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REACTIONS OF CARBON DIOXIDE WITH α-BROMOACYLOPHENONES: FORMATION OF OXAZOLIDONE DERIVATIVES

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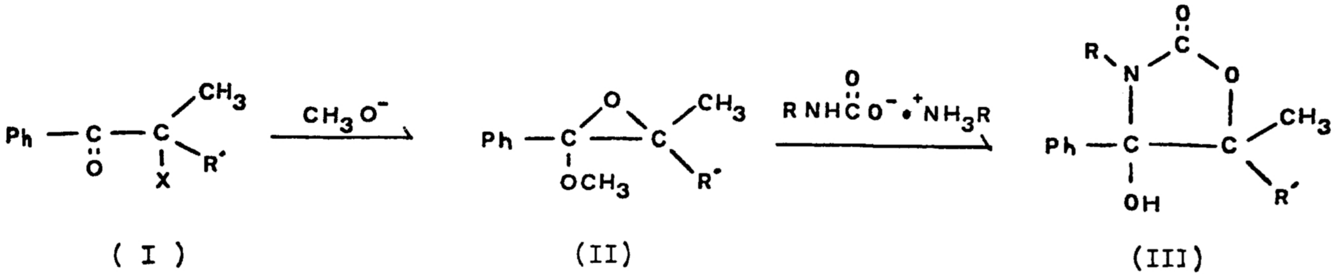
Reactions of carbon dioxide with α-bromoacylophenones in the presence of aliphatic primary amines in methanol afforded 3-alkyl-4-hydroxyoxazolidone-2 derivatives under mild conditions.

Although reactions of carbon dioxide with organic compounds have been extensively studied, such reactions are usually carried out in the presence of biotin[1] (or its analogues),[2] iodine,[3] metal complexes,[4] phosphorus compounds,[5] or strong bases.[6] We have also investigated this type of reactions in protic solvents under mild conditions without these catalysts. Here, we wish to present some preliminary results of reactions of α-haloacylophenones with carbon dioxide and aliphatic amines to give oxazolidone derivatives.

It is reported that carbon dioxide and some amines gave fairly stable carbamic acid ammonium salts.[7] The use of carbamic acids would appear to offer certain advantages for studying carbon dioxide incorporation into organic compounds under mild conditions. A typical example of the reactions is the following. To carbon dioxide saturated methanol, an aliphatic primary amine (3 equiv.; aqueous solutions of amines were used in the cases of methyl- and ethylamine) and α-bromoisobutyrophenone (1 equiv.) were dissolved in that order and heated gently for 10 - 12 hrs. During the reaction, carbon dioxide was bubbled through into the solution. Removal of the methanol followed by usual work-up gave corresponding 3-alkyl-4-hydroxy-5,5-dimethyl-4-phenyloxazolidone-2 derivatives (see the Table).[8] The N-methyl- and N-isopropyloxazolidones (1 and 3) were obtained by reactions of α-hydroxyisobutyrophenone[9] with methyl- and isopropylisocyanate. Thus, the structure of the oxazolidones was proved.

When the reactions were carried out with α-bromopropiophenone, a mixture of stereoisomers of 3-alkyl-4-hydroxy-5-methyl-4-phenyloxazolidone-2 was obtained. On the other hand, reactions of α-bromoacetophenone of α-chloroacetophenone resulted in the formation of resinous substances in the former, and recovery of the starting substances in the latter. Urethane derivatives were not obtained in the case of aromatic or secondary aliphatic amines.

A reasonable mechanism of the above reactions is as follows: 3-alkyl-2-methoxy-2-phenyloxiranes (II)[10] were formed at the first step of the reactions and subsequent attack of the carbamic acid ammonium salts on the oxiranes gave the oxazolidone derivatives (III). Actually, when the oxiranes were treated under similar conditions, the corresponding oxazolidones were obtained in much better yields.[11, 12]



Table

Oxazolidones (III)	R*	R'	Mp °C	Yield %	IR c=o cm^{-1} (KBr)
1	Methyl	Me	188.5	60	1740
2	Ethyl	Me	144	45	1740
3	i-Propyl	Me	180	50	1745
4	Cyclohexyl	Me	238	65	1745
5	Benzyl	Me	168	40	1740
6	Cetyl	Me	120	40	1740
7	i-Propyl	H	174**	40***	1740**

* Derived from amines (RNH_2). ** Mp and ir of a main product. *** Yield of a mixture.

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