May, 1986] © *1986 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 59, 1629—1631 (1986)* 1629

Formation of Bis(2-oxazolidinone) Derivatives by Reactions of 2-Methoxy-3,3-dimethyl-2-phenyloxirane or α-Bromoisobutyrophenone with Carbon Dioxide and Aliphatic α,ω-Diamines

Norio Saito,* Kiyotaka Hatakeda, Shota Ito, Takashi Asano,
and Takashi Toda*,†
Government Industrial Research Institute, Tohoku, Nigatake, Sendai 983
†Department of Industrial Chemistry, Faculty of Engineering, Utsunomiya University,
Ishii-cho, Utsunomiya 321

(Received December 4, 1985)

Synopsis. Reactions of 2-methoxy-3,3-dimethyl-2-phenyloxirane or α-bromoisobutyrophenone and carbon dioxide in the presence of aliphatic α,ω-diamines were investigated. 1,4-Butanediamine, 1,6-hexanediamine, 1,8-octanediamine, and 1,4-bis(aminomethyl)benzene afforded corresponding 3-(ω-aminoalkyl)-4-hydroxy-5,5-dimethyl-4-phenyl-2-oxazolidinones and 3,3′-polymethylenebis[4-hydroxy-5,5-dimethyl-4-phenyl-2-oxazolidinones] derivatives, while ethylenediamine gave only mono(2-oxazolidinone) derivative.

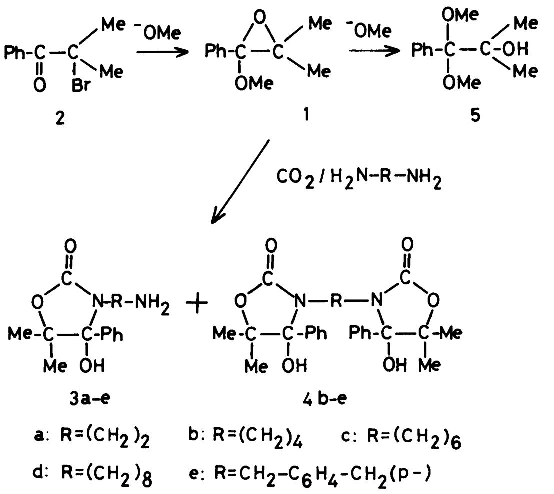
Since carbon dioxide is the most common, important and nontoxic C_1 resource, several attempts to utilize it have been reported.[1)] In such attempts, reactions are carried out under high pressure, at high temperature, in the presence of metal catalysts or caustic alkali, and/or combinations of those methods and so far.[1)] We noticed that carbon dioxide forms ammonium carbamates by the reactions with aliphatic amines, and some of the carbamate salts are fairly stable.[2,3)] We, and Yoshida and Inoue, found that carbon dioxide reacts with oxiranes (or their synthons) in the presence of aliphatic amines to give 2-oxazolidinones,[2)] carbamate derivatives,[4,5)] and tetrahydro-2*H*-1,3-oxazin-2-ones.[5)] Furthermore, we reported that thermolysis of the oxazolidone derivatives yielded isocyanate derivatives corresponding to the used amines.[6)] These results prompted us to study further extention of reactions of carbon dioxide with oxiranes (or thier synthons) in the presence of α,ω-diamines such as ethylenediamine or 1,6-hexanediamine expecting to obtain bis(2-oxazolidinone) derivatives. Because thermolysis of this type of bis(2-oxazolidinone) would give bis(isocyanate)s of which importance is well recognized in polymer chemistry.

The reactions were carried out as follows. After carbon dioxide was saturated in a methanol solution of a diamine, 2-methoxy-3,3-dimethyl-2-phenyloxirane (**1**) (or α-bromoisobutyrophenone (**2**)) was added to this solution, and then the solution was heated. IR spectrum of the product (**3a**) derived from ethylenediamine showed free amino group's frequencies at 3390 and 3210 cm^{-1}, and a carbonyl absorption at 1750 cm^{-1} corresponding to that of 2-oxazolidinone.[2)] The molecular formula and weight ($C_{13}H_{18}O_3N_2$, and *m/z*: M^+, 250) of **3a** indicate that only one amino group of ethylenediamine was incorporated into the 2-oxazolidinone skeleton. Thus, the structure of **3a** is presented as 3-(2-aminoethyl)-4-hydroxy-5,5-dimethyl-4-phenyl-2-oxazolidinone. On the other hand, 1,4-butanediamine, 1,6-hexanediamine, 1,8-octanediamine, and 1,4-bis(aminomethyl)benzene gave two different kind of oxazolidone derivatives, respectivily. The first ones are mono(2-oxazolidinone) derivatives which possess a free amino group at the end of the methylene chain as shown in their IR spectra (see the Table). The second products did not show any free amino group frequencies, but showed very strong carbonyl absorption around 1750 cm^{-1}. Therefore, the latter products are bis(2-oxazolidinone) derivatives as shown in the Scheme such as **4**. The elemental analyses of them also support that those structures are correct. Fairly large amount (25—50%) of 1,1-dimethoxy-2-methyl-1-phenyl-2-propanol (**5**) was obtained together with **3** and **4**.

Table 1. Yields and IR Data of Reaction Products

R	product	Yield/%[a)]		IR/cm^{-1}		
		1:1[b)]	1:2[b)]	C=O	NH	
$(CH_2)_2$	**3a**	37(Trace)	41(7)	1750	3320	3390
$(CH_2)_4$	**3b**	29(8)	25(20)	1750	3290	3365
	4b	1(1)	9(5)	1745		
$(CH_2)_6$	**3c**	35(21)	40(28)	1750	3310	3280
	4c	7(4)	5(3)	1750		
$(CH_2)_8$	**3d**	22(4)	21(19)	1745	3290	3360
	4d	7(8)	6(4)	1740		
$C_6H_4(CH_2)_2$(*p*-)	**3e**	13(Trace)	18(Trace)	1750	3300	3370
	4e	Trace(-)	Trace(-)	1750		

a) Yields are based on the oxirane (**1**), and yields in parenthesis are based on the bromo ketone (**2**). b) Mol ratio of **1** (or **2**): diamine.



Scheme 1.

The results are listed in the Table. Further treatment of 3-(8-aminooctyl)-4-hydroxy-5,5-dimethyl-4-phenyl-2-oxazolidinone (**3d**) with the oxirane in the presence of carbon dioxide gave the corresponding bis(2-oxazolidinone) derivative (**4d**, 53%). However, **3a** did not give any bis(2-oxazolidinone) derivative under the same conditions. Although the reason was not clear, formation of oxazolidinones was not observed when 1,3-bis(aminomethyl)benzene was adopted as the diamine.

One of the reason for the low yield of the oxazolidinones formation is presumed to be steric hindrance of big carbamates derived from the diamines. Also, intra- or intermolecular hydrogen bond formation between the remained amino group and the formed carbamate carbonyl seems to make those group's reactivity toward the oxirane inactive. Formation of fairly large amount of **5** indicate that the attack of methoxide anion and carbamate anion take place in the same probability. Contrarily to this, carbamate anions smoothly react with the oxirane to give the oxazolidinones in good yields in the case of monoamines.[2] It seems likely that the reason why the second oxazolidinone ring does not form **3a** is as follows; the formed oxazolidinone ring near the remained amino group causes steric hindrance, and intramolecular hydrogen bond formation between the amino group and the carbonyl group in the oxazolidinone makes the amino groups inactive. The more data than we have now are needed in order to come the conclusion about the low yield of bis(2-oxazolidinone).

The yields are rather poor to fair, but the bis(2-oxazolidinone) formation suggests possibility of the bis(isocyanate)s formation from carbon dioxide and α,ω-diamines.

Experimental

All melting points were uncorrected. IR spectra were recorded on a Hitachi 285 spectrophotometer by KBr disk method. Mass spectra were measured on a JEOL JMS-300 mass spectrometer by EI, CI, and FD methods. The oxirane and the bromo ketone were prepared by the methods as reported previously.[2]

3-(2-Aminoethyl)-4-hydroxy-5,5-dimethyl-4-phenyl-2-oxazolidinone (3a): Carbon dioxide was bubbled through the solution of ethylenediamine (4.2 g, 0.07 mol) in methanol (100 cm^3) until the colorless precipitates produced in the solution, and then the oxirane (**1**, 6.3 g, 0.035 mol) (or bromo ketone (**2**)) was added dropwise to the solution. The mixture was gently refluxed for 18 h with bubbling of carbon dioxide. The methanol was removed in vacuo, and the residue was dissolved in chloroform, washed with water, and dried ($MgSO_4$). After removal of the chloroform, the residue was treated with petroleum ether to afford **3a** as a precipitate. **5** was obtained from the petrolem ether layer. **3a**: Yield, 3.6 g (41%); colorless prisms (ethanol), mp 191—192 °C. Found: C, 62.41; H, 7.33; N, 11.21%; MS (*m/z*) 250 (M^+). Calcd for $C_{13}H_{18}O_3N_2$: C, 62.38; H, 7.25; N, 11.19%.

3-(4-Aminobutyl)-4-hydroxy-5,5-dimethyl-4-phenyl-2-oxazolidinone (3b) and 3,3′-Tetramethylenebis[4-hydroxy-5,5-dimethyl-4-phenyl-2-oxazolidinone] (4b): Under the same conditions as described above, **1** (6.3 g, 0.035 mol) was allowed to react with carbon dioxide and 1,4-butanediamine (6.3 g, 0.07 mol). After removal of the solvent, the residue was dissolved in chloroform, and washed with water. When the choloform was removed in vacuo and the residue was treated with petroleum ether, a white precipitates was obtained. The precipitate was treated with benzene to give colorless solid of **4b** as an insoluble part. The benzene filtrate was evaporated, and then the residue was recrystallized to afford **3b**. **5** was obtained from the petroleum ether layer. **3b**: Yield, 2.4 g (25%); colorless powder (benzene–hexane), mp 106—107 °C. Found: C, 64.11; H, 7.98; N, 9.77%; MS (*m/z*) 278 (M^+). Calcd for $C_{15}H_{22}O_3N_2$: C, 64.72; H. 7.97; N, 10.07%. **4b**: Yield, 0.7 g (9%); colorless powder (acetone), mp 294—295 °C. Found: C, 66.90; H, 7.12; N, 5.82%; MS (*m/z*) 469 (M^++1). Calcd for $C_{26}H_{32}O_6N_2$: C, 66.65; H, 6.88; N, 5.98%.

3-(6-Aminohexyl)-4-hydroxy-5,5-dimethyl-4-phenyl-2-oxazolidinone (3c) and 3,3′-Hexamethylenebis[4-hydroxy-5,5-dimethyl-4-phenyl-2-oxazolidinone] (4c): These compounds were synthesized in the manner similar to that of **3b** and **4b**. **3c**: Yield, 4.3 g (40%); colorless powder (ethanol–water), mp 80—81 °C. Found: C, 66.85; H, 8.29; N, 8.85%; MS (*m/z*) 306 (M^+). Calcd for $C_{17}H_{26}O_3N_2$: C, 66.64; H, 8.55; N, 9.14%. **4c**: Yield, 0.5 g (5%); colorless powder (chloroform), mp 239—240 °C. Found: C, 67.10; H, 7.41; N, 5.59%; MS (FD, *m/z*) 496 (M^+), 519 (M^++23). Calcd for $C_{28}H_{36}O_6N_2$: C, 67.52; H, 7.31; N, 5.64%.

3-(8-Aminooctyl)-4-hydroxy-5,5-dimethyl-4-phenyl-2-oxazolidinone (3d) and 3,3′-Octamethylenebis[4-hydroxy-5,5-dimethyl-4-phenyl-2-oxazolidinone] (4d): Under the same conditions described above, **1** (6.3 g, 0.035 mol) was allowed to react with carbon dioxide and 1,8-octanediamine (10.1 g, 0.07 mol). The methanol was removed in vacuo and the residue was dissolved in chloroform, and then the chloroform layer was washed with hydrochloric acid. **3d** was obtained as a precipitate from the aqueuos layer by addition of aqueous sodium hydroxide. The chloroform layer was washed with water, and concentrated under reduced pressure. The residue was treated with ether to afford **4d** as a precipitate. **5** was obtained from the ether layer. **3d**: Yield, 2.5 g (21%); colorless needless (ethanol–water), mp 79—80 °C. Found: C, 67.66; H, 8.77; N, 8.13%; MS (*m/z*) 334 (M^+). Calcd for $C_{19}H_{30}O_3N_2$: C, 68.23; H, 9.04%; N, 8.38%. **4d**: Yield, 0.7 g (6%); colorless prisms (ethanol), mp 197—198 °C. Found: C, 68.45; H, 7.88; N, 5.19%; MS (*m/z*) 525 (M^++1). Calcd for $C_{30}H_{40}O_6N_2$: C, 68.68; H, 7.69; N, 5.34%.

3-[*p*-(Aminomethyl)benzyl]-4-hydroxy-5,5-dimethyl-4-phenyl-2-oxazolidinone (3e): This compound was obtained in the manner similiar to that of **3d**. **3e**: Yield, 2.3 g (18%); colorless powder (ethanol), mp 68—69 °C. Found: C, 69.58; H, 6.95; N, 8.52%; MS (*m/z*) 327 ($M^{+}+1$). Calcd for $C_{19}H_{22}O_3N_2$; C, 69.92; H, 6.79; N, 8.58%.

1,1-Dimethoxy-2-methyl-1-phenyl-2-propanol (**5**, mp 54—55 °C, from hexane)[7] was obtained together with **3** and **4**; the yield of 5 varied (25—50%) for the each run of the reactions.

Preparation of 4d from 3d: After carbon dioxide was saturated in a methanol solution of **3d** (3.6 g, 0.02 mol), **1** (3.3 g, 0.01 mol) was added to the solution and then the mixture was gently refluxed for 24 h with bubbling of carbon dioxide. After the removal of the methanol in vacuo, the residue was dissolved in chloroform. The chloroform layer was washed with hydrochloric acid, water, and dried. The chloroform was evaporated in vacuo to afford a residue which was recrystallized from ethanol to give **4d** (2.8 g, 53%).

References

1) Y. Yoshida and S. Inoue, "Yuki Shigen no Kagaku," ed by S. Inoue, S. Sato, and H. Matsuda, Kagakudojin, Kyoto (1981), pp. 85—99; T. Osa, "Tansangasu no Kagaku," ed by Y. Kitani, M, Ichikawa, T. Osa, S. Inoue, and K. Asada, Kyoritu Shuppan, Tokyo (1976), Chap. 3.

2) T. Toda, *Chem. Lett.*, **1977**, 975; T. Toda, *Nippon Kagaku Kaishi,* **1982**, 282, and references therein.

3) T. Hayashi, *Riken Iho,* **11**, 1391 (1932); H. B. Wright and M. B. Moor, *J. Am. Chem. Soc.*, **70**, 3865 (1948).

4) Y. Yoshida and S. Inoue, *Chem. Lett.*, **1977**, 1375; Y. Yoshida and S. Inoue, *J. Chem. Soc., Perkin Trans. 1,* **1979**, 3146.

5) T. Asano, N. Saito, S. Ito, K. Hatakeda, and T. Toda, *Chem. Lett.*, **1978**, 311.

6) N. Saito, K. Hatakeda, S. Ito, T. Asano, and T. Toda, *Heterocycles,* **15**, 905 (1981).

7) T. I. Temnikova and N. I. Almashi, *Zh. Obshch Khim.*, **23**, 1338 (1953); *Chem. Abstr.*, **48**, 12025b (1954); C. L. Stevens and T. H. Coffield, *J. Am. Chem. Soc.*, **80**, 1919 (1958).