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Nucleophilic Reactions of Diethyl *N*-Phenyliminocarbonate

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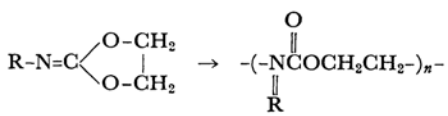
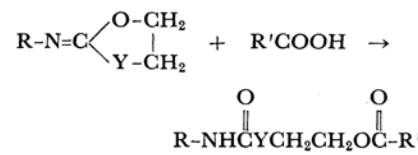
The reactions of diethyl *N*-phenyliminocarbonate with alkyl halide, acid chloride, lactone, and acid anhydride were studied in order to examine the nucleophilicity of the imino group. These reactions gave the corresponding carbamates at elevated temperatures, much as in the previously reported reactions of iminocarbonates with acids. On the other hand, from the reaction of the iminocarbonate with ethylene carbonate or ethylene sulfite, 3-phenyloxazolidone-2 was obtained along with the evolution of carbon dioxide or sulfur dioxide, respectively.

Previous papers[1,2] on 1, 4-addition-type ring-opening polymerization have shown that the cyclic iminocarbonates polymerize as follows to give polyurethanes in the presence of cationic catalysts:



R=aryl, alkyl or chlorine.

Furthermore, it has been reported that exo-imino cyclic compounds, such as ethylene *N*-phenyliminocarbonate, 2-phenylimino-3-methyl-1, 3-oxazolidine and *N*-substituted 2-iminotetrahydrofurans, react with carboxylic acids to give the corresponding addition compounds by a ring-opening 1, 4-addition reaction.[3]



Y=O, N-R'' or CH_2.

The reactivity of the iminocarbonate for such a 1, 4-addition-type reaction may be ascribed to the highly nucleophilic character of the imino

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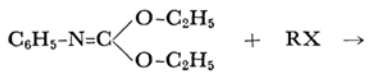
1) T. Mukaiyama, T. Fujisawa, H. Nohira and T. Hyugaji, *J. Org. Chem.*, **27**, 3337 (1962).

2) T. Fujisawa, Y. Tamura and T. Mukaiyama, This Bulletin, **37**, 793 (1964).

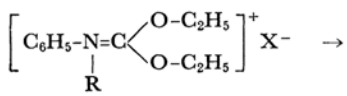
3) T. Mukaiyama, Y. Tamura and T. Fujisawa, *ibid.*, **37**, 628 (1964).

group. In the present experiment, nucleophilic reactions of diethyl *N*-phenyliminocarbonate (I) with several electrophiles, such as alkyl halide, acid chloride, lactone, and acid anhydride, to give corresponding carbamates have been investigated.

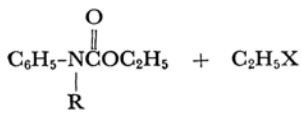
When a mixture of the iminocarbonate (I) and benzyl bromide was heated at 200°C for one hour, the expected ethyl *N*-benzyl-*N*-phenylcarbamate (IIa) was obtained in a 47% yield. Ethyl *N*-benzoyl-*N*-phenylcarbamate (IIb) was also produced in a quantitative yield by the treatment of I with benzoyl chloride at 200°C for 8 hr.



(I)

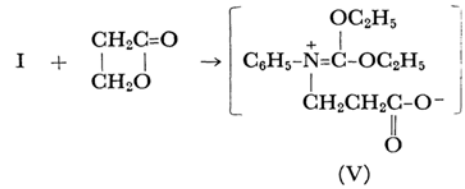


(III)

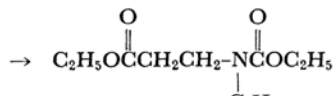


(IIa): R=$C_6H_5CH_2$–, X=Br
(IIb): R=C_6H_5CO–, X=Cl

The attempted reaction of I with β-propiolactone gave ethyl *N*-β-carboethoxyethyl-*N*-phenylcarbamate (IV) in a 59% yield; they were heated at 135—140°C for 16 hr.

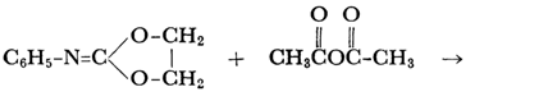


(V)

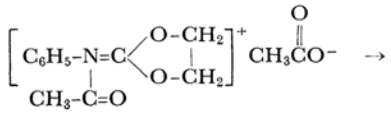


(IV)

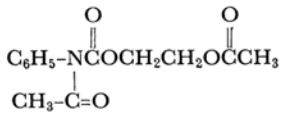
Further, the reaction of the iminocarbonate with acid anhydride as an electrophile was attempted. When I was refluxed in a large excess of acetic anhydride for 16 hr, ethyl acetate was obtained, but the expected ethyl *N*-acetyl-*N*-phenylcarbamate could not be isolated. On the other hand, when ethylene *N*-phenyliminocarbonate (VI) was used in place of I in the above experiment, a ring-opening addition compound, *i. e.*, β-acetoxyethyl *N*-acetyl-*N*-phenylcarbamate (VII), was obtained in a 20% yield.



(VI)



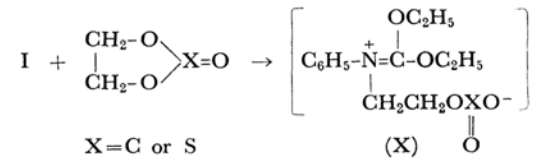
(VIII)



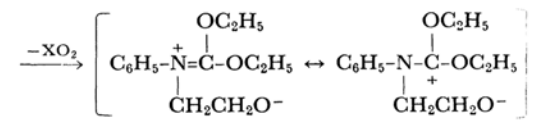
(VII)

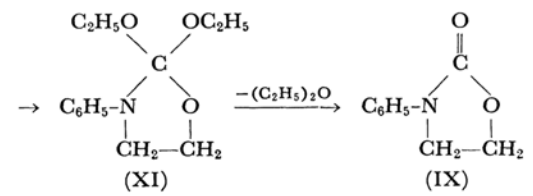
These reactions of iminocarbonate are considered to proceed through an initial formation of an intermediate salt, III, V or VIII, by an attack of electrophiles on the imino group. This salt in turn decomposes with oxygen-carbon linkage fission, to give the corresponding carbamate.

On the other hand, diethyl *N*-phenyliminocarbonate (I) was heated with ethylene carbonate at 200°C to give 3-phenyloxazolidone-2 (IX) in a 72% yield with the evolution of carbon dioxide. The same reaction was observed when I and ethylene sulfite were heated under the same conditions as the case of ethylene carbonate; 3-phenyloxazolidone-2 was thus obtained in a 60% yield with the evolution of sulfur dioxide.



X=C or S (X)





(XI) (IX)

These reactions may be explained by the above scheme, which involves an initial formation of the intermediate salt X produced by the ring-opening addition of ethylene carbonate or sulfite to the imino group of the iminocarbonate. This subsequently decomposes to form an ortho ester XI of cyclic urethane, with the loss of carbon dioxide or sulfur dioxide, followed by the elimination of diethyl ether, thus giving the oxazolidone IX.

This type of nucleophilic reaction of iminocarbonates is analogous to the Arbusov reaction,[4] which involves the reaction of the ester of trivalent

4) M. Grayson and E. J. Griffith, "Topics in Phosphorus Chemistry," Vol. I, Interscience Pub., New York, N. Y. (1964). p. 57.

phosphorus compound with alkyl halide to form the pentavalent phosphorus compound with a phosphoryl group, accompanied by the elimination of another alkyl halide.

Experimental

Diethyl *N*-Phenyliminocarbonate (I). This compound was prepared from phenylimidophosgene and sodium ethylate following the procedure of Smith.[5]

The Reaction of I with Benzyl Bromide. A mixture of 2.0 g (0.01 mol) of I and 1.7 g (0.01 mol) of benzyl bromide was heated on an oil bath at 200°C for one hour. Ethyl *N*-benzyl-*N*-phenylcarbamate (IIa) was then obtained by distillation; yield, 1.1 g. (47%); bp 120—122°C/0.1 mmHg.

Found: C, 75.24; H, 6.84; N, 5.76%. Calcd for $C_{16}H_{17}NO_2$: C, 75.29; H, 6.67; N, 5.49%.

The infrared absorption bands are at 2950 (ms), 1700 (s), 1600 (s), 1500 (s), 1300—1220 (s) broad, 1140 (s), 1025 (s), 770 (s), and 700 (s) cm^{-1}.

The Reaction of I with Benzoyl Chloride. A mixture of 2.0 g (0.01 mol) of I and 1.3 g (0.01 mol) of benzoyl chloride was heated on an oil bath at 200°C for 8 hr. Ethyl *N*-benzoyl-*N*-phenylcarbamate (IIb) was solidified when the mixture cooled; it was recrystallized from ethanol; yield, 2.5 g (100%); mp 65—66°C.

Found: C, 71.50; H, 5.69; N, 5.44%. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20%.

Its infrared absorption bands are at 1730(s), 1700(s), 1600 (m), 1500 (m), 1460 (m), 1380 (m), 1320 (s), 1265 (s), 1060 (s), 890 (m), 720 (m), and 700 (m)cm^{-1}.

The Reaction of I with β-Propiolactone. A mixture of 2.0 g (0.01 mol) of I and 0.7 g (0.01 mol) of β-propiolactone was heated on an oil bath at 135—140°C for 16 hr. Then ethyl *N*-β-carboethoxyethyl-*N*-phenyl-carbamate (IV) was obtained by distillation; yield, 1.5 g (57%); bp 120—122°C/0.3 mmHg.

Found: C, 63.32; H, 7.00; N, 5.57%. Calcd for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22; N, 5.28%.

Its infrared absorption bands are at 1740 (s), 1715 (s), 1605 (m), 1505 (m), 1415 (m), 1385 (m), 1300—1180 (m) broad, 1073 (m), 1030 (m), 770 (m), and 700 (m) cm^{-1}.

Ethylene *N*-Phenyliminocarbonate (VI). This compound was prepared from phenylimidophosgene and sodium glycolate.[6]

The Reaction of VI with Acetic Anhydride. A solution of 3.3 g (0.02 mol) of VI in 10.0 g (0.1 mol) of acetic anhydride was refluxed on an oil bath for 5 hr. After the excess anhydride had been removed, the distillation of the residue gave β-acetoxyethyl *N*-acetyl-*N*-phenylcarbamate (VII), which was then solidified and recrystallized from ether; yield, 1.1 g (20%); bp 120—130°C/0.15 mmHg; mp 45—46°C.

Found: C, 58.58; H, 5.83; N, 5.47%. Calcd for $C_{13}H_{15}NO_5$: C, 58.86; H, 5.70; N, 5.20%.

Its infrared absorption bands are at 1740 (s), 1710 (s), 1600 (m), 1500 (m), 1450 (m), 1370 (m), 1270 (m), 1230 (m), 1100 (s), 1060 (m), 1040 (m), 760 (m), and 700 (m) cm^{-1}.

The Reaction of I with Ethylene Carbonate. A mixture of 2.0 g (0.01 mol) of I and 2.0 g (0.025 mol) of ethylene carbonate was heated on an oil bath at 200°C for 10 hr; during this period the evolution of carbon dioxide was observed. Distillation then gave 3-phenyloxazolidone-2, which was solidified and recrystallized from ether; yield, 1.2 g (72%); bp 120—130°C/0.15 mmHg; mp 119—120°C.

Found: C, 66.62; H, 5.81; N, 8.50%. Calcd for $C_9H_9NO_2$: C, 66.24; H, 5.56; N, 8.58%.

Its infrared absorption spectrum is exactly the same as that of an authentic sample.[7]

The Reaction of I with Ethylene Sulfite. 3-Phenyloxazolidone-2 was obtained from 2.0 g (0.01 mol) of I and 2.2 g (0.02 mol) of ethylene sulfite in the same way as was used in the reaction of diethyl *N*-phenyliminocarbonate with ethylene carbonate; yield, 1.0 g (60%); bp 115—125°C/0.08 mmHg; mp 118—120°C.

5) W. R. Smith, *Am. Chem. J.*, **16**, 372 (1894).

6) T. Mukaiyama, T. Fujisawa and T. Hyugaji, This Bulletin, **35**, 687 (1962).

7) S. Pinchas and D. Ben-Ishai, *J. Am. Chem. Soc.*, **79**, 4099 (1957).