FORMATION OF ISOCYANATES BY THERMAL REACTIONS OF 4-HYDROXY-5,5-DIMETHYL-4-PHENYLOXAZOLIDONE-2 DERIVATIVES[1)]

Norio Saito, Kiyotaka Hatakeda, Shota Ito, and Takashi Asano*

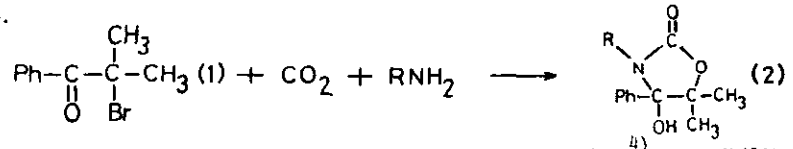
Government Industrial Research Institute Tohoku, Nigatake Haranomachi, Sendai 983

Takashi Toda*

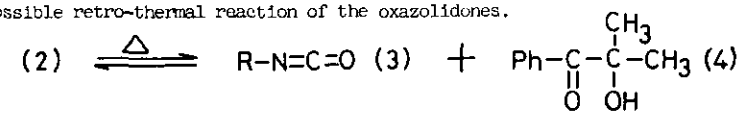
Department of Chemistry, Faculty of Science, Tohoku University, Aoba Aramaki, Sendai 980, Japan

Abstract —— Thermolysis of 3N-substituted 4-hydroxy-5,5-dimethyl-4-phenyloxazolidone-2 derivatives, which were prepared by the reaction of carbon dioxide and α-bromo-isobutyrophenone in the presence of primary amines, afforded corresponding isocyanates derived from 3N-substituents.

Recently we reported novel synthetic methods of 4-hydroxy-4-phenyloxazolidone-2 derivatives (2)[2)] or 4-hydroxyoxazinone-2 derivatives[3)] by the reactions of carbon dioxide and α-bromo-isobutyrophenone (1) or epichlorohydrin in the presence of aliphatic primary amines. As a part of utilization of carbon dioxide, we plan to synthesize isocyanates from the obtained oxazolidones, because isocyanates are important compounds in both chemical and industrial point of view. Isocyanates are usually synthesized by the reactions of amines with phosgene[4)]— very poisonous entity. Therefore it is an important and interesting task to synthesize isocyanates without using phosgene.



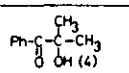
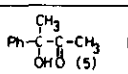
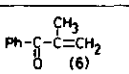
It is known that pyrolysis of some carbamates gave isocyanates derivatives[4)]. Possibility of isocyanates formation from the oxazolidones (2) was expected since our oxazolidones are cyclic carbamates. Synthesis of hydroxyoxazolidones from acylion derivatives (4) and isocyanates (3)[2,5)] also suggests possible retro-thermal reaction of the oxazolidones.



All oxazolidones (2a-e) used in this report were prepared by the method reported previously[2)]. The thermolysis was carried out by the following procedure : the oxazolidones as benzene solution or fine powder were dropped into a heated quartz tube which was packed with pieces of quartz under nitrogen stream. Decomposition began ca. 400 °C and the results obtained at 550 °C were presented in the Table. The reaction proceeded fairly clean and mainly gave four products; two different

acyloin (4 and 5), phenyl vinyl ketone (6) and urea detivatives (7), together with the desired isocyanates. The structure of each products were deduced from their spectral data[6] and comparison of retention time in the gas chromatography with those of the authentic samples. The acyloin (5)[7] and phenyl vinyl ketone (6)[8] are thermal and dehydration products of 2-hydroxy-2-methylpropiophenone (4)[2], respectively. Such rearrangements were reported previously[7], and thus

TABLE (yields and structures of the products)

(2)	isocyanates (3)		 (4)	 (5)	 (6)	$(RNH)_2CO$ (7)
a: R=Me	MeNCO	53 %	5 %	6 %	16 %	
b: Et	EtNCO	44	14	45	41	
c: i-Pr	i-PrNCO	17	6	17	27	9 %
d: Cyclohexyl	$C_6H_{11}NCO$	20	6	11	24	20
e; Phenyl*	C_6H_5NCO	76	9	24	12	ca. 3

* yield decomposed at 450 °C

retero-thermal reactions to isocyanates (3) and the acyloin (4) from the oxazolidones (2) occurred as expected. Since the urea derivatives (7) are secondary products from the formed isocyanates (3), the yields of isocyanates (3c-e) should be much better. Starting oxazolidones are prepared from carbon dioxide and amines, so that the present procedure provides a new synthetic method of isocyanates without using phosgene.

References and Notes

1) Dedicated to Professor T. Kametani on the occasion of his retirement anniversary.

2) T. Toda, Chemistry Letters, 1977, 957.

3) T. Asano, N. Saito, S. Ito, K. Hatakeda, and T. Toda, ibid., 1978, 311.

4) S. Ozaki, Chem Rev., 1972, 72, 457, and references cited therein.

5) N. R. Easton, D. R. Cassady, and R. D. Dillard, J. Org. Chem., 1962, 27, 2927.

6) Physical data of the reaction products. (5) [$\nu_{max}^{CHCl_3}$; 3475, 1705 cm^{-1} : M^+ at 25eV, 164 : δ_{CDCl_3} ; 1.60 (3H, s), 1.70 (3H, s), 4.54 (OH, s), 7.40 (Ph's H, m) :]. (6) [$\nu_{max}^{CHCl_3}$; 1645, 1630, 1595, 1515 cm^{-1} : M^+ at 25eV, 146 : δ_{CDCl_3} ; 2.05 (3H, t, J=4.0 Hz), 5.60 (1H, sextet, J=13.0 & 4.0 Hz), 5.85 (1H, sextet, J=13.0 & 4.0 Hz), 7.4-7.7 (Ph's H, m) :]. (7d) mp. 245 °C. (7e) mp. 255 °C.

7) I. Elphinoff-Felkin, G. Leny, and B. Tchouber, Bull. soc. chim. Fr., 1958, 552.

8) J. H. Burckhalter and R. C. Fusson, J. Am. Chem. Soc., 1948, 70, 4184.

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