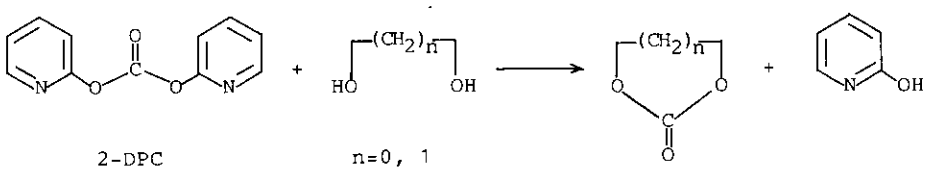
PREPARATION OF CYCLIC CARBONATES AND 2-OXAZOLIDONES USING DI-2-PYRIDYL CARBONATE

Sunggak Kim* and Young Kwan Ko
Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131, Korea

Abstract —— Cyclic carbonates and 2-oxazolidones are conveniently prepared in high yields by the reaction of diols and β-amino alcohols with di-2-pyridyl carbonate. It is of synthetic significance that the formation of cyclic carboantes in refluxing toluene occurs under essentially neutral conditions.

In connection with our ongoing research program on the synthetic utility of pyridin-2-yl related active esters and carbonates,[1] we have reported that di-2-pyridyl carbonate (2-DPC) is an efficient coupling agent for direct esterification of carboxylic acids.[2] We have found that 2-DPC can be successfully utilized as a carbonylating agent for the preparation of cyclic carbonates and 2-oxazolidones from diols and β-amino alcohols under very mild conditions.
Cyclic carbonates, prepared from 1,2- and 1,3-diols and several carbonylating agents,[3-8] have been widely used for the protection of vicinal hydroxy groups. Cyclic carbonates are readily hydrolized under basic conditions, whereas they are relatively stable to the acidic conditions.[9]

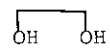
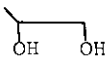
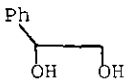
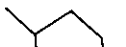
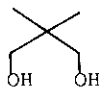
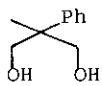
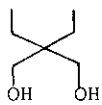
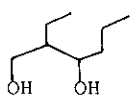
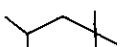
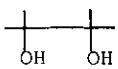


2-DPC n=0, 1

Table I shows some experimental results obtained in the preparation of cyclic carbonates using 2-DPC as a carbonylating agent and illustrates the efficiency, the scope, and limitations of the present method. First, the cyclic carbonate formation was carried out in refluxing toluene using a stoichiometric amount of 2-DPC (Method A). Under the present condition, the reaction was normally complete within 3 h. Furthermore, we have found that this reaction can be carried out in the presence of 0.1 equiv. of 4-dimethylaminopyridine (DMAP) as a catalyst in methylene chloride at room temperature (Method B), although the use of triethylamine and pyridine as catalysts was not effective in the preparation of cyclic carbonates. However, Method B required longer reaction times than Method A for completion of the reaction. As shown in Table I, the present method was successful for the preparation of cyclic carbonates from structurally different 1,2- and 1,3-diols with the exception of sterically hindered bis-tertiary substituted diols. In the case of bis-tertiary substituted diols, starting materials were recovered unchanged under prolonged stirring in refluxing toluene or in the presence of an excess amount of DMAP in methylene chloride at reflux. The cyclic carbonate formation using 1,1'-carbonyldiimidazole was briefly examined to compare the effectiveness of 2-DPC with that of 1,1'-carbonyldiimidazole as a carbonylating agent. Reaction of 1,2-propanediol and 1-phenyl-1,2-ethanediol with 1.2 equiv. of 1,1'-carbonyldiimidazole in refluxing toluene for 2 h gave 4-methyl-1,3-dioxolan-2-one and 4-phenyl-1,3-dioxolan-2-one in 83% and 85% yield, respectively. However, under similar conditions, ethylene glycol and 1,3-butanediol did not give satisfactory results, yielding 1,3-dioxolan-2-one and 4-methyl-1,3-dioxan-2-one in 49% and 39% yield along with several other by-products, respectively. Thus, it seems that the success of the reaction might depend on the nature of the substrates, although the reason for this is rather obscure.

Several noteworthy features of the present method are apparent as compared with previously known methods.[3-8] First, since 2-hydroxypyridine as the only other by-product formed is an essentially neutral compound, Method A proceeds under essentially neutral conditions, which is of synthetic significance. For instance, the use of 1,1'-carbonyldiimidazole for this purpose produces basic imidazole which might cause some problems in the synthesis of base-sensitive molecules. Second, the use of 2-DPC gave consistently satisfactory results with structurally

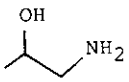
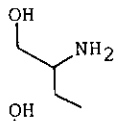
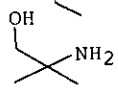
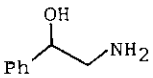
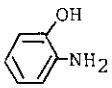
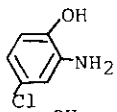
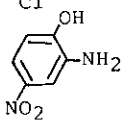
Table I. Preparation of Cyclic Carbonates Using Di-2-pyridyl Carbonate

diol	method[a]	time, h	yield, %[b] cyclic carbonate	bp,°C/torr or mp,°C found	reported
	A	1	85	69-71/1	248/760[10]
	A	1.5	83		
	B	2.5	85	73-75/2	110/10[10]
	A	0.5	94		
	B	1.5	83	54-55	
	A	1	80		
	B	1.5	82	117-119/0.4	113-115/0.2[4]
	B	3	90	109-110	109-110[4]
	A	1	92		
	B	2	96	99-100	100[4]
	A	1	94	44-45	44-45[4]
	A	3	91		
	B	10	94	117-119/0.46	
	A	1	89		
	B	5	83	97-98	
	A	24	0		
	B	24	0		

[a] Method A: in refluxing toluene. Method B: in the presence of 0.1 equiv of DMAP in methylene chloride at room temperature. [b] The yields refer to the isolated products.

different diols. Third, the present method is very simple and convenient because water-soluble 2-hydroxypyridine can be easily removed by the usual aqueous workup. Finally, 2-DPC is more stable than 1,1'-carbonyldiimidazole.

Table II. Preparation of 2-Oxazolidones from β-Amino Alcohols[a]

β-amino alcohol	time, min	yield, %[b] 2-oxazolidone	bp,°C/torr or mp,°C found	reported
	10	87	102-104/0.5	136-137/5[12]
	5	87	121-124/0.6	16-16.5[13]
	5	96	90-92/0.5	152-154/10[12]
	10	93	87-88	87-87.5[14]
	10	96	135-136	135-137[15]
	15	94	186-188	
	60	96	228-230	230-232[15]

[a] The reaction was carried out with an equimolar mixture of β-amino alcohols and 2-DPC in methylene chloride at room temperature. [b] The yields refer to isolated products.

2-Oxazolidones, an important class of heterocyclic compounds containing a five-membered ring, are very useful in the synthesis of biologically active compounds and polymers.[11] Many methods for the preparation of 2-oxazolidones have been reported.[11] We have found that 2-DPC can be successfully utilized for the preparation of 2-oxazolidones from β-amino alcohols.

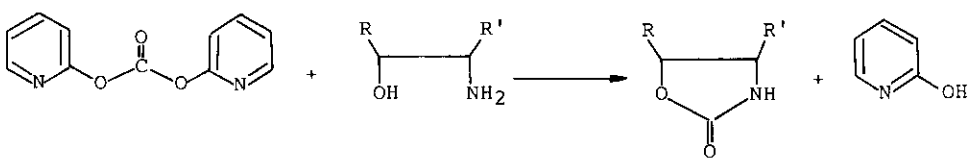


Table II shows some experimental results obtained in the preparation of 2-oxazolidones from β-amino alcohols. Reaction of β-amino alcohols with a stoichiometric amount of 2-DPC in methylene chloride proceeded smoothly and rapidly at room temperature, yielding the corresponding 2-oxazolidones in essentially quantitative yields. The reaction was normally complete within 10 min. In the case of relatively unreactive 2-amino-4-nitrophenol, the reaction required 1 h for completion of the reaction.

We felt that the present method, because of its simplicity, mildness, and effectiveness, might become the method of choice for the preparation of 2-oxazolidones from β-amino alcohols, although a number of methods such as using phosgene, dialkyl carboantes, and alkyl chloroformates are available for this conversion.[11]

EXPERIMENTAL

4-Methyl-1,3-dioxolan-2-one. (Method A): To a stirred solution of 1,2-propanediol (230 mg, 3.0 mmol) in toluene (8 ml) was added 2-DPC (670 mg, 3.1 mmol). After stirring at 110 °C for 1.5 h, the reaction mixture was allowed to cool to room temperature, diluted with methylene chloride (40 ml), washed with brine (30 ml), dried over anhydorus $MgSO_4$, and evaporated to dryness under reduced pressure. The crude product was distilled in vacuo with Kugelrohr apparatus to give 4-methyl-1,3-dioxolan-2-one (254 mg) in 83% yield. bp 73-75 °C/2 mmHg; ^{1}H-NMR($CDCl_3$) δ 1.46 (d, J=6 Hz, 3H, CH_3), 4.03 (dd, J=8 Hz, 1H, CH_2), 4.57 (dd, J=8 Hz, 1H, CH_2), 4.60-5.18 (m, 1H, OC<u>H</u>-CH_3); IR(film) 1790 cm^{-1}. (Method B): To a stirred solution of 1,2-propanediol (152 mg, 2.0 mmol) and 2-DPC (453 mg, 2.1 mmol) in methylene chloride (6 ml) at room temperature was added DMAP (23 mg, 0.2 mmol). The reaction mixture was stirred at room temperature for 2.5 h, diluted with methylene chloride (40 ml), washed with 5% aqueous hydrochloric acid (20 ml) and brine (20 ml), dried over anhydrous $MgSO_4$, and evaporated to dryness. The crude product was distilled in vacuo to give the desired product (174 mg, 85%).

5-Methyl-2-oxazolidone. A solution of 1-amino-2-propanol (150 mg, 2 mmol) and 2-DPC (432 mg, 2 mmol) in methylene chloride (6 ml) was stirred at room temperature. The reaction mixture was diluted with ethyl acetate (40 ml), washed with brine (20 ml), dried over anhydrous $MgSO_4$, and evaporated to dryness. The crude product was distilled in vacuo with Kugelrohr apparatus to

afford 5-methyl-2-oxazolidone (176 mg) in 87% yield. bp 102-104 °C/0.5 mmHg; ^{1}H-NMR($CDCl_3$)δ 1.42 (d, J=6 Hz, 3H, CH_3), 3.14 (dd, J=8 Hz, 1H, CH_2), 3.69 (dd, J=8 Hz, 1H, CH_2), 4.50-5.08 (m, 1H, OC<u>H</u>-CH_3), 6.35-6.96 (m, 1H, NH); IR(film) 1755 cm^{-1}.

ACKNOWLEDGMENT

We are grateful to the Korea Science and Engineering Foundation for generous support of this work.

REFERENCES

1. For our recent reports, see: (a) S. Kim and K. Y. Yi, Tetrahedron Lett., 1985, 1661. (b) S. Kim and Y. K. Ko, Bull. Korean Chem. Soc., 1985, 6, 175.
2. (a) S. Kim, J. I. Lee, and Y. K. Ko, Tetrahedron Lett., 1984, 4943. (b) S. Kim and Y. K. Ko, Chem. Comm., 1985, 474.
3. B. J. Ludwig and E. C. Piech, J. Am. Chem. Soc., 1951, 73, 5779.
4. S. Sarel, L. A. Pohoryles, and R. Ben-Shoshan, J. Org. Chem., 1959, 24, 1873.
5. R. L. Letsinger and K. K. Ogilvie, J. Org. Chem., 1967, 32, 296
6. A. Hampton and A. W. Nichol, J. Org. Chem., 1967, 32, 1688.
7. J. P. Kutney and A. H. Ratcliffe, Syn. Comm., 1975, 5, 47.
8. H. Komura, T. Yoshino, and Y. Ishido, Carbohydr. Res., 1975, 40, 391.
9. T. W. Greene, ' Protective Groups in Organic Synthesis ', John Wiley & Sons, New York, 1981, p 85.
10. Handbook of Chemistry and Physics, 60th Edit. CRC Press, Florida, 1980.
11. For an excellent review, see: M. E. Dyen and D. Swern, Chem. Rev., 1967, 67, 197.
12. E. Katchalski and D. B. Ishai, J. Org. Chem., 1950, 15, 1066.
13. A. H. Homeyer, Chem. Abstr., 1946, 40, 40849.
14. G. I. Poos, J. R. Carson, J. D. Rosenau, A. P. Roszkowski, N. M. Kelly, and J. McGowin, Chem. Abstr., 1963, 59, 1611f.
15. H. R. Kricheldorf, Chem. Ber., 1970, 103, 3353.

Received, 23rd January, 1986