nonbonded interaction between those hydrogens becomes least among any other confonfurmations such as $\delta\lambda$ or $\lambda\lambda$ conformations.

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Convenient Method for the Preparation of Active Carbonates, Active Carbamates, and Ureas Using *Di*-2-Pyridyl Carbonate

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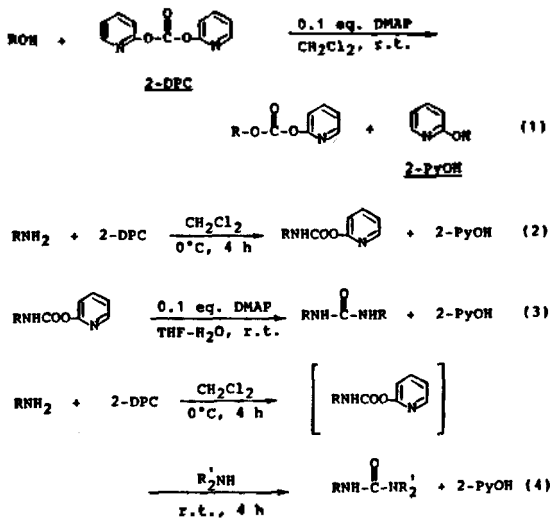
(Received Janaury 23, 1985)

As part of our research program directed toward the synthetic utility of active esters and carbonates containing 2-pyridyl[1-4] or 1-benzotriazolyl group,[5,6] we have recently reported that di-2-pyridyl carbonate (2-DPC) is an efficient coupling reagent for the direct esterification of carboxylic acids.[4] We now wish to report a convenient method for the preparation of active carbonate, active carbamates, and ureas using di-2-pyridyl carbonate.

Since a variety of active carbonates having *t*-butyl and benzyl group are well-known amino protective reagents for peptide synthesis,[7] reaction of an alcohol with *di*-2-pyridyl carbonate was studied and we found that several synthetically useful active carbonates could be conveniently prepared from di-2-pyridyl carbonate and an alcohol in the presence of 4-dimethylaminopyridine (DMAP)[8] (eq. 1). Reaction of benzyl alcohol with an equimolar amount of 2-DPC in the presence of 0.1 equiv of DMAP in methylene chloride at room temperature in 2 h gave benzyl 2-pyridyl carbonate in 70% yield, whereas the reaction did not occur in the presence of triethylamine. *t*-Butyl 2-pyridyl carbonate[2] was obtained in 80% yield by treatment of *t*-butyl alcohol with an equimolar amount of 2-DPC in the presence of 0.1 equiv of DMAP in methylene chloride at room temperature for 12 h. Similarly, methyl 2-pyridyl carbonate was obtained in 78 % yield within 1 h under the similar conditions.

When 2-DPC was reacted with several amines in methylene chloride at 0°C for 4 h, the corresponding 2-pyridyl carbamates were obtained in high yields along with a small amount of the corresponding ureas (eq. 2). For example, reaction of 2-DPC with an equimolar amount of benzylamine at 0 °C in 4 h gave N-benzyl, 2-pyridyl carbamate in 83% yield along with 4% of dibenzylurea after silica gel column chromatographic separation. Furthermore, it is noteworthy that the reaction did not afford the corresponding isocyanates and 2-pyridyl carbamates obtained here did not decompose thermally into the corresponding isocyanates and 2-hydroxypyridine. Some typical isolated yields of 2-pyridyl carbamates were: $CH_3CH_2CH_2NHCOO$-2-Py, 81%; $CH_3CH_2CH(CH_3)$ NHCOO-2-Py, 82%; cyclo-C_6H_{11}NHCOO-2-Py, 84%.

Reaction of 2-pyridyl carbamates with 0.1 equiv of DMAP in aqueous tetrahydrofuran did not give the original amines but the symmetrical ureas (eq. 3). The reaction proceeded cleanly at room temperature and required 12-24 h for completion of the reaction. Some typical isolated yields of the symmetrical ureas were: $C_6H_5CH_2NHCONHCH_2C_6H_5$, 99%; $CH_3CH_2CH_2NHCONHCH_2CH_2CH_3$, 92%; $CH_3CH_2(CH_3)$



$CHNHCONHCH(CH_3)CH_2CH_3$, 98%; cyclo-$C_6H_{11}NHCONH$-cyclo-C_6H_{11}, 95%.

Unsymmetrical ureas can be conveniently prepared using 2-DPC by a two-step, one-pot procedure (eq. 4). 2-Pyridyl carbamates prepared from an equimolar mixture of 2-DPC and amines were treated with equimolar amounts of amines to afford the corresponding unsymmetrical ureas in high yields. The reaction of 2-pyridyl cabamates with amines required 4 h at room temperature. Some typical isolated yields of unsymmetrical ureas were: $C_6H_5CH_2NHCON(CH_2CH_2CH_3)_2$, 81%; $CH_3CH_2CH_2NHCON(n\text{-}C_4H_9)_2$, 80%; $CH_3CH_2(CH_3)CHNHCON(\text{cyclo-}C_6H_{11})_2$, 87%; cyclo-$C_6H_{11}NHCON(n\text{-}C_3H_7)_2$, 87%.

Acknowledgment. This work was financially supported by a grant from Korea Science and Engineering Foundation.

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Catalytic Isomerization of Fumaronitrile to Maleonitrile with the Rhodium(I)-Perchlorato Compound $Rh(ClO_4)(CO)(P(C_6H_5)_3)_2$

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The isomerization of fumaronitrile (*trans*-NCCH = CHCN, FN) to maleonitrile (*cis*-NCCH = CHCN, MN) is catalyzed by iodine[1] and occurs when FN is treated with BuLi[2] or irradiated in the presence of a photosensitizer 1,2,3-triphenylpropene.[3]

TABLE 1: Isomerization and Hydrogenation of FN with Related Rhodium(I) Complexes.[a]

Catalyst	Temp, °C	Reaction Time, h	Product, mmol		
			MN[c]	SN[d]	FN
1	25	48	0	0	10.0
	70	24	2.9	0.1	7.0
	70	48	4.4	0.1	5.5
	120[b]	6	0	5.8	4.2
	120[b]	12	0	8.4	1.6
	120[b]	24	0	10	0
2	25	1	0	5.8	4.2
	25	2	0	8.6	1.4
3	25	48	0	0	10
	70	24	0	1.1	8.9
	70	48	0	2.0	8.0

[a] All experiments were carried out using 0.1 mmole of catalyst and 10 mmoles of FN (singlet, at 6.23 ppm relative to TMS in C_6H_5Cl) in 25 m*l* of monochlorobenzene under hydrogen (P^{H_2} + vapor pressure of the solution = 1 atm). Product ananlyses were obtained by ^1H-NMR spectroscopy at 60 MHz. [b] In a pressure bottle under hydrogen (P_{H_2} + vapor pressure of the solution = 1 atm at room temperature before the reactor was heated). [c] Singlet at 6.16 ppm relative to TMS in C_6H_5Cl. [d] Singlet at 2.23 ppm relative to TMS in C_6H_5Cl.

No reports have been made thus far on the isomerization of FN to MN with transition metal complexes.

We wish to report the catalytic isomerization of FN to MN by the rhodium(I)-perchlorato compound Rh (ClO_4) (CO) ($P(C_6H_5)_3)_2$ (**1**). Chlorobenzene solution of complex **1** and FN at 70°C under hydrogen selectively produces MN until 44% of FN is converted into MN. (See the footnotes of Table 1 for experimental details.) This isomerization of FN to MN with **1** does not proceed any further even for prolonged time under the same experimental conditions. A small amount of the hydrogenation product, succinonitrile ($NCCH_2CH_2CN$, SN) is also produced at 70°C (see Table 1). In the absence of hydrogen, the isomerization of FN to MN with complex **1** does not occur at all at 70°C. At 120°C, however, complex **1** exclusively catalyzes the hydrogenation of FN to give SN in 100% yield (see Table 1).

In the same manner, attempts have been made to catalyze the isomerization of FN to MN with the related compounds, RhCl ($P(C_6H_5)_3)_3$ and RhCl (CO) ($P(C_6H_5)_3)_2$. (See the footnotes of Table 1 for experimental details.) No catalytic isomerization, however, has been observed (see Table 1).

It may be noteworthy to compare our date (FN : MN = 56 : 44) with those obtained from the photolytic isomerization in the presence of photosensitizer 1,2,3-triphenylpropene where the isomerization of FN to MN proceeded until the ratio (FN : MN = 60 : 40) was obtained.[3] Practically the same ratio (FN : MN = 57 : 43) was also predicted in the laser photolysis experiments in the presence of photosensitizer.[4] Further investigation is being undertaken for the mechanism of the