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FORMATION OF CARBAMATE DERIVATIVES BY REACTION OF CHLOROMETHYLOXIRANE OR PHENYLOXIRANE WITH CARBON DIOXIDE AND ALIPHATIC AMINES

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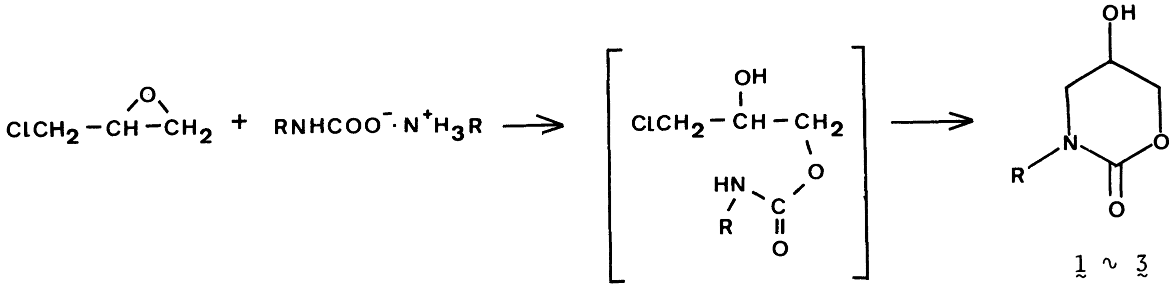
Reactions of chloromethyloxirane or phenyloxirane with carbon dioxide and aliphatic amines in methanol afforded corresponding hydroxyoxazinone or hydroxycarbamate derivatives under mild conditions.

In the previous paper we reported formation of oxazolidone derivatives by the reaction of α-bromoacylophenones with carbon dioxide and aliphatic amines.[1] As a part of our studies of reactions of carbon dioxide with organic compounds, we have investigated reactions of oxiranes with carbon dioxide and aliphatic amines (as carbamic acid ammonium salts) and wish to report some preliminary results to give carbamate derivatives.

Chloromethyloxirane and phenyloxirane were selected as oxiranes, because they are readily available, and also because chloromethyloxirane, especially, would give rise to cyclic carbamate (oxazinone) derivatives after carbamate formation followed by intramolecular ring cyclization.[2] Primary amines were mainly employed for the purpose of obtaining cyclic carbamates, and an aqueous methanol was used as the solvent in the case of methyl-, ethyl- and dimethylamine. Three equivalent moles of an amine and one equivalent mole of an oxirane were added successively in a carbon dioxide saturated methanol solution. Additional carbon dioxide was charged (10 kg/cm^2) to the above solution and then the mixture was heated gently in an autoclave (ca 60°C) for 10 - 15 hrs. The results are listed in the Table and the reactions are shown in the Scheme.

3-Alkyl-5-hydroxyoxazin-2-one and carbamate derivatives of 1-phenylethae-1,2-diol were obtained from chloromethyloxirane and from phenyloxirane, respectively. The structures of the oxazinones and the hydroxy carbamates were deduced from their elemental analyses[3] as well as from their ir, mass and nmr spectra,[4] and were confirmed by derivation to crystalline p-nitro- or 3,5-dinitrobenzoates as shown in the Table. The yields of carbamates were very poor in the cases of phenyloxirane However,the yields were improved, when the reactions were carried out in the presence of inorganic salts such as lithium bromide.

Although the yields of carbamates and oxazinones are rather poor, there are only few reports[1,5] of incorporation of carbamic acids into organic compounds under such mild conditions. Therefore, our results provide an interesting example of novel carbon dioxide incorporation reaction into organic compounds.



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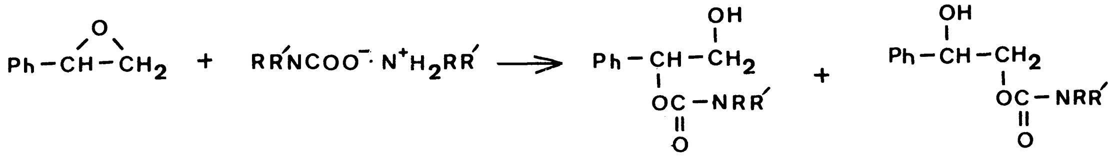

a b

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Table

Products	R	R'	Mp °C	Yield %*	IR c=o(CHCl$_3$) cm^{-1}
1	i-Pro		111	6	1675
2	Benzyl		110	10	1675
3	Cetyl		74	2.5	1680
4a	Me	H	109#	17**	1700
4b	Me	H			1705
5a	Et	H	118	13**	1705
6a	Benzyl	H	89	20**	1705
6b	Benzyl	H	111		1705
7a	Me	Me	112##	4.5**	1690
7b	Me	Me	103##		1690

*Isolated yield. **Yield of the mixtures of a and b except 5, in the presence of lithium bromide. #Mp of p-NO$_2$ benzoate. ##Mps of 3,5-diNO$_2$ benzoates.

References

1. T. Toda, Chemistry Letters, 1977, 957, and references cited therein.
2. S. Winstein and R. B. Henderson, "Heterocyclic Compounds," Vol I, ed. by R. C. Elderfield, John Wiley, New York, 1959, 1 - 60.
3. Satisfactory elemental analyses were obtained for all new compounds.
4. Details will be published elsewhere.
5. Y. Yoshida and S. Inoue, Chemistry Letters, 1977, 1375. Idem, ibid., 1978, 139.

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