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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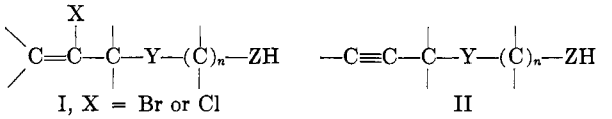
An N-alkyl-N-propargylethanolamine (III), as the alkoxide in ether, or on treatment with sodium hydroxide in dimethyl sulfoxide, or on treatment with potassium hydroxide in toluene or xylene, is converted to the corresponding 3-alkyl-2-vinyloxazolidine (VII). On treatment with aqueous sodium hydroxide, 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).

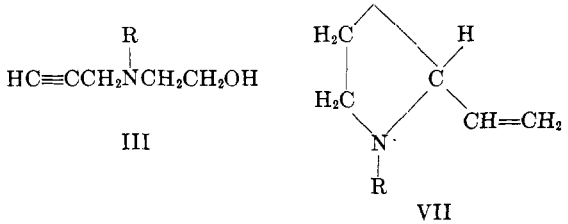
(5) N. R. Easton, D. R. Cassady, and R. D. Dillard, *J. Org. Chem.*, **28**, 448 (1963).

(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).

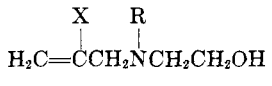
from simple N-(2-bromoallyl)alkylamines under optimum conditions for allenimine formation.[1b,8] Although the allenic amino alcohol, $CH_2{=}C{=}CHNHCH_2CHOHCH{=}CH_2$, an intermediate in the reaction leading to the allenimine, could conceivably undergo a ring-closure reaction in which a new carbon–oxygen bond is formed, no compound with an oxygen-containing ring was detected as a product.

As allenimine formation could be prevented by the simple expedient of replacing the amino hydrogen with an alkyl group, we treated N-ethyl-N-(2-bromoallyl)-ethanolamine (IVb) with an excess of sodium amide in liquid ammonia in order to determine if detectable quantities of an oxygen-containing ring compound could be formed from an N-(2-bromoallyl)ethanolamine under conditions similar to those used for preparation of an allenimine. When ether was added to the reaction mixture together with a small amount of water that was insufficient to convert all the excess base to sodium hydroxide, distillation of the ethereal solution gave in 10% yield an acrid liquid that was identified as 3-ethyl-2-vinyloxazolidine (VIIb). When excess water or ammonium chloride was added to the reaction mixture together with the ether, the only product isolated was N-ethyl-N-propargylethanolamine (IIIb), and yields were 78% and 88%, respectively. We concluded that little if any VIIb was formed in liquid ammonia from IVb[9] and that the ring-closure reaction occurred in ether. The latter conclusion was verified by the observation that N-ethyl-N-propargylethanolamine (IIIb) as the alkoxide in ether was converted in 40 hr. at room temperature to 3-ethyl-2-vinyloxazolidine (VIIb) in 21% yield.

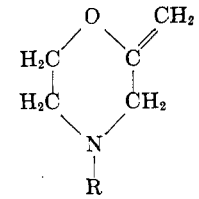


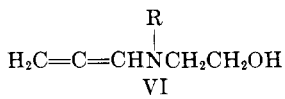
III

VII



IV, X = Br; V, X = Cl





VI

VIII

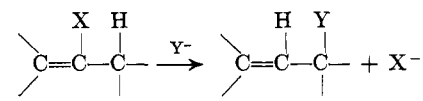
a, R = CH_3
b, R = C_2H_5
c, R = t-C_4H_9

Other 3-alkyl-2-vinyloxazolidines were prepared by treatment of the corresponding N-alkyl-N-propargylethanolamines with an equivalent of sodium amide in ether, and we have used this method to prepare a number of 3,5-dialkyl-2-vinyloxazolidines.[10] Yields, however, ranged from 13–35%, and the general utility of the method appears to be inferior to that used by Croxall and Mellema.[3]

We examined the reactions of the alkoxides of the N-t-butyl-N-(2-haloallyl)ethanolamines in ether in order to determine if cyclic products could be obtained directly from these compounds and, if so, if the mode of cyclization would be the same as observed for the corresponding propargyl compounds. N-t-Butyl-N-(2-chloroallyl)ethanolamine (Vc), on treatment with an equivalent amount of sodium amide in ether, gave after 40 hr. 3-t-butyl-2-vinyloxazolidine (VIIc) in 52% yield. Similar treatment of N-t-butyl-N-(2-bromoallyl)ethanolamine (IVc) gave only the corresponding propargylamino alcohol in 65% yield. These results are consistent with the interpretation that dehydrobromination of IVc occurs much more rapidly than dehydrochlorination of Vc and that oxazolidine formation occurs at about the same rate as the dehydrochlorination reaction. No detectable amount of VIIc is formed from Vc because the base necessary for prototropic rearrangement of N-t-butyl-N-propargylethanolamine (IIIc) has been destroyed during the rapid dehydrobromination reaction. Although the foregoing results show that dehydrobromination of IVc occurs exclusively across the double bond, they do not necessarily show that N-t-butyl-N-(2-chloroallyl)ethanolamine (Vc) dehydrohalogenates in the same way. Conceivably Vc can undergo dehydrochlorination directly to the intermediate allenic amino alcohol by either a concerted or stepwise process.

3-Methyl- and 3-ethyl-2-vinyloxazolidine (VIIa and VIIb) also were prepared from the corresponding N-(2-chloroallyl)ethanolamines, but the yields were less than 15%. In contrast, N-t-butyl-N-(2-chloroallyl)-1-amino-2-methyl-2-propanol, on treatment with a 28% excess of sodium amide in ether, gave a 51% yield of 3-t-butyl-5,5-dimethyl-2-vinyloxazolidine (IX).

We wish to note that formation of a 2-vinyloxazolidine from an N-(2-chloroallyl)ethanolamine appears to be the first example of a nucleophilic displacement reaction of the following type.



In the reaction, the nucleophile becomes bonded to the allylic carbon of the starting material which was adjacent to the vinylic carbon bonded to the leaving group.

We examined the ring-closure reactions of N-alkyl-N-propargylethanolamines (III) induced by sodium hydroxide in dimethyl sulfoxide at 70–90° and in water at 100°. The only products obtained from reactions of III carried out in dimethyl sulfoxide were the corresponding 3-alkyl-2-vinyloxazolidines (VII). Although the yields, which ranged from 36–58%, were higher than those obtained from reactions carried out in ether, they were less than those obtained by Croxall and Mellema.[3] In water, the sodium hydroxide-in-

(8) C. B. Pollard and R. F. Parcell, *J. Am. Chem. Soc.*, **73**, 2925 (1951).

(9) Failure to obtain a significant amount of VIIb from IVb in liquid ammonia does not allow one to conclude that little or no allenic amino alcohol (VIb) is formed during the reaction. Conceivably, under the particular reaction conditions, ring-closure reactions of the alkoxide of VIb are quite slow and do not compete successfully with rearrangement to the alkoxide of IIIb. J. J. Van Dealen, A. Kraak, and J. F. Arens, *Rec. trav. chim.*, **80**, 810 (1961), have observed that 1-t-butoxypropyne is isomerized to 3-t-butoxypropyne by sodamide in liquid ammonia, presumably *via* an allenic ether intermediate.

(10) We currently are examining the nature and degree of stereospecificity in the formation of 3,5-dialkyl-2-vinyloxazolidines from N-propargylalkanolamines. The diastereomers of 3-t-butyl-5-methyl-2-vinyloxazolidine appear to be formed in the ratio 3:2 as indicated by gas–liquid partition chromatography

TABLE I

YIELDS, PHYSICAL PROPERTIES, AND ANALYTICAL DATA OF UNSATURATED AMINO ALCOHOLS, 2-VINYLOXAZOLIDINES, AND 2-METHYLENEMORPHOLINES

Compound	R	Yield, %	B.p. (mm.), °C.	n_D	Temp., °C.	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N
III	CH_3	42[h]	62–65 (10)	1.4673	24	63.68	9.80	12.38	63.64	9.98	12.16
III	C_2H_5	60[i]	59–61 (3)	1.4660	25	66.11	10.30	11.02	65.99	10.12	10.94
III	t-C_4H_9	51[h]	93–95 (10)	1.4677	24	69.63	11.03	9.02	69.52	11.08	9.21
IV	CH_3	52[i]	80–84 (15)	1.4951	25	37.13	6.23	7.22	37.31	6.25	7.31
IV	C_2H_5	40[i]	82–86 (4)	1.4886	25	40.40	6.78	6.73	40.66	6.78	6.32
IV	t-C_4H_9	74[h]	113 (10)	1.4908	22	45.97	7.71	5.96	45.63	7.41	5.87
V	CH_3	69[h]	85–90 (16)	1.4746	21	48.16	8.08	9.36	48.28	7.89	9.10
V	C_2H_5	58[i]	67–68 (2)	1.4700	25	51.37	8.62	8.56	51.39	8.30	8.39
V	t-C_4H_9	51[h]	84–85 (2)	1.4726	22	56.39	9.46	7.31	56.60	9.32	7.31
VII	CH_3	32[j]	36–38 (41)	1.4450	22	63.68	9.80	12.38	63.32	9.60	12.43
VII	C_2H_5	21[j]	52–53 (18)	1.4450	26	66.11	10.30	11.02	66.53	10.53	10.69
VII	t-C_4H_9	52[k]	70–73 (15)	1.4520	23	69.63	11.03	9.02	69.45	10.95	9.21
VIII	CH_3	39	46–48 (22)	1.4592	25	63.68	9.80	12.38	63.60	9.68	12.46
VIII	C_2H_5	48	44–46 (9)	1.4596	25	66.11	10.30	11.02	65.86	10.12	11.04
VIII	t-C_4H_9	65	75–77 (14)	1.4612	25	69.63	11.03	9.02	69.79	11.40	8.89
IX	t-C_4H_9	48[k]	73–75 (18)	1.4471	23	72.08	11.54		71.70	11.34	
XIV[a]	CH_3	86[h]	58 (10)	1.4534	24	66.11	10.30	11.02	65.92	10.39	10.90
XIV[a]	C_2H_5	71[l]	63–64 (6)	1.4510	26	68.05	10.70	9.92	68.11	10.57	10.06
XIV[a]	i-C_3H_7	72[k]	74–76 (6)	1.4550	20	69.63	11.03	9.02	69.81	10.81	8.91
XIV[a]	t-C_4H_9	61[i]	102–105 (19)	1.4579	22	70.96	11.31	8.28	71.09	11.26	8.30
XV[b]	CH_3	69[i]	91 (10)	1.4807	26	40.40	6.78	6.73	40.72	6.70	6.56
XV[b]	C_2H_5	74[i]	91 (10)	1.4800	25	43.25	7.26	6.30	43.27	7.22	6.17
XV[b]	i-C_3H_7	72[i]	60 (1)	1.4787	25	45.97	7.71		45.70	7.46	
XV[b]	t-C_4H_9	62[h]	115 (11)	1.4850	25			5.60			6.09
XVI[c]	CH_3	72[i]	65–67 (4)	1.4593	27	51.37	8.62	8.56	51.59	8.57	8.52
XVI[c]	t-C_4H_9	61[h]	95–97 (7)	1.4658	28	58.38	9.80	6.81	58.51	9.82	6.77
XVII[d]	t-C_4H_9	77[h]	85–87 (9)	1.4597	19	72.08	11.54	7.64	71.98	11.25	7.78
XVIII[e]	t-C_4H_9	37[h]	100–108 (10)	1.4673	22	60.12	10.09	6.38	59.85	9.88	6.46
XIX[f]	CH_3	13[j]	45–48 (10)	1.4351	26	66.11	10.30	11.02	65.95	10.39	10.85
XIX[f]	C_2H_5	14[j]	67 (30)	1.4379	28	68.05	10.70	9.92	67.86	10.51	9.61
XIX[f]	i-C_3H_7	6[j]	30 (3)	1.4418	28			9.02			8.64
XIX[f]	t-C_4H_9	54[m]	68–70 (13)	1.4464	23	70.96	11.31	8.28	71.10	11.09	8.41
XX[g]	CH_3	47	58 (42)	1.4518	26	66.11	10.30	11.02	65.92	10.53	11.12

[a] XIV is N-alkyl-N-propargyl-1-amino-2-propanol. [b] XV is N-alkyl-N-(2-bromoallyl)-1-amino-2-propanol. [c] XVI is N-alkyl-N-(2-chloroallyl)-1-amino-2-propanol. [d] XVII is N-t-butyl-N-propargyl-1-amino-2-methyl-2-propanol. [e] XVIII is N-t-butyl-N-(2-chloroallyl)-1-amino-2-methyl-2-propanol. [f] XIX is 3-alkyl-5-methyl-2-vinyloxazolidine. [g] XX is 4,6-dimethyl-2-methylenemorpholine. [h] From unsaturated halide and amino alcohol. [i] From unsaturated amine and oxirane. [j] From propargylamino alcohol in ether. [k] From 2-chloroallylamino alcohol in ether. [l] From dehydrobromination of XII, R = C_2H_5. [m] From XI, R = t-C_4H_9, in dimethyl sulfoxide.

duced reaction of N-alkyl-N-propargylethanolamines (III) took a different course, and the reactions gave the corresponding 4-alkyl-2-methylenemorpholines (VIII). Several 4-alkyl-2-methylenemorpholines were prepared in yields ranging from 45–67%, and conversions ranged from 39–56%.

Tentative assignment of the 4-alkyl-2-methylenemorpholine (VIII) structure to the products obtained from aqueous media was made on the basis of their infrared and n.m.r. spectra. The infrared spectrum of each VIII possessed an intense band at 1660 cm.$^{-1}$, which indicated the presence of a polar carbon–carbon double bond[11] and an intense band at 835–845 cm.$^{-1}$, which we could assign to the exocyclic methylene group. The n.m.r. spectrum of neat 4-methyl-2-methylenemorpholine (VIIIa), which has the bands common to other 4-alkyl-2-methylenemorpholines, consists of singlets at τ 5.57 and 5.79,[12] which are assigned to the exocyclic methylene protons, apparent triplets with J = 4.8 c.p.s. at τ 6.01 and 7.44, which are assigned to the C-6 and C-5 protons, respectively, and singlets at τ 6.99 and 7.63 which are assigned to the C-3 and N-methyl protons, respectively. The resonance frequencies and relative intensities of the bands are consistent with the 4-methyl-2-methylenemorpholine structure and are inconsistent with those expected for the isomeric 2,4-dimethyl-5,6-dihydro-1,4-oxazine. The skeletal structure of the 2-methylenemorpholines was established by hydrogenation of 4-ethyl-2-methylenemorpholine (VIIIb) to 4-ethyl-2-methylmorpholine (X), which was indistinguishable from X prepared from N-ethyl-N-(2-hydroxypropyl)ethanolamine by Médard's procedure.[13]

We interpret the difference in products obtained from N-alkyl-N-propargylethanolamines (III) on treatment with sodium hydroxide in dimethyl sulfoxide and in water as due to the difference in rates of prototropic rearrangement in the two solvents.[14] Prototropic rearrangement of III to the corresponding allenic amino alcohol (VI), which then rapidly cyclizes to the 2-vinyloxazolidine (VII), apparently occurs rapidly

(11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 3.

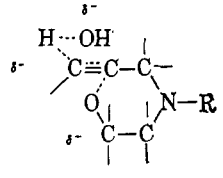
(12) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(13) L. Médard, *Bull. soc. chim. France*, [5] **3**, 1338 (1936).

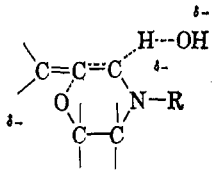
(14) Examples of the dependence of rates of prototropic rearrangements on solvent are given by C. C. Price and W. H. Snyder, *J. Am. Chem. Soc.*, **83**, 1773 (1961); see also C. C. Price and W. H. Snyder, *J. Org. Chem.*, **27**, 4639 (1962).

enough in dimethyl sulfoxide to overshadow completely the competing ring-closure reaction of III to the 2-methylenemorpholine (VIII). Direct cyclization of III to VIII in dimethyl sulfoxide appeared conceivable because the alkoxide of III can be expected to exhibit enhanced basicity and nucleophilicity in dimethyl sulfoxide.[15] In water, rearrangement of III to VI apparently occurs sufficiently slowly so that the formation of VIII by nucleophilic addition of the alkoxide oxygen to acetylenic carbon can occur *via* a transition state represented by XI.[16]

We considered it necessary to obtain proof that the 4-alkyl-2-methylenemorpholines (VIII) were indeed formed by cyclization of the alkoxide of the corresponding III. Conceivably, formation of VIII could occur by cyclization through a transition state represented by XII of the allenic amino alcohol (VI) formed from III. Examples of reactions involving nucleophilic attack at the digonal carbon of a substituted allene are known,[2,17] and sodium hydroxide in dimethyl sulfoxide and in toluene (following) induces rearrangement of III to VI. Also, in this regard, a 3-alkyl-2-vinyloxazolidine (VIII) is destroyed within minutes when treated with aqueous sodium hydroxide under conditions used by us for the preparation of a 4-alkyl-2-methylenemorpholine (VIII). As material balances of only 70% or less were obtained in preparations of VIII, 30% or more of the N-alkyl-N-propargylethanolamine (III) used could have been converted to the corresponding VII *via* the allenic amino alcohol VI.



XI



XII

In order to determine the mechanism of 2-methylenemorpholine formation, we prepared 4-methyl-2-methylenemorpholine (VIIIa) by treatment of N-methyl-N-propargylethanolamine (IIIa) with 3 *N* sodium deuterioxide in deuterium oxide and examined its n.m.r. spectrum. If the methylenemorpholine were formed by cyclization of the conjugate base of IIIa *via* a transition state represented by XI, no deuterium would be incorporated at C-3 of VIIIa. If the methylenemorpholine were formed by cyclization of the conjugate base of the allenic amino alcohol *via* a transition state represented by XII, one deuterium would be incorporated at C-3 of VIIIa. The n.m.r. spectra of deuterated and undeuterated VIIIa were indistinguishable except for the absence of bands due to the vinyl protons in the spectrum of deuterated VIIIa. Compound VIIIa and other 4-alkyl-2-methylenemorpholines also could be prepared from the corresponding N-alkyl-N-(2-bromoallyl)ethanolamines (IV). The VIIIa obtained by treatment of N-methyl-N-(2-bromoallyl)ethanolamine (IVa) with sodium deuterioxide in deuterium oxide had an n.m.r. spectrum identical with that of VIIIa obtained from similar treatment of IIIa. These results establish that an allenic amino alcohol is not involved significantly in the formation of a methylenemorpholine induced by aqueous sodium hydroxide at 100° and that the transition state leading to a methylenemorpholine is approximated by XI.

Reactions of several N-alkyl-N-propargyl-1-amino-2-propanols and N-alkyl-N-(2-bromoallyl)ethanolamines under conditions identical with those used for preparation of a 4-alkyl-2-methylenemorpholine (VII) gave conversions of only ~3–22% to the corresponding 2-methylenemorpholines. A propargylamino-2-propanol, a secondary alcohol, is a weaker acid than an N-propargylethanolamine, a primary alcohol. Therefore, on treatment with aqueous sodium hydroxide under identical conditions, the concentration of the conjugate base of a propargylamino-2-propanol is less than the concentration of the conjugate base of an N-propargylethanolamine. The presumed greater nucleophilicity of a secondary alkoxide as compared with that of a primary alkoxide is apparently insufficient to compensate for its lower concentration.

We found that treatment of N-*t*-butyl-N-propargylethanolamine (IIIc) with sodium hydroxide in refluxing toluene gave a 78% yield of a mixture consisting of 77% VIIc and 23% VIIIc. From a similar reaction using potassium hydroxide[3] instead of sodium hydroxide, the vinyloxazolidine (VIIc) was obtained free of 4-*t*-butyl-2-methylenemorpholine in over 80% yield. We examined the products obtained by treatment of several N-alkyl-N-propargylamino-2-propanols with sodium hydroxide in refluxing toluene, and these products were the corresponding 2-vinyloxazolidines containing less the 2% of the corresponding 2-methylenemorpholine.

We observed that 4-*t*-butyl-2-methylenemorpholine (VIIIc) is converted by treatment with potassium *t*-butoxide in ether to an unidentified, ether-insoluble material. Approximately 1 mole of potassium *t*-butoxide is required per mole of VIIIc, and the reaction occurs as fast or faster than the formation in ether of a 3-alkyl-2-vinyloxayolidine from either an N-alkyl-N-propargylethanolamine (III) or an N-alkyl-N-(2-chloroallyl)ethanolamine (V). This indicates that, if any VIII has been formed together with a 3-alkyl-2-vinyloxazolidine in ether in the presence of excess alkoxide, VIII would have been destroyed and not detected in the product.

We also treated VIIIc with sodium hydroxide in dimethyl sulfoxide and with potassium hydroxide in toluene under other conditions used by us for the preparation of 3-*t*-butyl-2-vinyloxazolidine (VIIc) from N-*t*-butyl-N-propargylethanolamine (IIIc). 4-*t*-Butyl-2-methylenemorpholine (VIIIc) was more stable under these conditions than in ether in the presence of potassium *t*-butoxide. The results of our control experiments indicated that, if more than 10% of the IIIc had been converted to VIIIc in toluene or dimethyl sulfoxide, the VIIIc would have been detected in the product. No VIIIc was detected in either of the products.

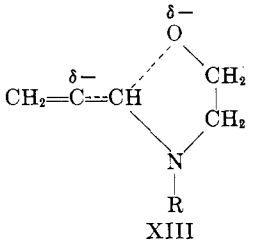
Interestingly, isolation of a 2-vinyloxazolidine in over 50% yield from reactions in dimethyl sulfoxide and toluene shows that the transition state leading to VII, which is represented by XIII, is of lower energy

(15) In this regard, see D. J. Cram, B. Rickborn, and G. R. Knox, *J. Am. Chem. Soc.*, **82**, 6412 (1960); and D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfield, *ibid.*, **83**, 3678 (1961).

(16) A significant paper concerning the addition of an alkoxide to an acetylene is by S. I. Miller and G. Shkapenko, *ibid.*, **77**, 5038 (1955).

(17) A. N. Pudovik and I. M. Alajeva, *Zh. Obshch. Khim.* **33**, 708 (1963).

than the corresponding XII or analogous transition state that would lead to the 2-methyl-4-alkyl-5,6-dihydro-1,4-oxazine. Any electronic factors that might tend to make the transition states leading to six-membered ring products more stable than XIII are apparently more than counteracted by the lesser amount of angle strain in XIII.



XIII

Experimental

Boiling points are uncorrected. Infrared spectra were obtained with a Beckman IR-4 or a Beckman IR-5 spectrophotometer. N.m.r. spectra were obtained at 56.4 Mc. or 60 Mc. with a Varian Associates HR-60 system with samples contained in 5-mm. o.d. tubes. Resonance frequencies in n.m.r. spectra were determined relative to tetramethylsilane (TMS) using the side-band technique with a Packard OD-200 audiooscillator. Gas–liquid partition (g.l.p.) chromatograms were obtained using a 5-m. column that contained a packing of Carbowax 20M alkaline on firebrick in an Aerograph Model A-700 (Wilkens Instrument and Research, Inc., Walnut Creek, Calif.). Microanalyses were performed by Mr. V. H. Tashinian, Berkeley, Calif.

Unsaturated Amino Alcohols.—The N-alkyl-N-propargylalkanolamines and N-alkyl-N-(2-haloallyl)alkanolamines were prepared either by treatment of a propargyl halide or 2,3-dihalopropene with the corresponding N-alkylalkanolamine or by treatment of an N-alkylpropargylamine or N-(2-haloallyl)-alkylamine[1b,8] with the necessary oxirane. Procedures used for reactions of the unsaturated halides with N-alkylethanolamines were patterned after the procedure described for the preparation of (−)-N-(2-bromoallyl)-2-hydroxy-3-butenylamine.[7] Procedures used for reactions of unsaturated secondary amines with oxirane were patterned after a procedure described for the preparation of N-isopropylethanolamine.[18] A typical procedure for the preparation and isolation of an unsaturated amino alcohol from a substituted oxirane follows. To a cold stirred solution of 88 g. (0.69 mole) of N-*t*-butylpropargylamine and 50 ml. of 80% aqueous ethanol by volume contained in a 500-ml. round-bottomed flask equipped with a Dry Ice condenser charged with an ice–salt mixture was added dropwise 92 g. (1.6 moles) of propylene oxide. When the addition was complete, the reaction mixture was allowed to warm to room temperature, and it was heated at 50° for 16 hr. (Reaction times of >50 hr. were used for reactions of isobutylene oxide.) Distillation of the reaction mixture gave 78 g. (61%) of N-*t*-butyl-N-propargyl-1-amino-2-propanol, b.p. 102–105° (19 mm.), $n^{23}D$ 1.4579. The yields, physical constants, and analytical data for all unsaturated amino alcohols, as well as 3-alkyl-2-vinyloxazolidines and 4-alkyl-2-methylenemorpholines, are given in Table I.

Attempted Ring-Closure Reaction of N-Ethyl-N-(2-bromoallyl)-ethanolamine (IVb) with Sodium Amide in Liquid Ammonia.—Compound IVb (52 g., 0.25 mole) was added dropwise to a stirred slurry of 35.1 g. (0.90 mole) of sodium amide and 2 l. of liquid ammonia. The mixture was stirred 4 hr., and 300 ml. of ether and 10 ml. (0.55 mole) of water were added cautiously with continued stirring. The ammonia was allowed to evaporate overnight. The ethereal solution was decanted from the reaction flask, and the residual material in the flask was washed three times with 100-ml. portions of ether. The ethereal solutions were combined, and most of the ether was removed by distillation through a 35 × 0.8 mm. column packed with glass helices. A yellow-orange precipitate with the consistency of ferric hydroxide separated from the ether solution during this distillation. The residue was distilled under vacuum in a nitrogen atmosphere through a semimicro Vigreux column, and two fractions were taken. The first fraction (3.3 g.) was an acrid colorless liquid, which had b.p. 52–53° (18 mm.), $n^{21}D$ 1.4469, an elemental analysis, an infrared spectrum, and an n.m.r. spectrum that were compatible with the 3-ethyl-2-vinyloxazolidine (VIIb) structure, and were identical with VIIb obtained by the method of Croxall and Mellema.[3] The second fraction (3.4 g.) was a colorless, slightly viscous liquid, which had b.p. 52–53° (1 mm.), $n^{25}D$ 1.4656, and was shown to be N-ethyl-N-propargylethanolamine (IIIb) by comparison with material prepared from N-propargylethylamine and ethylene oxide.

Compound IVb (52 g., 0.25 mole) was treated with 19.7 g. (0.51 mole) of sodium amide and 1 l. of liquid ammonia. After 3 hr., 250 ml. of ether and 22.1 g. (0.41 mole) of ammonium chloride were added to the mixture with continued stirring. The reaction mixture was worked up as described for the first run, and 28 g. (88%) of IIIb, $n^{25}D$ 1.4650, was collected at 72–74° (6 mm.).

Compound IVb (52 g., 0.25 mole) was treated with 22 g. (0.56 mole) of sodium amide and 1 l. of liquid ammonia. After 5 hr., 100 ml. of ether and 18 ml. (1.0 mole) of water were added to the mixture with continued stirring. The reaction mixture was worked up as usual, and 24.6 g. (78%) of IIIb, $n^{25}D$ 1.4667, was collected at 72–75° (6 mm.).

3-Alkyl-2-vinyloxazolidones. A. From N-Alkyl-N-propargylethanolamines and Sodium Amide in Ether.—A typical procedure follows. To a magnetically stirred slurry of 3.45 g. (0.088 mole) of sodium amide in 80 ml. of dry ether was added dropwise 10.0 g. (0.088 mole) of N-methyl-N-propargylethanolamine (IIIa) in 15 min. After the evolution of ammonia had slowed appreciably, the flask was stoppered with a cork containing an inverted capillary, and stirring was continued for 48 hr. The ether solution was decanted from a grey precipitate in the flask, and most of the ether was removed by distillation at atmospheric pressure. The residue was distilled under a pressure of 10 mm. of nitrogen, and 3.4 g. (34%) of 3-methyl-2-vinyloxazolidine (VIIa), $n^{22}D$ 1.4455, was collected. Duplication of the prior procedure resulted in the isolation of 3.2 g. of VIIa, $n^{22}D$ 1.4450. When 4.7 g. (0.088 mole) of ammonium chloride was added to the stirred reaction mixture after the 48-hr. reaction time, removal of the excess ammonium chloride and other solids by filtration and distillation of the ether solution gave 2.3 g. of VIIa, $n^{21}D$ 1.4462. A duplication of this run gave 1.8 g. of VIIa, $n^{22}D$ 1.4460. The infrared spectra of all samples of VIIa indicated that they were free of IIIa and 4-methyl-2-methylenemorpholine (VIIIa).

B. From N-Alkyl-N-(2-chloroallyl)ethanolamines and Sodium Amide in Ether.—The following procedure is typical. The mixture obtained by the addition of 10.0 g. (0.052 mole) of N-*t*-butyl-N-(2-chloroallyl)ethanolamine (Vc) to a stirred slurry of 2.04 g. (0.052 mole) of sodium amide and 80 ml. of dry ether was stirred at room temperature for 40 hr. The mixture was filtered, and most of the ether was removed from the filtrate by distillation. The residue was distilled under nitrogen, and 4.2 g. (52%) of 3-*t*-butyl-2-vinyloxazolidine (VIIc), $n^{23}D$ 1.4250, was collected at 75–80° (15 mm.). The VIIc had an infrared spectrum and an n.m.r. spectrum that were identical with those of VIIc obtained in 83% yield by the method of Croxall and Mellema.[3]

Treatment of 10.0 g. (0.0424 mole) of N-*t*-butyl-N-(2-bromoallyl)ethanolamine (IVc) with 1.65 g. (0.0424 mole) of sodium amide in 80 ml. of dry ether gave 4.3 g. (65%) of light yellow N-*t*-butyl-N-propargylethanolamine (IIIc), $n^{22.5}D$ 1.4693.

N-*t*-Butyl-N-(2-chloroallyl)-1-amino-2-methyl-2-propanol (8.4 g., 0.038 mole) was treated with 1.79 g. (0.046 mole) of sodium amide in 80 ml. of dry ether as described for IVc. The product was collected in two fractions: the first fraction (1.9 g.) had b.p. 73–75° (18 mm.), $n^{23}D$ 1.4471, and the second fraction (1.7 g.) had b.p. 75–85° (18 mm.), $n^{23}D$ 1.4508. Present in the infrared spectrum of each fraction was a band at 1740 cm.$^{-1}$, and the band was more intense in the spectrum of the second fraction. G.l.p. chromatograms of the two fractions indicated that the first fraction consisted of about 98% 3-*t*-butyl-5,5-dimethyl-2-vinyloxazolidine and that the second fraction consisted of about 90% of the oxazolidine. The impurity, which appeared to be the same in both fractions, had a slightly greater retention time than the oxazolidine. Interestingly, the products from reactions of N-*t*-butyl-N-(2-chloroallyl)-1-amino-2-propanol and N-*t*-butyl-N-(2-chloroallyl)-1-amino-2-methyl-2-propanol with 1 equiv. of sodium amide possessed bands at 1670 cm.$^{-1}$. As the 2-methylenemorpholines possess bands at 1660 cm.$^{-1}$, these minor

(18) J. H. Biel, *J. Am. Chem. Soc.*, **71**, 1306 (1949).

impurities may be the isomeric 2-methyl-5,6-dihydro-1,4-oxazines.

C. From N-Alkyl-N-propargylethanolamines and Sodium Hydroxide in Dimethyl Sulfoxide.—A mixture prepared from 50 ml. of dry dimethyl sulfoxide, 5.8 g. (0.142 mole) of coarsely powdered sodium hydroxide, and 8.0 g. (0.047 mole) of N-*t*-butyl-N-propargyl-1-amino-2-propanol was heated with stirring at 75–85° for 2 hr. The mixture was cooled, and 150 ml. of ether and 150 ml. of water were added in that order. The phases were separated, and the organic layer was washed successively with 150 ml. of water and 50 ml. of 6 *N* sodium chloride. Most of the ether was removed by distillation at atmospheric pressure, and the residue was distilled under nitrogen. 3-*t*-Butyl-5-methyl-2-vinyloxazolidine (4.3 g., 54%), $n^{23}D$ 1.4464, was collected at 68–70° (13 mm.).

4-Alkyl-2-methylenemorpholines.—The following is a typical procedure. A heterogeneous mixture of 66 g. (0.428 mole) of N-*t*-butyl-N-propargylethanolamine (IIIc) and 425 ml. of 3 *N* aqueous sodium hydroxide was stirred under reflux for 20 hr. The reaction mixture was cooled in an ice bath and extracted with 250 ml. of ether. The aqueous phase was extracted twice with 50-ml. portions of ether, and the ether extracts were combined and dried with sodium hydroxide. Most of the ether was removed by distillation at atmospheric pressure, and the residue was distilled under nitrogen through a 60 × 0.8 mm. Podbielniak column equipped with a total reflux head. 4-*t*-Butyl-2-methylenemorpholine (VIIIc), $n^{25}D$ 1.4612, was collected at 75–77° (14 mm.), and 17 g. of IIIc was collected at 96–100° (14 mm.). The VIIIc weighed 32 g. (48% conversion, 65% yield).

N-*t*-Butyl-N-propargyl-1-amino-2-propanol (10 g., 0.059 mole) was treated with 60 ml. of 3 *N* aqueous sodium hydroxide at reflux for 16 hr., and the reaction mixture was worked up in a manner similar to that described before. A 2.3-g. fraction, b.p. 82–88° (11 mm.), $n^{21}D$ 1.4570, and a 5.7-g. fraction, b.p. 86–92° (11 mm.), $n^{21}D$ 1.4588, were obtained by dist llation of the ether solution. In the g.l.p. chromatogram of the first fraction, the area of the band due to 4-*t*-butyl-6-methyl-2-methylenemorpholine was approximately 20% of the area of the band due to the amino alcohol; in the g.l.p. chromatogram of the second fraction, the area of the band due to the 2-methylenemorpholine was 2% that of the band due to the amino alcohol. The infrared spectrum of the first fraction had a band of moderate intensity at 1660 cm.$^{-1}$.

4-Ethyl-2-methylmorpholine.—A mixture of 4.3 g. of 4-ethyl-2-methylenemorpholine (VIIIb), 100 ml. of absolute ethanol, and 0.2 g. of platinic oxide was shaken under 2.5 atm. of hydrogen for 4 hr. The catalyst was removed by filtration, and the filtrate was distilled. 4-Ethyl-2-methylmorpholine (3.0 g., 70%) was collected at 76–78° (67 mm.). It had $n^{25}D$ 1.4344 and an infrared spectrum that was superimposable on that of 4-ethyl-2-methylmorpholine, b.p. 80–82° (86 mm.), $n^{25}D$ 1.4350, which was prepared in 42% yield from 118 g. of N-ethyl-N-(2-hydroxyethyl)-1-amino-2-propanol and 262 g. of 96% sulfuric acid following the procedure of Médard.[13]

Spectral Characteristics of 3-Alkyl-2-vinyloxazolidines and 4-Alkyl-2-methylenemorpholines.—In contrast to the 2-methylenemorpholines, which have intense bands at 1660 cm.$^{-1}$, the 2-vinyloxazolidines have bands of weak intensity at 1630 cm.$^{-1}$.

Common to the n.m.r. spectra of the 2-vinyloxazolidines is a complex series of bands from approximately −355 to −285 c.p.s. relative to TMS at 56.4 Mc., which are assigned to the vinyl and allyl protons. The bonds common to the n.m.r. spectra of VIIIa–c have been noted in the discussion.

The n.m.r. spectra of 3-*t*-butyl-2-vinyloxazolidine (VIIIc) and 3-*t*-butyl-5,5-dimethyl-2-vinyloxazolidine (IX) at 56.4 Mc. are surprisingly simple, but the spectra of the other 2-vinyloxazolidines are complex as might be expected for compounds that contain an ABCD system (the C-4 and C-5 protons) or for mixtures of diastereomers. The spectrum of neat VIIIc consists of the vinyl and allyl bands from −355 to −287 c.p.s. relative to TMS, two apparent triplets (J_{app} = 6.4 c.p.s.) at τ 6.05 and 6.85, which are assigned to the C-5 and C-4 protons, respectively, and an intense singlet at τ 8.65, which is assigned to the *t*-butyl protons. The spectrum of neat IX at 56.4 Mc. consists of the vinyl and allyl bands from −364 to −280 c.p.s. relative to TMS, an AB quartet due to the C-4 protons centered at τ 6.92 (J = 8.3 c.p.s., δ_H = 9.8 c.p.s.), the bands due to the C-5 methyl protons centered at τ 8.42 (δ_H = 3.0 c.p.s.), and the singlet due to the *t*-butyl protons at τ 8.59.

For purposes of comparison, 3-*t*-butyl-2-phenyloxazolidine, b.p. 102–104° (2 mm.), $n^{23}D$ 1.5130, was prepared in 38% yield from 21 g. of benzaldehyde and 21 g. of N-*t*-butylethanolamine.

Anal. Calcd. for $C_{13}H_{19}NO$: C, 76.05; H, 9.33; N, 6.82. Found: C, 75.51; H, 9.07; N, 6.65.

The n.m.r. spectrum at 56.4 Mc. of 3-*t*-butyl-2-phenyloxazolidine as a 16 mole % solution in benzene possesses bands from −428 to −403 c.p.s. relative to TMS, which are due to the aromatic protons, a singlet at τ 4.5, which is assigned to the C-2 proton, 2 apparent triplets (J_{app} = 6.4 c.p.s.) at τ 6.5 and 7.3, which are assigned to the C-5 and C-4 protons, respectively, and an intense singlet at τ 9.0, which is assigned to the *t*-butyl protons. In the n.m.r. spectrum at 56.4 Mc. of VIIc as a 12 mole % solution in benzene, the bands due to the C-5, C-4, and *t*-butyl protons appear at τ 6.5, 7.35, and 9.1, respectively.

4-Methyl-2-deuteriomethylenemorpholine. A. From N-methyl-N-propargylethanolamine (IIIa).—Sodium (6.9 g.) was divided into approximately 30 pieces, and each piece was treated under a stream of nitrogen with 1.5–2.0 ml. of 99.83 % deuterium oxide (Bio-Rad Laboratories, Richmond, Calif.). The sodium deuterioxide solutions were combined and made up to a volume of 100 ml. with deuterium oxide. Compound IIIa (11.6 g., 0.10 mole) was added, and the heterogeneous mixture was stirred and heated under reflux overnight. The product was isolated as described for the isolation of VIIIa, and the 4.2-g. fraction with b.p. 30–32° (11 mm.), $n^{24}D$ 1.4588, was examined. The n.m.r. spectrum of VIIIa was taken, and the n.m.r. spectrum of deuterated VIIIa was taken immediately after using identical instrument settings. The portions of the two spectra from τ 7.0–7.7, which contain the bands due to the C-3 protons and N-methyl protons as well as the triplet due to the C-5 protons, were superimposable. The bands due to the C-6 protons were also superimposable, but the spectrum of deuterated VIIIa did not have the bands at τ 5.6 and 5.8, which are due to the vinyl protons of VIIIa. The infrared spectra of VIIIa and deuterated VIIIa were markedly similar from 1060–4000 cm.$^{-1}$. A weak band at 2240 cm.$^{-1}$ was noted in the spectrum of deuterated Va, and the band at 1660 cm.$^{-1}$ in the spectrum of VIIIa was observed at 1630 cm.$^{-1}$ in the spectrum of deuterated VIIIa. The spectra of VIIIa and deuterated VIIIa from 650–1060 cm.$^{-1}$ were significantly different. The only band common to the two spectra in this region was at 840 cm.$^{-1}$, and the intensity of the band in the spectrum of deuterated VIIIa was considerably less than the intensity of the band in the spectrum of VIIIa.

B. From N-Methyl-N-(2-bromoallyl)ethanolamine (IVa).—Compound IVa (10.0 g., 0.05 mole) and 50 ml. of 3 *N* sodium deuterioxide were heated with stirring at 100° for 18 hr. The 1.2-g. fraction of VIIIa, which had b.p. 44–48° (22 mm.) and $n^{23}D$ 1.44588, was examined and was found to be identical with the 4-methyl-2-deuteriomethylenemorpholine prepared from IIIa.

N-*t*-Butyl-N-propargylaminoethanol (IIIc) and Sodium Hydroxide in Toluene.—To a vigorously stirred slurry of 0.4 g. (0.01 mole) of coarsely powdered sodium hydroxide and 25 ml. of refluxing toluene was added dropwise 15.5 g. (0.1 mole) of IIIc in 20 min. The mixture was stirred for 2 hr. at reflux and cooled. The toluene solution was decanted from the solids and distilled at reduced pressure under nitrogen. The colorless product (12.1 g., 78%) was collected at 77–80° (19 mm.). It had $n^{26}D$ 1.4537 and an infrared spectrum that indicated it was a mixture of 3-*t*-butyl-2-vinyloxazolidine (VIIc) and 4-*t*-butyl-2-methylenemorpholine (VIIIc). Analysis by g.l.p.c. of the product and mixtures prepared from known amounts of the product and VIIIc showed that the product was 77% VIIc and 23% VIIIc.

Treatment of 4-*t*-Butyl-2-methylenemorpholine (VIIIc) with Various Bases.—To a stirred mixture of 3.62 g. (0.032 mole) of potassium *t*-butoxide and 180 ml. of dry ether was added dropwise 10.0 g. (0.064 mole) of VIIIc. During the addition a flocculent white precipitate formed in the mixture. The mixture was stirred for 45 hr. at room temperature, and the solids were removed by suction filtration. The filtrate was distilled, and 4.5 g. of Vc was collected at 74–76° (16 mm.). A small amount of *t*-butyl alcohol, b.p. 27–30° (25 mm.), also was collected.

A stirred slurry of 1.8 g. of coarsely powdered potassium hydroxide, 20 ml. of toluene, and 5.0 g. of VIIIc was heated under reflux for 2 hr. and cooled. The solids were removed by suction filtration, and the filtrate was distilled. Compound VIIIc (3.4 g.) was collected at 68–71° (11 mm.), and the residue (0.7 g.) was mainly VIIIc.

A mixture of 3.6 g. of sodium hydroxide, 5.0 g. of VIIIc, and 30 ml. of dry dimethyl sulfoxide was stirred for 19 hr. at 80–85°. The mixture was cooled, and 100 ml. of ether and 100 ml. of water were added in that order. The phases were separated, and the organic layer was washed successively with 100 ml. of water and 30 ml. of 6 *N* sodium chloride. The ether solution was distilled, and 3.3 g. of VIIIc was collected. The residue, which was mainly VIIIc, weighed 0.8 g.

Glycidyl Ether Reactions with Urethanes and Ureas. A New Synthetic Method for 2-Oxazolidones

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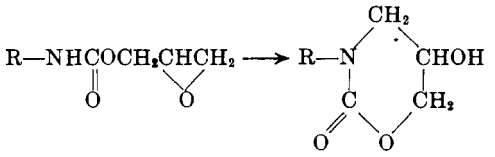
Tertiary amines and quarternary ammonium salts have been found to be efficient catalysts for the intermolecular addition reaction between urethane linkages and epoxy rings. Addition products of urethanes and epoxides undergo an intramolecular exchange of alcohols to give the oxazolidone derivatives in good yields.

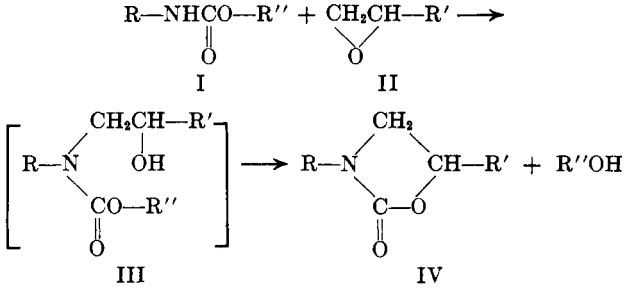
Epoxy compounds are known to produce ring-opened addition products with nucleophilic reagents,[1-4] but up to this time there has been no report about the reaction between epoxy compounds and the imide group of urethane linkages. Imide groups of urethane linkages are not reactive enough nucleophiles to react with epoxy rings without catalysts.

As we reported previously,[5] glycidyl urethanes are isomerized by heating to give N-substituted 5-hydroxytetrahydro-1,3-oxazin-2-ones. We attempted to extend these intramolecular reactions to intermolecular



addition reaction between urethanes and epoxides using catalysts.

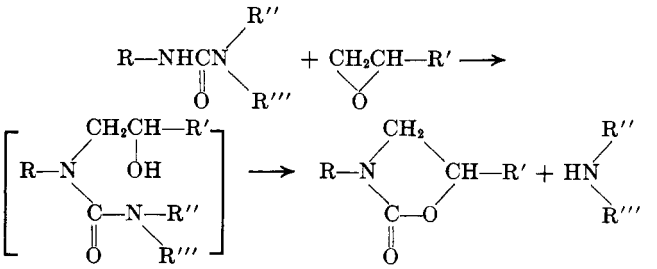
Tertiary amines and quarternary ammonium salts are useful catalysts to accelerate the intermolecular nucleophilic addition reactions between imide groups of urethane linkages and epoxy compounds, and, since



the reaction products (III) obtained by this addition split off alcohols rather rapidly to give the oxazolidone derivatives (IV), we can only isolate the oxazolidone derivatives as the final products in the intermolecular addition reactions between urethanes and epoxides.

As explained in detail in a later section, there is sufficient evidence that these reactions giving oxazolidone derivatives do not proceed *via* dissociation of urethanes to isocyanates and alcohols. According to Homeyer,[6] alkali-catalyzed reaction of α-amino alcohols and diethyl carbonate gives oxazolidones. From our experiments, it was found that condensation reactions of α-amino alcohols and ethyl chlorocarbonate also gave oxazolidones even at room temperature. These two results give support to reaction mechanisms involving nucleophilic addition and intramolecular exchange of alcohols as indicated by the previous formula.

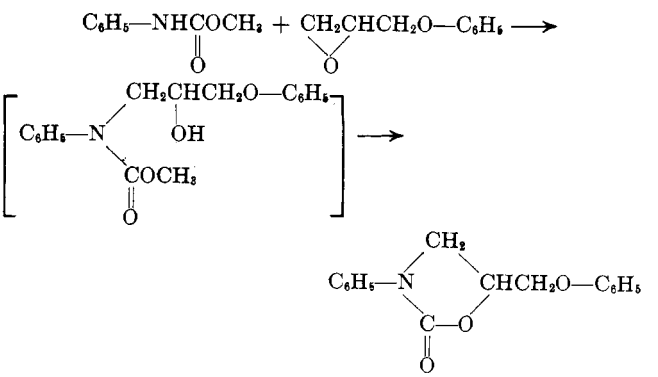
From the analogy of the mechanism of this reaction, we expect that ureas also would give the oxazolidones. In fact the intermolecular addition reaction between di- and trisubstituted ureas and epoxy



compounds gave the oxazolidone derivatives. In this case, the primary or secondary amines which are produced react with other epoxy compounds quickly; thus it is necessary that two or three molar equivalents of epoxy compounds be added.

Results and Discussion

Reaction between Urethanes and Epoxides.—To investigate the ability of intermolecular addition reaction of urethane linkages and epoxy rings, the reaction of N-phenylmethylurethane with phenyl glycidyl ether was examined expecting the following reaction. On



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