. Y., 1962, p. 437 ff.

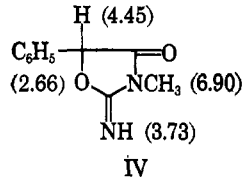
(8) G. N. Walker, *J. Org. Chem.*, **27**, 4227 (1962).

(9) (a) G. O. Dudeck and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 2099, 3914 (1961); (b) J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

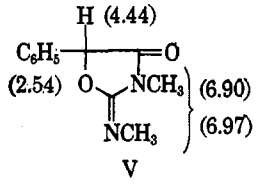
(10) However, Katritzky (ref. 5) has described the *cis* and *trans* forms (i and ii) of an aminopyrimidone cation which may be regarded as protonated

π-system. This restricts rotation about the bond from C-2 to the dimethylamino substituent and places the two methyl groups in different magnetic environments (near O and near N) as shown, while the amino nitrogen atom acquires a degree of planar (sp^2) character.

The proton resonances in IV and V are similar to those in II and III. The similarity of the N-methyl



IV

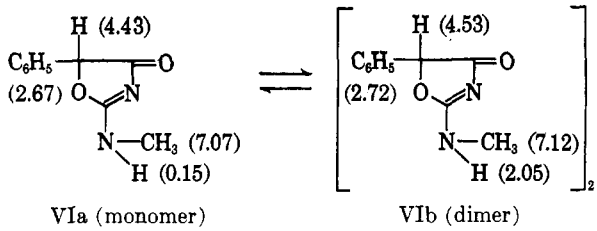


V

resonances suggests that the magnetic environments near N-3 and the 2-amino and 2-imino groups are similar. Compound V appears to exist in only one of the two possible *cis* and *trans* forms or the chemical shifts of the *cis*- and *trans*-N-methyl groups are indistinguishable.

The n.m.r. spectrum of a 13 mole % solution of VI in deuteriochloroform at room temperature was also unexpectedly complex (see Fig. 1, curve A). All the expected resonances appeared as pairs of peaks in a ratio of about 9:7.5 for each signal except for the N-methyl resonance at *ca.* τ 7.1 which is too broad for useful interpretation. Several alternative explanations of this behavior were discarded before the concentration dependence of these ratios was established. It seemed possible that a mixture of tautomeric forms like Ia and Ib might be involved. This interpretation was discarded when it was found that acetonitrile solutions of VI, which also exhibited doubled n.m.r. resonances, had essentially the same extinction coefficient in the ultraviolet spectrum [λ_{max} 223 mμ (ϵ 29,000)] as in methanol [λ_{max} 221 mμ (ϵ 27,800)].[1] In II, with a similar extinction coefficient, this type of tautomerism is impossible. Compound VI has been found to exist in two crystalline forms (one recrystallized from water, the other from ethyl acetate) which have different infrared spectra as solids (potassium bromide).[1] However, solutions of these forms had identical infrared, ultraviolet, and n.m.r. spectra.

The observed behavior is concentration dependent and is explained by the equilibrium formation of a dimer[11] in chloroform (or acetonitrile) solutions in



VIa (monomer) VIb (dimer)

which the lifetime of the dimer is sufficiently long (about 1.5×10^{-3} sec.)[12] and the chemical shifts are slightly different for monomer and dimer.

Magnetic shielding by the π-electrons[13a] in VI is

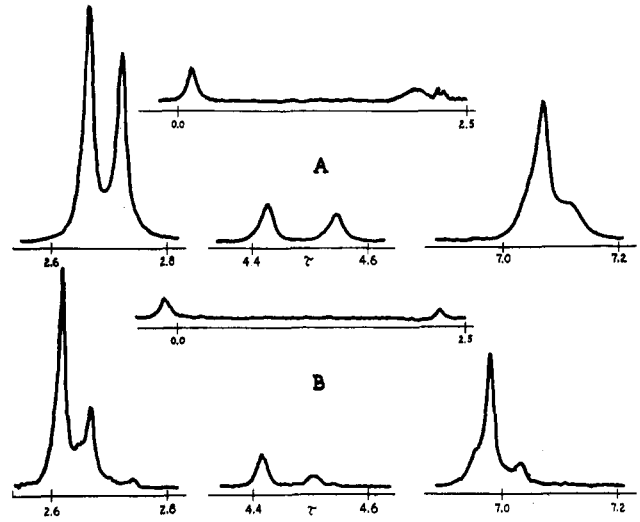


Fig. 1.—N.m.r. spectra of 2-methylamino-5-phenyl-2-oxazolin-4-one (VI) in deuteriochloroform: curve A, 13 mole %; curve B, 2.5 mole %.

responsible both for the relative positions of signals from VIa and VIb and for the general downfield shifts upon dilution. The π-systems effectively contribute more shielding in the dimer than in the monomer so that the dimer resonances appear at higher fields. In more dilute solutions all the signals appear at lower fields because there is less shielding by the reduced concentration of π-systems in the solution. The signals at τ 2.25 in Fig. 1 (curves A and B) appear to be spinning satellites of the aromatic signal and result from field inhomogeneity.[13a] Broad N–H resonances are centered at τ 0.15 and 2.05. Assignment of the τ 2.05 signal to the hydrogen-bonded NH of the dimer is necessitated by its virtual disappearance upon dilution even though hydrogen-bonded protons are usually shifted to lower fields,[9] *e.g.*, in aliphatic amines.[14] The N–H signals of associated pyrrole[15a] and porphyrins,[15b] however, shift to higher fields in more concentrated solutions.

The ratios of the integrated intensities of the two signals from the proton at C-5 (better separated than the other sharp pairs) in the monomer and the dimer are presented in Table I. From these values an association constant (k_2) of 0.3 l./mole was estimated.

TABLE I

DIMERIZATION OF 2-METHYLAMINO-5-PHENYL-2-OXAZOLIN-4-ONE (VI)

Mole % of VI	Ratio of dimer/monomer signals	k_2,[a] l./mole
2.6	0.22	0.37
4.8	0.37	0.29
7.7	0.43	0.26
12.7	0.83	0.34

[a] Association constant estimated on the assumption that dissolving VI in deuteriochloroform does not affect the volume.

(11) The "monomer" may also be hydrogen bonded to the solvent deuteriochloroform. Evidence (infrared) has been presented by C. M. Huggins and G. C. Pimentel [*J. Chem. Phys.*, **23**, 896 (1955)] for such association between N-ethylacetamide and deuteriochloroform.

(12) A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5126 (1956); **80**, 5203 (1958).

(13) (a) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959; (b) several hydrogen-bonded systems are reviewed (ref. 13a) where exchange is slow enough to produce nonaveraged n.m.r. signals, *e.g.*, ethanol and water in the absence of acid (p. 418), acetyl acetone and acetic acid (p. 439), and alkylammonium ions and aqueous acid (p. 454).

(14) J. Feeney and L. H. Sutcliffe, *J. Chem. Soc.*, 1123 (1962).

(15) (a) J. A. Happe, *J. Phys. Chem.*, **65**, 72 (1961); (b) R. J. Abraham, P. A. Burbidge, A. H. Jackson, and G. W. Kenner, *Proc. Chem. Soc.*, 134 (1963).

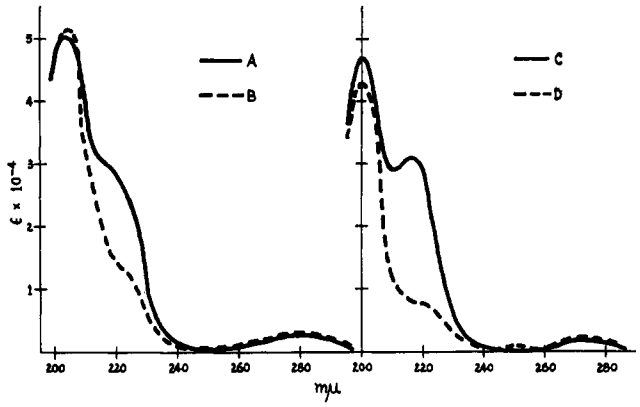
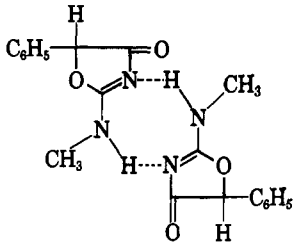


Fig. 2.—Ultraviolet spectra (in methanol) of A, 2-amino-5-(2,3-dimethoxyphenyl)-2-oxazolin-4-one (VIIIa); B, 5-(2,3-dimethoxyphenyl)-2-imino-3-methyl-4-oxazolidinone (IX); C, equimolar mixture of 2,3-dimethoxybenzyl alcohol and 2-amino-2-oxazolin-4-one; and D, 2,3-dimethoxybenzyl alcohol.

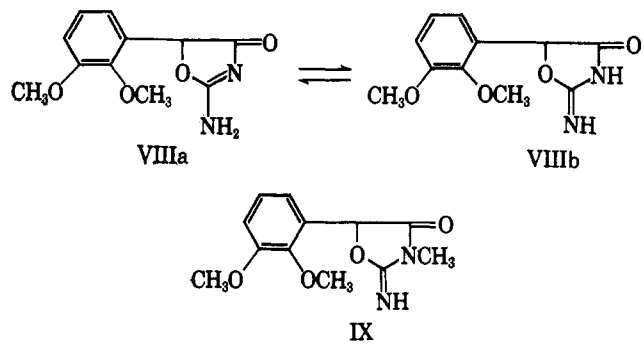
The signals from the dimer increased on cooling from +30° to −43° and disappeared when the temperature was raised from 53° to 77°. Only the relative intensity of the pairs of signals was affected rather than their shapes and positions as in II and III and is consistent with an exothermic dimerization.

The infrared spectra of chloroform solutions of VI are also concentration dependent and entirely parallel the n.m.r. spectra. Absorption at 2.9 (nonbonded N–H)[16] and 7.25 μ is more intense in dilute solutions and is associated with monomeric[12] VIa while bands at 3.4 (bonded N–H)[16] and 7.1 μ are associated with the dimer VIb. The intensities of bands due to bonded and nonbonded N–H stretching in aminopyridines have been studied[17] and used to calculate an association constant for 2-aminopyridine of *ca.* 0.1 l./mole in chloroform. By analogy to this association dimer of 2-aminopyridine,[17] the dimer of VI, an amphoteric compound, may be depicted as VII.



VII

The ultraviolet spectrum of VIIIa was recently reported[4a,b] and absorption at 206 mμ (ε 44,600) was interpreted to indicate a preponderance of VIIIb since derivatives of 2-imino-4-oxazolidinone absorb near this wave length.[1,4] The spectra in Fig. 2 indicate that most of the absorption at *ca.* 206 mμ results from a chromophore similar to 2,3-dimethoxybenzyl alcohol.[18] Although this chromophore is obviously not identical with the aromatic chromophore in VIII, the spectrum of an equimolar mixture of the alcohol and 2-amino-2-oxazolin-4-one[2] closely resembles that of VIII, particularly near 218 mμ where other 2-amino-2-oxazolin-4-ones absorb.[1] In contrast, the spectrum of the 2-imino compound IX (prepared from VIII and methyl iodide in dimethylformamide and characterized by hydrolysis to 5-(2,3-dimethoxyphenyl)-3-methyl-2,4-oxazolidinedione) is significantly different in this region. While these results cannot exclude the presence of small amounts of VIIIb, VIIIa appears to be the predominant tautomer.[1,4] The published spectrum[4] of 5-(3,4-dimethoxyphenyl)-2-amino-2-oxazolin-4-one suggests that it also exists predominantly as the 2-amino tautomer in ethanol.



VIIIa VIIIb

IX

Experimental

General.—N.m.r. spectra were determined with a Varian A-60 instrument operating at 60 Mc. except for the temperature dependence studies where a Varian HR-60 instrument operating at 6.4 Mc. was employed. Chemical shift values are relative to a tetramethylsilane internal standard.[19] Ultraviolet spectra were determined using a Cary Model 14 spectrophotometer, except that of IX where a Cary Model 11 was used. Melting points are uncorrected. The preparations of II, IV, V, VI,[1] and VIII[3a] have been described previously.

2-Dimethylamino-2-oxazolin-4-one (III).—A solution of 25 ml. (0.25 mole) of ethyl glycolate (Eastman, technical) in 300 ml. of benzene was distilled until 50 ml. of distillate was collected. The residual solution was cooled and treated with 1.8 g. of 50% sodium hydride–mineral oil dispersion followed by 20 ml. (0.25 mole) of dimethylcyanamide and refluxed for 3 hr.[1] The mixture was stored at room temperature for 60 hr., clarified by filtration, and concentrated to about 30 ml. Cooling gave 12.1 g. (38%) of colorless 2-dimethylamino-2-oxazolin-4-one, m.p. 107–109°. A sample for analysis was sublimed *in vacuo* and had m.p. 108.5–110.5°, λ_{max}^{MeOH} 227 mμ (ε 27,000).

Anal. Calcd. for $C_5H_8N_2O_2$: C, 46.85; H, 6.30; N, 21.87. Found: C, 47.15; H, 6.18; N, 21.59.

5-(2,3-Dimethoxyphenyl)-2-imino-3-methyl-4-oxazolidinone (IX).—A solution of 4.1 g. (0.017 mole) of 2-amino-5-(2,3-dimethoxyphenyl)-2-oxazolin-4-one[3a] in 17 ml. of freshly opened dimethylformamide was treated with 7.2 ml. of methyl iodide and stored in the dark at room temperature for 7 days.[1] The dark solution was then treated with 1.5 g. of sodium bicarbonate and concentrated under reduced pressure. The residue was suspended in 80 ml. of methylene chloride and then was filtered. The residue was washed with two more 25-ml. portions of methylene chloride. The combined solutions were extracted with 25 ml. of 0.1 *N* sodium thiosulfate, cooled, washed with 17 ml. of ice-cold 1 *N* sodium hydroxide, and dried over sodium sulfate. Concentration yielded an oil that resisted crystallization. This material was dissolved in 17 ml. of cold benzene and extracted with two 17-ml. portions of ice-cold 10% hydrochloric acid which were added at once to excess solid potassium carbonate. The product was extracted into methylene chloride and dried over sodium sulfate. Concentration yielded 1.2 g. (28%) of 5-(2,3-dimethoxyphenyl)-2-imino-3-methyl-4-oxazolidinone, m.p. 88–92°. A sample sublimed with the aid of a mercury diffusion pump had m.p. 94–96° and infrared absorption at 2.9 (sharp, =NH), 5.65, 5.75 and 5.9 μ.

(16) L. J. Bellamy ["The Infrared Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1958, p. 205] gives 2.9 and 3.0–3.25 μ for nonbonded and bonded N–H stretching of secondary amines.

(17) K. V. Ramiah and P. G. Puranik, *J. Mol. Spectry.*, **7**, 89 (1961).

(18) J. H. Burckhalter and S. H. Johnson, Jr., *J. Am. Chem. Soc.*, **73**, 4832 (1951).

(19) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

Anal. Calcd. for $C_{12}H_{14}N_2O_4$: C, 57.59; H, 5.64; N, 11.20. Found: C, 57.38; H, 5.82; N, 10.83.

5-(2,3-Dimethoxyphenyl)-3-methyl-2,4-oxazolidinedione. A.—The benzene solution from the preceding reaction, which had been washed with hydrochloric acid, was concentrated and the solid residue was recrystallized from benzene–cyclohexane to give 1.5 g. (34%) of 5-(2,3-dimethoxyphenyl)-3-methyl-2,4-oxazolidinedione, m.p. 92–95°. A sample for analysis was recrystallized and dried *in vacuo* over phosphorus pentoxide and had m.p. 95–96° and infrared absorption at 5.5 and 5.75 μ.

Anal. Calcd. for $C_{12}H_{13}NO_5$: C, 57.35; H, 5.22; N, 5.58. Found: C, 57.10; H, 5.16; N, 5.35.

B.—Hydrolysis of 62 mg. of IX in 0.6 ml. of 10% hydrochloric acid at 90–100° for 10 min. gave 57 mg. (91%) of 5-(2,3-dimethoxyphenyl)-3-methyl-2,4-oxazolidinedione, m.p. 95.5–97°, with the characteristic infrared spectrum.

Acknowledgment.—We wish to thank G. Morton, L. Brancone, and Dr. J. E. Lancaster for generous assistance with spectral studies, microanalyses, and n.m.r. spectra at elevated temperatures, respectively. Our thanks also are extended to Dr. M. G. Howell for many helpful discussions and for assistance with the technical literature. Appreciation is extended to Dr. H. Najer (Labs Dausse, Paris) for reference samples of IX and 5-(3,4-dimethoxyphenyl)-2-amino-2-oxazolin-4-one.

2-Vinyloxazolidines and 2-Methylenemorpholines from N-Propargylethanolamines and N-(2-Haloallyl)ethanolamines[1]

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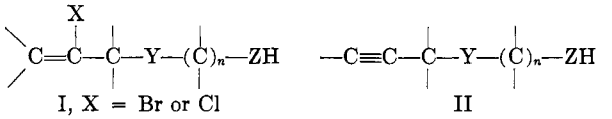
An N-alkyl-N-propargylethanolamine (III), as the alkoxide in ether, or on treatment with sodium hydroxide in dimethyl sulfoxide, or on treatment with potassium hydroxide in toluene or xylene, is converted to the corresponding 3-alkyl-2-vinyloxazolidine (VII). On treatment with aqueous sodium hydroxide, III is converted to the corresponding 4-alkyl-2-methylenemorpholine (VIII). Formation of VII is best understood as occurring *via* an intramolecular nucleophilic addition at C-1 of the allene moiety of the allenic amino alcohol (VI) formed by base-induced prototropic rearrangement of III. That an allenic amino alcohol is not an intermediate in the reaction leading to a 2-methylenemorpholine has been shown by tracer experiments. Treatment of an N-alkyl-N-(2-chloroallyl)ethanolamine (V) with an equivalent amount of sodium amide in ether gave the corresponding VII, but similar treatment of a 2-bromoallyl analog of V gave only the corresponding N-alkyl-N-propargylethanolamine (III).

Formation of an N-alkylallenimine (1-alkyl-2-methyleneaziridine) by the reaction of an N-(2-bromoallyl)-alkylamine with sodium amide in liquid ammonia occurs predominantly, if not exclusively, *via* an intramolecular nucleophilic addition to the central carbon of an intermediate allenic amine.[2] Another reaction that can be best interpreted as occurring by an intramolecular nucleophilic addition to an allenic amine intermediate is that of an N-propargylethanolamine with potassium hydroxide in boiling toluene or xylene.[3] The product is the 2-vinyloxazolidine, and nucleophilic addition occurs at C-1 of the allene moiety of the allenic amino alcohol, which can arise from the N-propargylethanolamine by base-induced prototropic rearrangement.[4] Substituted N-propargylethanolamines, which contain no propargylic hydrogens, were found recently to undergo cyclization to 2-methylenemorpholines when treated with potassium hydroxide in boiling toluene or xylene.[5]

The work described here was undertaken to determine the range of conditions under which N-(2-haloallyl)-ethanolamines and N-propargylethanolamines could be converted conveniently to cyclic products by treatment with base and, where practical, to learn the detailed mechanisms by which the products are formed. A large number of base-induced ring-closure reactions of suitably constituted 2-haloallyl and propargyl compounds, which are represented generally by I and II, are conceivable,[6] and the results reported here have already proved of value in further studies in these laboratories directed toward determining the scope and limitations of ring-closure reactions of compounds represented by I and II.



I, X = Br or Cl II

The reaction in liquid ammonia of N-(2-bromoallyl)-2-hydroxy-3-butenylamine with 2.1 equiv. of sodium amide gives a yield of the corresponding allenimine[7] that is comparable with yields obtained

(1) (a) Part VI, Amines Derived from Dihalopropenes; (b) previous paper in the series, A. T. Bottini, B. J. King, and R. E. Olsen, *J. Org. Chem.*, **28**, 3241 (1963); (c) presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., September, 1963. This work was supported by Grant CA-05528 from the National Cancer Institute and Grant GM-10606 from the Division of General Medicine of the Public Health Service.

(2) A. T. Bottini and R. E. Olsen, *J. Am. Chem. Soc.*, **84**, 195 (1962).

(3) (a) W. J. Croxall and J. H. Mellema, U. S. Patent 2,960,508 (November 15, 1960); *Chem. Abstr.*, **55**, 14482 (1961); (b) see also W. J. Croxall, N. D. Dawson, P. D. Arseneau, J. H. Mellema, and J. Mirza, Abstracts, 138th National Meeting of the American Chemical Society, New York, N. Y., September, 1960, p. 77P.

(4) A significant paper concerning prototropic rearrangements of acetylenes is by T. L. Jacobs, R. Akawie, and R. G. Cooper, *J. Am. Chem. Soc.*, **73**, 1273 (1951).

(5) N. R. Easton, D. R. Cassady, and R. D. Dillard, *J. Org. Chem.*, **28**, 448 (1963).

(6) Some recent examples of base-induced ring-closure reactions of 2-chloroallyl and propargyl compounds other than those already mentioned are given by W. J. Croxall and N. D. Dawson, U. S. Patent 3,021,341 (February 13, 1962); *Chem. Abstr.*, **57**, 11,205 (1962); K. Sisido, K. Hukuoka, M. Tuda, and K. Nozaki, *J. Org. Chem.*, **27**, 2663 (1962); N. R. Easton, D. R. Cassady, and R. D. Dillard, *ibid.*, **27**, 2927 (1962); E. Kaiser, E. Domba, and M. Skibbe, *ibid.*, **27**, 2931 (1962); N. Shachat and J. J. Bagnell, Jr., *ibid.*, **28**, 991 (1963); and W. J. Croxall and N. D. Dawson, U. S. Patent 3,048,598 (August 7, 1962); *Chem. Abstr.*, **59**, 2828 (1963). See also I. Iwai, *Takamine Kenkyusho Nempo*, **14**, 1 (1962), and references cited therein to recent Japanese work.

(7) A. T. Bottini and V. Dev, *J. Org. Chem.*, **27**, 968 (1962).