Russian Journal of General Chemistry, Vol. 71, No. 1, 2001, pp. 143–144. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 1, 2001, pp. 157–158.

Original Russian Text Copyright © 2001 by Onys'ko, Kim, Kiseleva, Sinitsa.

LETTERS TO THE EDITOR

First Example of Stereoselective Aza-Perkow Reaction

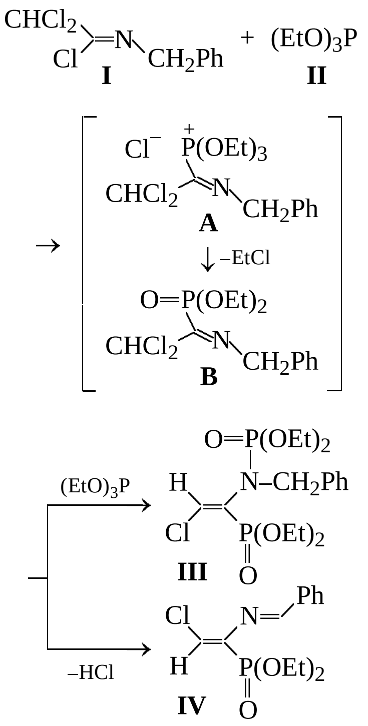
P. P. Onys'ko, T. V. Kim, E. I. Kiseleva, and A. D. Sinitsa

Institute of Organic Chemistry, Ukrainian National Academy of Sciences, Kiev, Ukraine

Received April 13, 2000

Reactions of *N*-benzylpolychloroalkylimidoyl chlorides $R_{Hlg}CCl{=}NCH_2Ph$ with trialkyl phosphites proceed unusually and, depending on the number of α-atoms of chlorine, yield either *C*,*N*-diphosphorylated vinylamides (R_{Hlg} = CCl_3) [1] or *C*-phosphorylated azadienes (R_{Hlg} = Me_2CCl) [2]. The behavior of *N*-benzyldichloroacetimidoyl chloride **I** in this reaction is of particular interest, because it furnishes information not only on the direction but also on stereochemistry of the process.

We have found that imidoyl chloride **I**, irrespective of the reactant ratio, reacts with 2 mol of triethyl phosphite to give chlorovinylphosphoroamidate **III**. Note that it is the first example of the reaction of aza-Perkow type involving the $CHCl_2$ group. Analogous transformations were previously known only for the derivatives containing CCl_3 and CF_3 groups at the C=N bond [3].



(1)

Only one geometric isomer of **III** was detected, which shows that the reaction of the aza-Perkow type is highly stereoselective. Large coupling constant between the phosphorus and the proton at the double bond ($^3J_{HP}$ 30.6 Hz) indicates the *trans* arrangement of the proton and phosphoryl group (cf. [4]).

Formation of diphosphorylated product **III** even at an excess of imidoyl chloride **I** shows that intermediates **A** and **B** exhibit considerably higher reactivity in relation to phosphite than the starting imidoyl chloride. For example, the ^{31}P NMR data show that the final mixture obtained in the reaction of equimolar amounts of compounds **I** and **II** (80–90°C, 1 h) contains bisphosphorylated vinylamide **III** (~65 mol %), azadiene **IV** (5–10%), and unidentified products (~25%). At a 1 : 2 ratio of **I** and **II** the yield of vinylamide decreases. Phosphorylated azabutadiene **IV** is evidently formed by dehydrochlorination of intermediates **A** and **B** (cf. [2]). It was prepared independently by the reaction of dichloroazadiene **V** with triethyl phosphite.

$$\mathbf{I} \xrightarrow{Et_3N} \underset{\mathbf{V}}{CHCl{=}C(Cl)N{=}CHPh} \xrightarrow{(EtO)_3P} \mathbf{IV} \qquad (2)$$

It is noteworthy that reactions (1) and (2) yield the same geometric isomer of phosphonate **IV**, and dehydrochlorination of **I** also yields a single geometric isomer of chloroazabutadiene **V**. The coupling constant between the phosphorus atom and the proton in azadiene **IV** ($^3J_{HP}$ 9.4 Hz) is considerably smaller than that in vinylamide **III** and suggests the *cis* location of hydrogen and the phosphoryl group. Thus, the aza-Perkow reaction as well as phosphorylation of chloroazadiene **V** yield sterically less hindered isomers of **III** and **IV**.

***N*-Benzyldichloracetimidoyl chloride I** was prepared by the reaction of *N*-benzyldichloroacetamide with phosphorus pentachloride. Yield 72%, bp 98–99°C/0.09 mm. ^1H NMR spectrum ($CDCl_3$), δ, ppm:

1070-3632/01/7101-0143 $25.00 © 2001 MAIK "Nauka/Interperiodica"

4.75 s (2H, CH_2), 6.37 s (1H, Cl_2CH), 7.4 m (5H, Ph). Found, %: Cl 45.15; N 6.01. $C_9H_8Cl_3N$. Calculated, %: Cl 44.97; N 5.92.

(*Z*)-1-Chloro-2,3-bis(diethoxyphosphoryl)-4-phenyl-3-aza-1-butene III. A mixture of equimolar amounts of imidoyl chloride **I** and triethyl phosphite was heated in a Claisen flask at 80–90°C until the gas evolution ceased (~1 h) and then was distilled. Yield 35%, bp 173–179°C/0.05 mm Hg. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.4 m (12H, Me), 4.2 m (8H, OCH_2), 4.69 d (2H, CH_2N, $^3J_{CH_2NP}$ 9.6 Hz), 6.45 d.d (1H, =CH, $^3J_{HP}$ 30.6, $^4J_{HP}$ 2.6 Hz), 7.3 m (5H, Ph). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 5.0 m (1P, NP), 9.7 d.m (1P, =CP, $^3J_{PC=CH}$ 30.6 Hz). Found, %: Cl 7.60; N 3.32; P 14.28. $C_{17}H_{18}ClNO_6P_2$. Calculated, %: Cl 8.06; N 3.18; P 14.08.

4-Chloro-3-(diethoxyphosphoryl)-1-phenyl-2-aza-1,3-butadiene IV was prepared by heating of a 1 : 2 mixture of dichloroazadiene **V** and $(EtO)_3P$ at 90–100°C for 1 h. Yield 35%. The compound was not isolated analyticaly pure; after distillation it contained about 25 mol % unidentified admixtutes (δ_P 12, 7.1, and 3.8 ppm). The spectral characteristics of **IV** were close to those of the previously synthesized phosphorylated azadienes [2]. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.34 t (Me, J_{HH} 7.5 Hz), 4.2 m (OCH_2), 6.78 d (1H, CHCl, $^3J_{HP}$ 9.4 Hz), 7.5 m and 7.8 m (Ph), 8.45 d (1H, CH=N, $^4J_{HP}$ 1.8 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 9.8.

1,2-Dichloro-4-phenyl-2-aza-1,3-butadiene V. To a solution of imidoyl chloride **I** in ether an equimolar amount of triethylamine was added at 20°C. A day later the precipitate was filtered off, the filtrate was evaporated, and the residue was distilled in a vacuum. Yield 88%, bp 97–100°C/0.09 mm Hg. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.88 s (1H, =CHCl), 7.4 m (3H) and 7.8 m (2H) (Ph), 8.44 (1H, =CHN). Found, %: Cl 34.82; N 6.79. $C_9H_7Cl_2N$. Calculated, %: Cl 35.44, N 7.0.

The ^1H and ^{31}P NMR spectra were recorded on a Varian VXR-300 spectrometer, working frequencies 299.5 and 121.42 MHz, respectively. The chemical shifts were measured against internal TMS (^1H) and external 85% phosphoric acid (^{31}P).

ACKNOWLEDGMENTS

The work was financially supported by the Ukrainian State Foundation for Basic Research (project no. 3.4/207).

REFERENCES

1. Sinitsa, A.D., Onys’ko, P.P., Kim, T.V., Kiseleva, E.I., and Pirozhenko, V.V., *Zh. Obshch. Khim.*, 1986, vol. 56, no. 12, pp. 2681–2689.
2. Sinitsa, A.D., Maidanovich, N.K., Onys’ko, P.P., and Shurubura, A.K., *Zh. Obshch. Khim.*, 1989, vol. 59, no. 11, pp. 2492–2497.
3. Sinitsya, A.A., Kolotilo, M.V., and Onis’ko, P.P., *Ukr. Khim. Zh.*, 1998, vol. 64, no. 5, pp. 48–67.
4. Quian, D.Q., Shi, X.D., Cao, R.Z., and Liu, L.Z., *Heteroatom Chem.*, 1999, vol. 10, no. 4, pp. 271–276.