Dehydration Reactions of Benzaldoxime by Means of Compounds Having a Nitrogen-Carbon Double Bond

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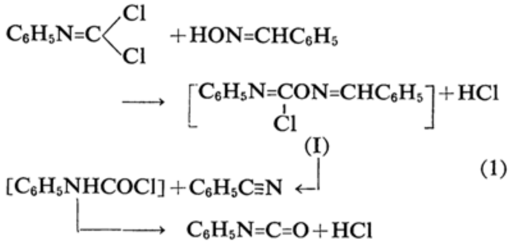
Preceding papers of this series have shown that acetylenic ethers, vinyl ethers, vinyl acetate, ketene acetals, isocyanates and carbodiimides dehydrate aldoximes, primary nitroparaffins and hydroxamic acids, giving nitriles, nitrile oxides and isocyanates respectively[1-6]. These results lead to the conclusion that compounds having either a cumulate double bond or a multiple bond, with alkoxyl or acyloxyl groups, are effective as dehydrating reagents. This paper reports a further study of the dehydration reactions of benzaldoxime by means of phenylimidophosgene, ethyl *N*-phenyliminochloroformate and ethyl *N*-phenylformimidate. These substances are nitrogen-carbon double bond compounds which have halogen(s) and/or an alkoxyl group as substituents attached to the carbon atom.

First, when 1 mol. of phenylimidophosgene was treated with 1 mol. of benzaldoxime in dry benzene under stirring, an evolution of heat was noticeable, and phenyl isocyanate and benzonitrile were obtained in good yields, along with hydrogen chloride and a small amount of aniline hydrochloride (Eq. 1).



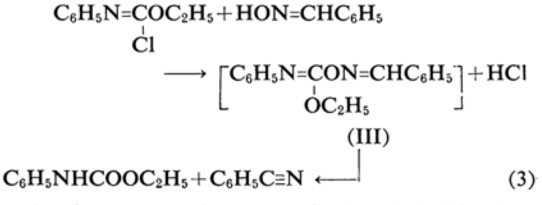
$$\begin{aligned}&C_6H_5N{=}C\begin{smallmatrix}\diagup Cl\\ \diagdown Cl\end{smallmatrix} + HON{=}CHC_6H_5\\ &\longrightarrow \left[C_6H_5N{=}\underset{\displaystyle Cl}{C}ON{=}CHC_6H_5\right] + HCl \quad (I)\\ &[C_6H_5NHCOCl] + C_6H_5C{\equiv}N \longleftarrow (I)\\ &\quad\longrightarrow C_6H_5N{=}C{=}O + HCl\end{aligned}\tag{1}$$

It is reasonable to postulate that the reaction proceeds through the intermediate I, which in turn decomposes to give benzonitrile and *N*-phenylcarbamyl chloride. The latter subsequently decomposes to produce phenyl isocyanate and hydrogen chloride. The formation of aniline hydrochloride may be attributed to the decomposition of adduct II of phenyl isocyanate and benzaldoxime by hydrogen chloride, as is shown in the following equation:

$$\begin{aligned}&C_6H_5N{=}C{=}O + HON{=}CHC_6H_5\\ &\longrightarrow \underset{(II)}{C_6H_5NHCOON{=}CHC_6H_5}\\ &\longrightarrow C_6H_5NH_2 + C_6H_5C{\equiv}N + CO_2\\ &\qquad \xrightarrow[HCl]{} C_6H_5NH_2HCl\end{aligned}\tag{2}$$

In order to confirm the above assumption, the reaction of 2 mol. of benzaldoxime with 1 mol. of phenylimidophosgene was tested. When they were allowed to react in dry benzene at room temperature under vigorous stirring for a while, a violent reaction suddenly took place and aniline hydrochloride and benzonitrile were obtained in good yields, along with the evolution of hydrogen chloride and carbon dioxide. The results show that the violent reaction is initiated by the hydrogen chloride initially formed.

Secondly, the treatment of ethyl *N*-phenyliminochloroformate with benzaldoxime was attempted. When they reacted in dry benzene, the evolution of hydrogen chloride and carbon dioxide was observed, and ethyl *N*-phenylcarbamate and benzonitrile were produced in good yields, along with a small amount of aniline hydrochloride and *sym*-diphenylurea (Eq. 3).



$$\begin{aligned}&C_6H_5N{=}\underset{\displaystyle Cl}{C}OC_2H_5 + HON{=}CHC_6H_5\\ &\longrightarrow \left[C_6H_5N{=}\underset{\displaystyle OC_2H_5}{C}ON{=}CHC_6H_5\right] + HCl \quad (III)\\ &C_6H_5NHCOOC_2H_5 + C_6H_5C{\equiv}N \longleftarrow (III)\end{aligned}\tag{3}$$

Analogous to the case of phenyl imidophosgene, the reaction can be explained by assuming the existence of the intermediate III, which is the condensation product of ethyl *N*-phenyliminochloroformate and benzaldoxime. This readily decomposes to give ethyl *N*-phenylcarbamate and benzonitrile. Further, since ethyl *N*-phenyliminochloroformate is decomposed with hydrogen chloride or at temperatures over 100°C, yielding phenyl isocyanate and ethyl chloride (Eq. 4), the formation of

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[1] T. Mukaiyama and T. Hoshino, *J. Am. Chem. Soc.*, **82**, 5339 (1960).

[2] T. Mukaiyama and T. Hata, This Bulletin, **33**, 1382 (1960).

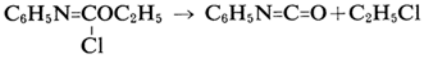
[3] T. Mukaiyama and T. Hata, ibid., **33**, 1712 (1960).

[4] T. Mukaiyama and T. Hata, ibid., **34**, 99 (1961).

[5] T. Mukaiyama and H. Nohira, *J. Org. Chem.*, **26**, 782 (1961).

[6] T. Mukaiyama, K. Tonooka and K. Inoue, ibid., **26**, 2202 (1961).

aniline hydrochloride and *sym*-diphenylurea is attributed to the reactions of the isocyanate with benzaldoxime (Eq. 2) and with aniline (Eq. 5) respectively.

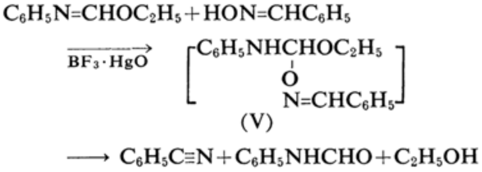


$$\underset{\displaystyle Cl}{C_6H_5N{=}COC_2H_5} \rightarrow C_6H_5N{=}C{=}O + C_2H_5Cl \qquad (4)$$

$$C_6H_5N{=}C{=}O + C_6H_5NH_2 \rightarrow (C_6H_5NH)_2CO \qquad (5)$$

On the other hand, it is noteworthy that diethyl *N*-phenyliminocarbonate, which has two alkoxyl groups to the carbon atom of the nitrogen-carbon double bond, hardly reacted with benzaldoxime, even in the presence of basic or acidic catalyst, such as triethylamine or boron trifluoride, and most of the starting materials were recovered[7].

Finally, the reaction of ethyl *N*-phenylformimidate with benzaldoxime gave benzonitrile and formanilide, in 83 and 66% yields respectively, when refluxed in dry benzene with boron trifluoride and yellow mercuric oxide as catalysts (Eq. 6).



$$C_6H_5N{=}CHOC_2H_5 + HON{=}CHC_6H_5 \xrightarrow{BF_3\cdot HgO} \underset{(V)}{\left[\begin{array}{l} C_6H_5NH\underset{\displaystyle O}{C}HOC_2H_5 \\ \quad N{=}CHC_6H_5 \end{array}\right]} \qquad (6)$$
$$\longrightarrow C_6H_5C{\equiv}N + C_6H_5NHCHO + C_2H_5OH$$

This reaction can be represented by the above scheme, which involves the initial formation of the intermediate V, the adduct of ethyl *N*-phenylformimidate and benzaldoxime, analogous to the explanation proposed for the dehydrations of aldoxime with vinyl ethers[3]. The V subsequently decomposes to give benzonitrile, formanilide and alcohol.

Experimental

Phenylimidophosgene.—This compound was prepared from phenyl isothiocyanate and chlorine according to the procedure of Bly, Perkins and Lewis; b. p., 102～104°C/28 mmHg[8].

Reaction of Phenylimidophosgene with Benzaldoxime (1 : 1).—When a solution of phenylimidophosgene (3.5 g. 0.02 mol.) and benzaldoxime (2.4 g. 0.02 mol.) in dry benzene (20 ml.) was stirred vigorously, an evolution of heat was noticeable and aniline hydrochloride precipitated. Then the reaction mixture was refluxed for an hour. The hydrochloride was filtered and was recrystallized from ethanol; yield, 0.3 g. (11%); m. p. and mixed m. p., 195～197°C. Benzene was removed from the filtrate, and the residual materials were fractionated. Two grams (84% yield) of phenyl isocyanate (b. p., 48～50°C/10 mmHg) and 1.5 g. (72% yield) of benzonitrile (b. p., 70～72°C/10 mmHg) were obtained.

Reaction of Phenylimidophosgene with Benzaldoxime (1 : 2).—A solution of phenylimidophosgene (3.5g., 0.02 mol.) and benzaldoxime (4.8g., 0.04 mol.) in dry benzene (20 ml.) was stirred. After a while, a violent reaction suddenly took place and aniline hydrochloride precipitated. By the same procedure as described above, the hydrochloride (yield, 2.3 g., 92%; m. p. and mixed m. p., 195～197°C) and benzonitrile (yield, 3.1 g., 75%; b. p., 66～68°C/10 mmHg) were obtained.

Ethyl *N*-Phenyliminochloroformate.—This compound was prepared from phenylimidophosgene and sodium ethylate according to the procedure of Smith; b. p., 114～116°C/12 mmHg[9].

Reaction of Ethyl *N*-Phenyliminochloroformate with Benzaldoxime.—Into an ice cold solution of ethyl *N*-phenyliminochloroformate (3.7 g. 0.02 mol.) in dry benzene (20 ml.) was vigorously stirred, drop by drop, a solution of benzaldoxime (2.4 g., 0.02 mol.) in dry benzene (20 ml.). The reaction mixture was refluxed for an hour, and the precipitated aniline hydrochloride was filtered; yield, 0.2 g. (8%); m. p. and mixed m. p., 197～199°C. After the removal of the benzene from the filtrate, 1.6 g. (78% yield) of benzonitrile (b. p., 85～87°C/25 mmHg) and 2.5 g. (76% yield) of ethyl *N*-phenylcarbamate (b. p., 106～115°C/2 mmHg) were obtained by distillation. The latter solidified on cooling and was recrystallized from petroleum ether; m. p. and mixed m. p., 48～50°C. *sym*-Diphenylurea remained in a distillation flask and was recrystallized from acetic acid; yield, 0.6 g. (14%); m. p. and mixed m. p., 234～236°C.

Decomposition of Ethyl *N*-Phenyliminochloroformate with Hydrogen Chloride.—Into a solution of ethyl *N*-phenyliminochloroformate (1.8 g., 0.01 mol.) in dry benzene (20 ml.) was passed dry hydrogen chloride, with refluxing for an hour. After the removal of the benzene, phenyl isocyanate was distilled; yield, 0.8 g. (66%); b. p., 58～60°C/15 mmHg.

Ethyl *N*-Phenylformimidate. — This compound was prepared from aniline and ethyl orthoformate according to the procedure of Roberts and Vogt; b. p., 117～118°C/40 mmHg.[10]

Reaction of Ethyl *N*-Phenylformimidate with Benzaldoxime.—A solution of ethyl *N*-phenylformimidate (3.0 g., 0.02 mol.), benzaldoxime (2.4 g., 0.02 mol.), boron trifluoride etherate (5 drops) and a catalytic amount of mercuric oxide in dry benzene (5 ml.) was refluxed for 5 hr. and was then filtered. The benzene was removed from the clear filtrate, and 1.7 g. (85% yield) of benzonitrile (b. p., 76～78°C/18 mmHg) and 1.6 g. (67% yield) of formanilide (b. p., 108～112°C/0.35 mmHg) were obtained by distillation. The latter solidified on cooling; m. p., 40～44°C.

Summary

The dehydration reactions of benzaldoxime with such nitrogen-carbon double bond compounds having halogen and alkoxyl groups as

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7) T. Mukaiyama, T. Fujisawa and T. Hyugaji, This Bulletin, **95**, 687 (1962).

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

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

10) R. M. Roberts and P. J. Vogt, *Org. Syn.*, **35**, 65 (1955).

phenylimidophosgen, ethyl *N*-phenyliminochloroformate and ethyl *N*-phenylformidate were studied.

One mole of phenyl imidophosgene, when reacted with 1 mol. of benzaldoxime, gave phenyl isocyanate and benzonitrile as main products. On the other hand, with 2 mol. of the aldoxime, aniline hydrochloride and benzonitrile were obtained in good yields. The aldoxime was also dehydrated effectively by ethyl *N*-phenyliminochloroformate to give, among other byproducts, the nitrile and ethyl *N*-phenylcarbamate. The nitrile and formanilide were obtained by the reaction of the aldoxime with ethyl *N*-phenylformimidate.

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