

$$\begin{aligned} \Psi &= (1/\sqrt{6})(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) & \epsilon &= 2\beta \\ \Psi &= (1/\sqrt{6})(e^{\pi i/3}\phi_1 + e^{2\pi i/3}\phi_2 + e^{\pi i}\phi_3 + \\ & \quad e^{-2\pi i/3}\phi_4 + e^{-\pi i/3}\phi_5 + \phi_6) & \epsilon &= \beta \\ \Psi &= (1/\sqrt{6})(e^{-\pi i/3}\phi_1 + e^{-2\pi i/3}\phi_2 + \\ & \quad e^{-\pi i}\phi_3 + e^{2\pi i/3}\phi_4 + e^{\pi i/3}\phi_5 + \phi_6) & \epsilon &= \beta \\ \Psi &= (1/\sqrt{6})[e^{2\pi i/3}(\phi_1 + \phi_4) + \\ & \quad e^{-2\pi i/3}(\phi_2 + \phi_5) + (\phi_3 + \phi_6)] & \epsilon &= -\beta \\ \Psi &= (1/\sqrt{6})[e^{-2\pi i/3}(\phi_1 + \phi_4) + \\ & \quad e^{2\pi i/3}(\phi_2 + \phi_5) + (\phi_3 + \phi_6)] & \epsilon &= -\beta \\ \Psi &= (1/\sqrt{6})(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6) & \epsilon &= -2\beta \end{aligned}$$

Quantities derivable from wave functions. From the normalized molecular orbital wave functions

$$\Psi_j = a_1\phi_1 + a_2\phi_2 + \dots + a_n\phi_n, j = 1, 2, \dots, n$$

and the number of electrons ν_j in each molecular orbital j , one may calculate in the usual way the total energy of the π -electrons:

$$E = \sum \nu_j(\epsilon_j + \alpha) = \sum \nu_j \int (\Psi_j H \Psi_j) dv$$

the resonance (delocalization) energy relative to a localized structure with d double bonds:

$$\text{R.E.} = \sum_j \nu_j \epsilon_j - d(2\beta)$$

the π -electron density q_r or the net positive charge Q_r on any atom r :

$$q_r = \sum_j \nu_j a_{jr}^2 = 1 - Q_r$$

the π -bond order p_{rs} or the total bond order N_{rs} of the bond between atoms r and s :

$$p_{rs} = \sum_j \nu_j a_{jr} a_{js} = N_{rs} - (\text{No. of } \sigma\text{-bonds})$$

and the free valence on any atom:

$$F_r = 4.732 - \sum_s N_{rs}$$

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Isomerization of *N*-Substituted Glycidyl Carbamates

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Glycidyl aryl- or alkylcarbamate undergoes a pyrolytic rearrangement to give 3-aryl- or alkyl-5-hydroxytetrahydro-1,3-oxazine-2-one in good yields.

In connection with a research on the addition reaction of glycidyl *N*-aryl- or alkylcarbamates, it happened that they thermally isomerized to give *N*-substituted 5-hydroxytetrahydro-1,3-oxazine-2-one (*N*-substituted 5-hydroxy-2-pentoxazolidone). On the isomerization of three-membered ring compounds, it was reported that *N*-acyl-^{1,2} or *N*-phenylthiocarbonyl ethyleneimine³ and their derivatives⁴ underwent a rearrangement to give 2-substituted oxazoline-2 or thiazoline-2. No literature was found, however, on the ring expansion of *N*-substituted glycidyl carbamates. In the first place from the reactivity of epoxy ring to imino group, it is considered that the isomerization of glycidyl carbamate to substituted tetrahydro-1,3-oxazine-2-one will be caused by intramolecular addition reaction of epoxy ring to urethane linkage.

To confirm the structure of isomers, isomerization of glycidyl phenylcarbamate and some of the alkylcarbamates prepared from phenyl or alkyl isocyanate and glycidol were studied in detail.

When glycidyl phenylcarbamate (I) was heated without solvent in a test tube at 125° for 1 hr., crystalline II was obtained in 95% yield, the molecular weight and microanalysis of which were found to be similar to those of I. Phenyl isocyanate or acetic anhydride reacts with II to give phenylcarbamate (III) or acetate (IV) of II. II was also obtained from 1-chloro-2-hydroxy-3-phenylcarbamoyloxypropane (V), prepared from I and hydrogen chloride.⁵ This confirms II to be 3-phenyl-5-hydroxytetrahydro-1,3-oxazine-2-one. From 1-chloro-2,3-bis(phenylcarbamoyloxy)propane (VI), 3-phenyl-5-phenylcarbamoyloxymethyl-2-oxazolidone (VII) was obtained without forming III. This might be because of the fact that five-membered cyclic urethane was more stable and easier to form than six-membered one.⁶⁻⁸ An attempt to obtain IV from 1-chloro-2-acetoxy-3-phenylcarbamoyloxypropane by ring closure with sodium methoxide, gave unexpectedly 10% yield of II and 90% yield of oily polymeric substance.

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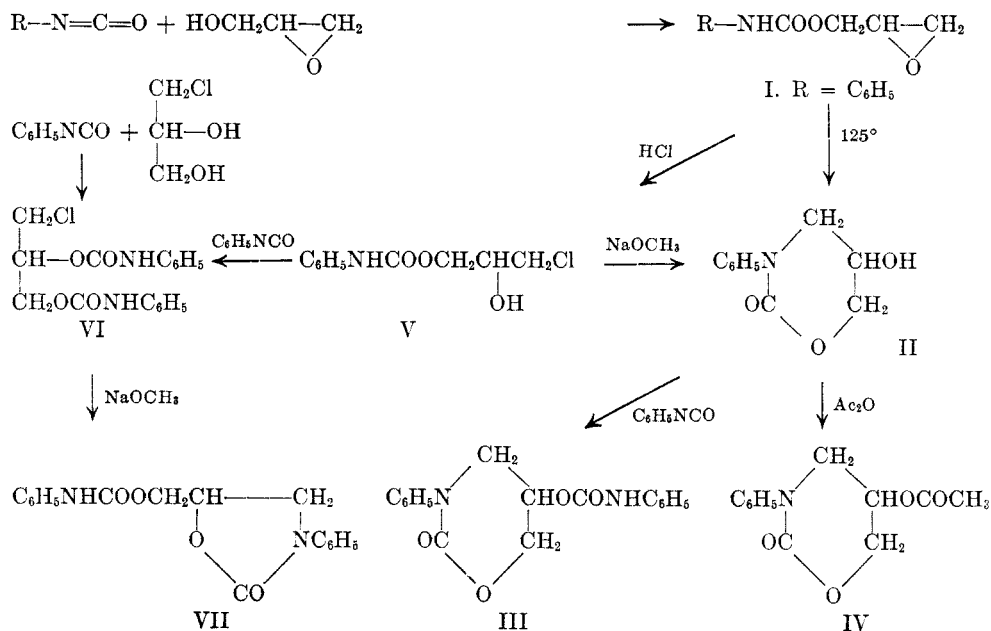
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Structures of isomer (II) and its derivatives were also confirmed by the comparison of the infrared spectra of I, II, and IV.

Glycidyl alkylcarbamates were easily converted to 3-alkyl-5-hydroxytetrahydro-1,3-oxazine-2-one at 80–100° for 1 hr., and methylcarbamate happened to isomerize during distillation at 80–82°/1 mm. Physical properties and analytical data of glycidyl alkylcarbamates and substituted tetrahydro-1,3-oxazine-2-ones are listed in Tables I and II.

EXPERIMENTAL⁹

Glycidyl phenylcarbamate (I). To a boiling solution of 11.9 g. (0.1 mol.) of phenyl isocyanate in 200 ml. of benzene, was added dropwise with stirring during 1 hr. 7.2 g. (0.1 mol.) of newly distilled glycidol in 50 ml. of benzene, and the mixture was heated under reflux for an additional 3 hr. After removal of benzene at reduced pressure, the residue was recrystallized from ether-petroleum ether (2:1) to give 17.5 g. (92%) of glycidyl phenylcarbamate, m.p. 59.8–60.0° (lit.¹⁰ m.p. 60°, lit.¹¹ m.p. 60–61°).

In the infrared spectra are found strong absorption bands arising from N—H vibrations at 1449, 1555, and 3370 cm.⁻¹, and from epoxy group at 865, 910, and 1260 cm.⁻¹

Anal. Calcd. for C₁₀H₁₁O₃N: N, 7.25. Found: N, 7.25.

3-Phenyl-5-hydroxytetrahydro-1,3-oxazine-2-one (II). Five g. of I was heated in an oil bath kept at 125° for 1 hr. Oily viscous substance was crystallized from benzene in 95% yield. Pure sample melted at 109.5–110.5°. A mixed melting point with authentic sample showed no depression.

In the infrared spectra are found strong O—H absorption bands at 1090, 1350, and 3420 cm.⁻¹, and no absorption band arising from N—H and epoxy group was recognized.

(9) Melting points and boiling points are uncorrected. Microanalyses were performed by A. Kondo in Laboratory of Organic Chemistry, Tokyo Institute of Technology. Infrared measurements were made by Government Chemical Industrial Research Institute, Tokyo.

(10) T. H. Rider and A. J. Hill, *J. Am. Chem. Soc.*, **52**, 1521 (1930).

(11) A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **74**, 2100 (1952).

Anal. Calcd. for C₁₀H₁₁O₃N: C, 62.16; H, 5.74; N, 7.25; mol. wt. 193. Found: C, 62.35; H, 5.75; N, 7.54; mol. wt. 198.

3-Phenyl-5-phenylcarbamoyloxyltetrahydro-1,3-oxazine-2-one (III). II, 1.93 g. (0.01 mol.), and 1.19 g. (0.01 mol.) of phenyl isocyanate in 30 ml. of benzene were heated under reflux for 1 hr. After cooling, the adduct was precipitated and recrystallized from ethanol to give 3.0 g. (96%) of 3-phenyl-5-phenylcarbamoyloxyltetrahydro-1,3-oxazine-2-one, m.p. 175–175.5°.

Anal. Calcd. for C₁₇H₁₆O₄N₂: N, 8.97. Found: N, 9.29.

3-Phenyl-5-acetoxytetrahydro-1,3-oxazine-2-one (IV). II, 1.93 g. (0.01 mol.), 13.5 g. of pyridine, and 10.0 g. of acetic anhydride were allowed to stand overnight. After removal of pyridine and excess of acetic anhydride, the crystalline solid was obtained and recrystallized from ether to give 1.74 g. (90%) of 3-phenyl-5-acetoxytetrahydro-1,3-oxazine-2-one, m.p. 70.8–71.6°.

The infrared spectra had neither N—H, O—H nor epoxy group absorption.

Anal. Calcd. for C₁₂H₁₃O₄N: C, 62.27; H, 5.57; N, 5.96. Found: C, 61.49; H, 5.54; N, 6.33.

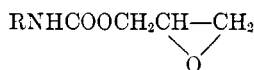
1-Chloro-2-hydroxy-3-phenylcarbamoyloxypropane (V). Into 50 ml. of ether containing 9.7 g. (0.05 mol.) of I was bubbled gradually dry hydrogen chloride at 10° for 30 min. After removal of the solvent, the liquid residue (11.5 g.) was distilled at 155–157°/0.05 mm. or 180–183°/1 mm. to give 9.0 g. (79%) of 1-chloro-2-hydroxy-3-phenylcarbamoyloxypropane, which was solidified by cooling and melted at 55–59°.

Anal. Calcd. for C₁₀H₁₂O₃NCl: N, 6.10. Found: N, 5.95.

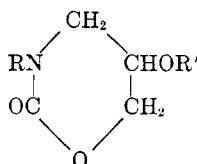
1-Chloro-2,3-bis(phenylcarbamoyloxy)propane (VI). A mixture of 2.29 g. (0.01 mol.) of V and 1.19 g. (0.01 mol.) of phenyl isocyanate in 50 ml. of benzene was heated under reflux for 1 hr. After cooling, the precipitate was collected and recrystallized from ethanol to give 2.4 g. (69%) of 1-chloro-2,3-bis(phenylcarbamoyloxy)propane, m.p. 128–130°. A mixed melting point with authentic sample prepared from α-chloroglycerin and phenyl isocyanate showed no depression.

Anal. Calcd. for C₁₇H₁₇O₄N₂Cl: N, 8.03. Found: N, 7.74.

Authentic 2-phenyl-5-hydroxytetrahydro-1,3-oxazine-2-one (II). To 1.15 g. (0.05 mol.) of V in 30 ml. of methanol was added dropwise 0.27 g. of sodium methoxide in 5 ml. of methanol, the solution being kept at 20° for 3 hr. After removal of the solvent, the residue was washed with water

TABLE I
 GLYCIDYL ALKYL CARBAMATES.


R	B.P.	Refractive Index, n_D^{25}	Formula	N, %	
				Calcd.	Found
Ethyl	112-116 (4 mm.)	1.4502	$\text{C}_6\text{H}_{11}\text{O}_3\text{N}$	9.65	9.85
<i>n</i> -Propyl	103-108 (1.6 mm.)	1.4516	$\text{C}_7\text{H}_{13}\text{O}_3\text{N}$	8.80	8.89
<i>n</i> -Hexyl	126-128 (2 mm.)	1.4537	$\text{C}_{10}\text{H}_{19}\text{O}_3\text{N}$	6.96	7.20

 TABLE II
 3,5-DISUBSTITUTED TETRAHYDRO-1,3-OXAZINE-2-ONES


R	R'	M.P.	Refractive Index, n_D^{25}	Formula	N, %	
					Calcd.	Found
Me	H	214-216	1.4880	$\text{C}_8\text{H}_9\text{O}_3\text{N}$	10.68	10.87
	PhNHCO			$\text{C}_{12}\text{H}_{14}\text{O}_4\text{N}_2$	11.20	11.27
Et	H	172.0-172.5	1.4743	$\text{C}_8\text{H}_{11}\text{O}_3\text{N}$	9.65	
	PhNHCO			$\text{C}_{13}\text{H}_{15}\text{O}_4\text{N}_2$	10.60	10.60
<i>n</i> -Pr	H	161-162	1.4680	$\text{C}_7\text{H}_{13}\text{O}_3\text{N}$	8.80	
	PhNHCO			$\text{C}_{14}\text{H}_{18}\text{O}_4\text{N}_2$	10.07	9.98
<i>n</i> -Hex	H	72-75		$\text{C}_{10}\text{H}_{19}\text{O}_3\text{N}$	6.96	
	PhNHCO	137-139		$\text{C}_{17}\text{H}_{24}\text{O}_4\text{N}_2$	8.84	8.70

and recrystallized from benzene. Yield of the product was 0.7 g. (72%).

3-Phenyl-5-phenylcarbamyloxymethyl-2-oxazolidone (VII). Into 1.74 g. (0.05 mol.) of VI in 30 ml. of methanol was added dropwise 0.27 g. of sodium methoxide in 5 ml. of methanol, the mixture being kept at 20° for 3 hr. After removal of the solvent, the residue was washed with water and recrystallized from methanol to give 1.22 g. (78%) of 3-phenyl-5-phenylcarbamyloxymethyl-2-oxazolidone, m.p. 156.2-157.5°. A mixed melting point with III was 140-148°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{16}\text{N}_4\text{O}_2$: C, 65.37; H, 5.16; N, 8.97. Found: C, 65.12; H, 5.50; N, 9.19.

1-Chloro-2-acetoxy-3-phenylcarbamyloxypropane. V, 2.3 g. (0.01 mol.), in 10 g. of acetic anhydride containing a small amount of *p*-toluenesulfonic acid as a catalyst was heated under reflux for 1 hr. After removal of excess of acetic anhydride, the residue was distilled at 160-164°/0.07 mm. to give 1.85 g. (88%) of 1-chloro-2-acetoxy-3-phenylcarbamyloxypropane. The index of refraction was n_D^{25} 1.4990.

Anal. Calcd. for $\text{C}_{12}\text{H}_{14}\text{O}_4\text{NCl}$: N, 5.16. Found: N, 5.00.

Glycidyl alkyl carbamates. A mixture of equimolecular amount of glycidol and alkyl isocyanate was allowed to stand for 3 days and distilled under reduced pressure to obtain glycidyl alkyl carbamates. Glycidyl methyl carbamate was not isolated, however, which underwent the rearrangement during distillation to give 3-methyl-5-hydroxytetrahydro-1,3-oxazine-2-one, b.p. 80-82°/1 mm.

3-Alkyl-5-hydroxytetrahydro-1,3-oxazine-2-ones. Isomerization proceeded while glycidyl alkyl carbamates were heated at 100° for 1 hr. to yield 3-alkyl-5-hydroxytetrahydro-1,3-oxazine-2-ones. They were confirmed by their phenyl carbamates.

3-Alkyl-5-phenylcarbamyloxytetrahydro-1,3-oxazine-2-ones. A mixture of 3-alkyl-5-hydroxytetrahydro-1,3-oxazine-2-one and equimolecular amount of phenyl isocyanate was heated with 30 ml. of benzene for 3 hr. After cooling, the crystalline precipitate was collected and recrystallized from ethanol.

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