

SYNTHESIS OF URETHANE DERIVATIVES BY REACTIONS OF  $\alpha$ -BROMOACYCLOPHENONES OR EPICHLOROHYDRIN WITH CARBON DIOXIDE AND ALIPHATIC AMINES AND REACTIONS OF THE OBTAINED URETHANE DERIVATIVES

Takashi Toda and Takashi Asano<sup>†</sup>

Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Aramaki, Sendai 980, and <sup>†</sup>Government Industrial Research Institute, Tohoku, Nigatake, Haranomachi, Sendai 983

Reactions of carbon dioxide with organic compounds have been extensively studied from a biochemical or biomimetic point of view and for the utilization of natural resources. We have also investigated these types of reactions and wish to report our results of reactions of  $\alpha$ -bromoacyclophenones or epichlorohydrin with carbon dioxide and primary aliphatic amines to give cyclic urethane derivatives.

Carbon dioxide readily reacts with amines to form carbamic acid ammonium salts even though free carbamic acids are said to be very unstable entities. The use of carbamic acids would appear to offer certain advantage for studying carbon dioxide incorporation into organic compounds under mild conditions.

The reactions of  $\alpha$ -bromoisobutyrophenone with carbon dioxide and primary aliphatic amines in methanol gave corresponding 3-alkyl-4-hydroxy-5,5-dimethyl-4-phenyl-1,3-oxazolidone-2 derivatives. The structure of the oxazolidones was deduced from their elemental analyses and spectral data; especially the ir spectra show a carbonyl band at  $1740\text{ cm}^{-1}$ . Acid hydrolysis of the oxazolidones afforded  $\alpha$ -hydroxyisobutyrophenone. Catalytic reduction in acidic methanol followed by hydrolysis gave corresponding 1-alkylamino-2-hydroxy-2-methyl-1-phenylpropanes. The mechanism of the oxazolidone formation is as follows: 2,2-dimethyl-3-methoxy-3-phenyloxirane was formed at the first step of the reaction and then attack of the carbamic acids to the oxirane gave the corresponding oxazolidones. Actually, when the oxirane was treated under similar conditions, the oxazolidones were obtained in much better yields.

The reactions of epichlorohydrin with carbamic acids also gave cyclic urethane derivatives; 5-hydroxy-3-alkyl-1,3-oxazinone-2 derivatives whose ir spectra show a strong carbonyl band at  $1675\text{ cm}^{-1}$ .

Incorporation of carbon dioxide into organic compounds under such mild conditions seems to be very important.