Reactions of Iminocarbonates with Acids

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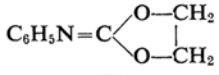
(Received September 2, 1961)

Intramolecular dehydrations of primary nitroparaffins[1,2], aldoximes[3,4,5] and hydroxamic acids[6] into nitrile oxides, nitriles and isocyanates respectively, by means of unsaturated organic reagents, such as isocyanates, carbodiimides, acetylenic ethers, ketene acetals and vinyl ethers, have been described in preceding papers. Further study has now been carried out on the reactions of iminocarbonates, which are considered to be the acetals of isocyanates, with a view to extending the scope of the organic dehydrating reagents.

In the first place, diethyl *N*-phenyl iminocarbonate (I) was chosen. This compound has been reported to be stable towards alkalies and water, but to be split by dilute hydrochloric acid, even while cold, into aniline and diethyl carbonate[7]. Contrary to the cases of isocyanates, however, the reaction of I with benzaldoxime could hardly be observed even at 100°C or in the presence of basic or acidic catalysts, such as triethyl amine or boron trifluoride, and most of the starting materials could be recovered. In the presence of hydrogen chloride, a protonic acid, as a catalyst, the reaction gave the expected ethyl *N*-phenyl carbamate, but the dehydration of benzaldoxime did not take place and the aldoxime was recovered.

1) T. Mukaiyama and T. Hoshino, *J. Am. Chem. Soc.*, **82**, 5339 (1960).
2) T. Mukaiyama and T. Hata, This Bulletin, **33**, 1382 (1960).
3) T. Mukaiyama and T. Hata, ibid., **33**, 1712 (1960).
4) T. Mukaiyama and T. Hata, ibid., **34**, 99 (1961).
5) T. Mukaiyama, K. Tonooka and K. Inoue, *J. Org. Chem.*, **26**, 2202 (1961).
6) T. Mukaiyama and H. Nohira, ibid., **26**, 782 (1961).
7) W. R. Smith, *Am. Chem. J.*, **16**, 372 (1894).

When hydrogen chloride was passed into a solution of I in dry benzene, a violent reaction occurred, forming ethyl *N*-phenyl carbamate in a quantitative yield. This reaction is of the same type as that of diethyl iminocarbonate with hydrogen chloride by which Sandmeyer[8] obtained ethyl chloride and ethyl carbamate. Ethylene *N*-phenyl iminocarbonate (II), which was prepared from phenyl imidophosgene and sodium salt of ethylene glycol, also reacted with hydrogen chloride, giving β-chloroethyl *N*-phenyl carbamate in a 63% yield.

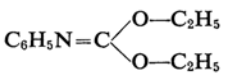


(II)

$$\rightarrow C_6H_5NHCOOCH_2CH_2Cl$$

Since it was found that dehydration did not take place in the reaction with the iminocarbonates and that they were readily decomposed by hydrogen chloride, their reactions with carboxylic and with phosphoric acids studied further.

The reaction of I with acetic acid did not take place at room temperature, but it did proceed well after they had been heated on a water bath at 100°C for 1 hr., giving ethyl *N*-phenyl carbamate and ethyl acetate in high yields. Similarly, I reacted with benzoic acid, giving ethyl *N*-phenyl carbamate and ethyl benzoate, when they had been refluxed in dry benzene for 1 hr.



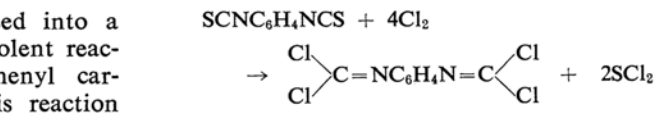
(I)

$$\rightarrow C_6H_5NHCOOC_2H_5 + RCOOC_2H_5$$

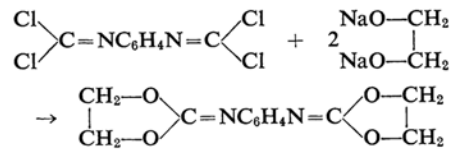
Treatments of II with acetic and benzoic acids also afforded the corresponding β-acyloxyethyl *N*-phenyl carbamate in high yields when refluxed in dry benzene for 2 hr.

$$II + RCOOH \rightarrow C_6H_5NHCOOCH_2CH_2OCOR$$

Next, in order to apply these reactions to the field of polymer chemistry, a compound containing two iminocarbonate groups was treated with acids. As the bifunctional iminocarbonate has not been reported on so far, the preparation of *N*, *N'*-*p*-phenylene bis(ethylene iminocarbonate) (III) was tried by a procedure similar to that for II. *p*-Phenylene diimidophosgene was produced by passing dry chlorine through a solution of *p*-phenylene diisothiocyanate in chloroform instead of the carbon tetrachloride which had been used as a solvent in the case of phenyl imidophosgene.



The use of chloroform is better than that of carbon tetrachloride because the latter leads to the decomposition of the reaction products, giving a dark-stained thick oil. *p*-Phenylene diimidophosgene is unstable towards moisture and is subject to decomposition into *p*-phenylene diamine hydrochloride; it is also desirable to keep it in a vacuum desiccator. One mole of *p*-phenylene diimidophosgene and 2 mol. of sodium salt of ethylene glycol gave III in a 25% yield when refluxed in dry benzene for 5 hr.



(III)

$$+ 4NaCl$$

When a solution of 1 mol. of III and 2 mol. of benzoic acid in dry benzene was refluxed for 2 hr., *p*-phenylene bis(benzoyloxyethyl carbamate) was obtained in a good yield.

$$III + 2C_6H_5COOH \rightarrow C_6H_5COOCH_2 \cdot CH_2OCONHC_6H_4NHCOOCH_2CH_2OCOC_6H_5$$

Further, the reactions of III with dicarboxylic acids, such as adipic and terephthalic acids, in dry dimethyl formamide were tried, producing substances with alternating ester and urethan linkages.

$$III + HOCORCOOH \rightarrow [-OCORCOOCH_2 \cdot CH_2OCONHC_6H_4NHCOOCH_2CH_2-]_n$$

Finally, when the reaction of I with diethyl phosphate was tried, ethyl *N*-phenyl carbamate and triethyl phosphate were obtained in about 85% yields.

$$I + (C_2H_5O)_2POOH \rightarrow C_6H_5NHCOOC_2H_5 + PO(OC_2H_5)_3$$

This type of reaction of iminocarbonates with acids resembles the so-called Pinner decomposition[9], which involves the reactions of imidoesters with acids to form the amides and esters of the corresponding acids; the reactions seem to proceed through an initial formation of intermediate IV, which in turn decomposes to give urethans and esters of the corresponding acids.

8) T. Sandmeyer, *Ber.*, **19**, 862 (1886).

9) F. Cramer, K. Pawelzik and F. W. Lichtenthaler, *Chem. Ber.*, **91**, 1555 (1958).

$$R'N=C\begin{matrix}OR\\OR\end{matrix} + HX \rightarrow \left[R'\overset{+}{N}H=C\begin{matrix}OR\\OR\end{matrix}\right]X^- \quad (IV)$$

$$\rightarrow R'NHCOOR + RX$$

The initial formation of salt by the interaction of acids because of the strongly basic character attributed to their two alkoxyl groups leads to the formation of ester and urethan, in contrast with the reaction of isocyanates with acids, which yields addition compounds.

Experimental

Diethyl *N*-Phenyl Iminocarbonate (I).—This compound was prepared from phenyl imidophosgene and sodium ethylate following the procedure of Smith[7].

Phenyl Imidophosgene.—This was prepared from phenyl isothiocyanate and chlorine according to the procedure of Bly, Perkins and Lewis[10].

Reaction of I with Hydrogen Chloride.—Into a solution of 3.9 g. (0.02 mol.) of I in 10 ml. of dry benzene was passed dry hydrogen chloride. An evolution of heat was noticeable, and when it was over, the mixture was heated on a water bath at 100°C for half an hour in order to complete the reaction. Then the benzene was removed, and ethyl *N*-phenyl carbamate was obtained and was recrystallized from petroleum ether. Yield 3.3 g. (100%); m. p. 49~51°C, while the mixed melting point with the authentic sample was the same.

Ethylene *N*-Phenyl Iminocarbonate (II).—Into 5.3 g. (0.05 mol.) of sodium salt of ethylene glycol suspended in 30 ml. of dry benzene was added, vigorously stirred, over a period of 10 min., 20 ml. of dry benzene, dissolving 8.0 g. (0.05 mol.) of phenyl imidophosgene. Then the reaction mixture was refluxed on a water bath for 2 hr. while the stirring was continued. It was then poured into water and extracted with benzene, and the benzene solution was washed twice with water. The solution was dried with calcium chloride, and the benzene was removed completely in vacuo. II was solidified and was recrystallized from ether to give needles; yield 6.0 g. (80%); m. p. 73~75°C.

Found: C, 66.03; H, 5.72; N, 8.74. Calcd. for $C_9H_9O_2N$ (II): C, 66.24; H, 5.56; N, 8.58%.

Reaction of II with Hydrogen Chloride.—Dry hydrogen chloride was saturated into a solution of 1.3 g. (0.008 mol.) of II in 40 ml. of dry benzene by warming on a water bath for 1 hr. On evaporation of the benzene, crude β-chloroethyl *N*-phenyl carbamate was obtained and was recrystallized from ether-cyclohexane, yield 1 g. (63%); m. p. 49~51°C.

Reaction of I with Acetic Acid.—A mixture of 7.7 g. (0.04 mol.) of I and 2.4 g. (0.04 mol.) of acetic acid was heated on a water bath at 100°C for 1 hr. Then 2.8 g. (80% yield) of ethyl acetate was obtained by distillation at 78~80°C at ordinary pressure. After the residue had been cooled, ethyl *N*-phenyl carbamate was obtained and was recrystallized from petroleum ether; yield 5.8 g. (88%); m. p. and mixed m. p. 49~51°C.

Reaction of I with Benzoic Acid.—A mixture of 7.7 g. (0.04 mol.) of I and 4.9 g. (0.04 mol.) of benzoic acid in 20 ml. of dry benzene was refluxed on a water bath for 1 hr., and then the benzene was removed. Distillation gave 5.7 g. (95% yield) of ethyl benzoate at 88~90°C/12 mmHg. When the residue was cooled, ethyl *N*-phenyl carbamate was solidified and was recrystallized from petroleum ether; yield 5.8 g. (88%); m. p. and mixed m. p. 49~51°C.

Reaction of II with Acetic Acid.—A solution of 4.0 g. (0.025 mol.) of II and 1.5 g. (0.025 mol.) of acetic acid in 20 ml. of dry benzene was refluxed on a water bath for 2 hr. When the benzene had been removed and the brown oily residue kept standing for three weeks, then there were obtained colorless chunky prisms of β-acetoxyethyl *N*-phenyl carbamate which could not be recrystallized from any solvent; yield 2.3 g. (42%); m. p. 43~45°C.

Found: C, 59.06; H, 6.29; N, 6.33. Calcd. for $C_{11}H_{13}O_4N$: C, 59.18; H, 5.87; N, 6.28%.

Reaction of II with Benzoic Acid.—A mixture of 1.6 g. (0.01 mol.) of II and 1.2 g. (0.01 mol.) of benzoic acid in 20 ml. of dry benzene was refluxed on a water bath for 1 hr. After the removal of the benzene, β-benzoxyethyl *N*-phenyl carbamate was obtained and was recrystallized from benzene to give needles; yield 2.3 g. (81%); m. p. 115~116°C.

Found: C, 67.27; H, 5.46; N, 5.03. Calcd. for $C_{16}H_{15}O_4N$: C, 67.36; H, 5.30; N, 4.91.

***p*-Phenylene Diimidophosgene.**—A solution in 100 ml. of chloroform of 19.2 g. (0.1 mol.) of *p*-phenylene diisothiocyanate, which had been prepared according to the procedure of van der Kerk, Pluygers and de Vries[11] and which had been recrystallized from petroleum ether[12], was saturated with dry chloride. As an evolution of heat was noticeable during the reaction, the solution was cooled in ice-water. The color of the reaction mixture gradually became red. After the chloroform and sulfur chloride had been partially removed by distillation, the resulting crude *p*-phenylene diimidophosgene was kept standing in vacuo in order to remove them completely. Recrystallization from ether afforded pale yellow needles; yield 23.0 g. (85%); m. p. 94~96°C.

Found: C, 35.87; H, 1.58; N, 10.45. Calcd. for $C_8H_4N_2Cl_4$: C, 35.55; H, 1.48; N, 10.37%.

***N*,*N'*-*p*-Phenylene Bis(ethylene iminocarbonate) (III).**—To 8.7 g. (0.04 mol.) of sodium salt of ethylene glycol suspended in 200 ml. of dry benzene was added dropwise, by vigorous stirring and refluxing on a water bath, a solution of 5.4 g. (0.02 mol.) of *p*-phenylene diimidophosgene in 200 ml. of dry benzene at such a rate that the addition was completed in about 1 hr., while the stirring and the refluxing were continued for an additional 4 hr. Then the reaction mixture was filtered while still hot, and from the filtrate about two-thirds of the benzene was distilled off. When it was cooled, III

10) R. S. Bly, G. A. Perkins and W. L. Lewis, *J. Am. Chem. Soc.*, **44**, 2896 (1922).

11) G. J. M. van der Kerk, C. W. Pluygers and G. de Vries, *Rec. trav. chem.*, **74**, 1262 (1955).

12) This compound, which was recrystallized from glacial acetic acid, did not give a good result.

was obtained as a white precipitate. By extracting the filtered mass with hot benzene, a considerable increase in the yield was observed. Several recrystallizations from acetone afforded a white solid; yield 1.3 g. (25%); m. p. 188~190°C.

Found: C, 58.13; H, 5.13; N, 11.45. Calcd. for $C_{12}H_{12}O_4N_2$ (III): C, 58.06; H, 4.87; N, 11.29%.

Reaction of III with Benzoic Acid.—A mixture of 0.62 g. (0.0025 mol.) of III and 0.61 g. (0.005 mol.) of benzoic acid in 50 ml. of dry benzene was refluxed on a water bath while being stirred for 2 hr. After the removal of the benzene, *p*-phenylene bis(benzoyloxyethyl carbamate) was obtained and recrystallized from methanol many times to give a white solid; yield 1.0 g. (81%); m. p. 180~182°C.

Found: C, 62.62; H, 5.19; N, 5.69. Calcd. for $C_{26}H_{24}O_8N_2$: C, 63.41; H, 4.91; N, 5.68%.

Reaction of III with Adipic Acid.—A mixture of 0.62 g. (0.0025 mol.) of III and 0.37 g. (0.0025 mol.) of adipic acid in 10 ml. of dry dimethyl formamide was heated and stirred on a water bath at 85°C for 2 hr. and was then vigorously stirred into water to precipitate a polymer, alternating poly(adipate/*p*-phenylene bis(ethylene carbamate)), which separated as a brown solid. The polymer was filtered off and washed several times by stirring with water and dried in vacuo overnight; yield 0.81 g. (81%); m. p. 140°C.

Found: N, 7.59. Calcd. for $(C_{18}H_{22}O_8N_2)_n$: N, 7.10%.

Reaction of III with Terephthalic Acid.—A mixture of 0.62 g. (0.0025 mol.) of III and 0.42 g. (0.0025 mol) of terephthalic acid in 15 ml. of dry dimethyl formamide was heated and stirred on a water bath at 85°C for 2 hr. and then filtered. The clear solution was vigorously stirred into water to precipitate a polymer, alternating poly(terephthalate/*p*-phenylene bis(ethylene carbamate)), which separated as a white solid. The polymer was filtered off and washed several times by stirring with water and dried in vacuo overnight; yield 1.01 g. (97%); m. p. 236°C.

Found: N, 7.44. Calcd. for $(C_{20}H_{18}O_8N_2)_n$: N, 6.76%.

Reaction of I with Diethyl Phosphate.—A solution of 3.1 g. (0.02 mol.) of diethyl phosphate and 3.9 g. (0.02 mol.) of I in 10 ml. of dry benzene was refluxed on a water bath for 3 hr. After the benzene had been removed, distillation gave 3.1 g. (86% yield) of triethyl phosphate at 96~98°C/13 mmHg (Found: P, 16.98%).

When the residue was cooled, ethyl *N*-phenyl carbamate was obtained and was recrystallized from petroleum ether; yield 2.6 g. (87%); m. p. and mixed m. p. 49~51°C.

Summary

Iminocarbonates, whose chemical properties have been little investigated, were prepared from sodium alkoxides and corresponding imidophosgene.

Diethyl *N*-phenyl iminocarbonate gave urethan and esters by reaction with acids, such as hydrogen chloride, carboxylic acids and diethyl phosphate. β-Acyloxyethyl *N*-phenyl cabamates were prepared from the reactions of ethylene *N*-phenyl iminocarbonate with carboxylic acids.

These reactions were applied to the syntheses of polymers, and the alternating poly(urethan/ester)s were obtained.

The authors wish to express their hearty thanks to Mr. Keiji Naruse for his microanalyses.

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