Russian Journal of General Chemistry, Vol. 71, No. 6, 2001, pp. 979–980. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 6, 2001, pp. 1041–1042.

LETTERS TO THE EDITOR

Unsaturated Phosphorus Compounds on the Basis of *O*-Vinyloximes

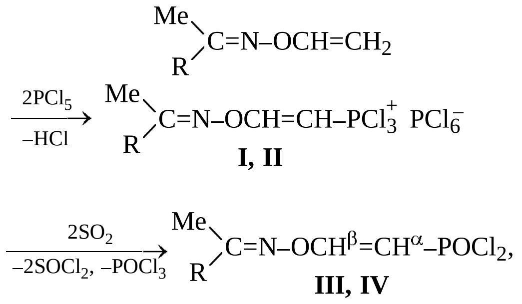
V. G. Rozinov, M. Yu. Dmitrichenko, L. I. Larina, E. Yu. Shmidt, and A. I. Mikhaleva

Institute of Petroleum and Coal Chemical Synthesis, Irkutsk State University, Irkutsk, Russia
Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, Russia

Received July 11, 2000

It is known that under the action of phosphorus pentachloride not only ketoximes, but also esters derived from them undergo Beckmann rearrangement [1]. Acid catalysts can induce rearrangements of oxime ethers [2]. The reaction of oxime *O*-vinyl ethers with phosphorus pentachloride would be expected to involve, along with the Beckmann rearrangement, formation of organophosphorus compounds like those isolated on phosphorylation of vinyl ethers [3].

We found that propan-2-one *O*-vinyloxime and 3-methylbutan-2-one *O*-vinyloxime are easily phosphorylated with phosphorus pentachloride at room temperature by the *O*-vinyl group to form alkenyltrichlorophosphonium hexachlorophosphorates **I**, **II**.



$$\mathrm{Me(R)C{=}N{-}OCH{=}CH_2} \xrightarrow[-\mathrm{HCl}]{2\mathrm{PCl_5}} \mathrm{Me(R)C{=}N{-}OCH{=}CH{-}\overset{+}{P}Cl_3\ PCl_6^-}\ \ \mathbf{I,\ II} \xrightarrow[-2\mathrm{SOCl_2},\ -\mathrm{POCl_3}]{2\mathrm{SO_2}} \mathrm{Me(R)C{=}N{-}OCH^{\beta}{=}CH^{\alpha}{-}POCl_2},\ \ \mathbf{III,\ IV}$$

R = Me (**I, III**), *i*-Pr (**II, IV**).

Under the action of sulfur dioxide hexachlorophosphorates **I, II** convert to (2-isopropylideneaminooxyethenyl)phosphonic and [2-(1,2-dimethylpropylidene)aminooxyethenyl]phosphonic dichlorides **III, IV** as *E* isomers (NMR data).

To a suspension of 2.1 g of phosphorus pentachloride in 15 ml of benzene, a solution of 0.5 g of propan-2-on *O*-vinyloxime in 3 ml of benzene was added dropwise with stirring. A gray finely crystalline precipitate formed. A day after, it got colorless. Filtration and vacuum drying gave 1.8 g (74%) of compound **I** as a white powder susceptible to hydrolysis.

Sulfur dioxide was passed through a dispersion of 1.35 g of compound **I** until complete homogenization. The solvent and volatile by-products were removed in a vacuum to obtain ca. 100% of compound **III** as a light brown liquid decomposing during vacuum distillation. IR spectrum, ν, cm^{-1}: 540 (P–Cl), 1260 (P=O), 1590 (C=C), 1620 (C=N), 3050 (=C–H). ^{1}H MNR spectrum, δ, ppm: 7.70 d.d (1H, H_β, $^3J_{\mathrm{HH}}$ 13.2 Hz, $^3J_{\mathrm{PH}}$ 14.7 Hz), 5.80 ppm d.d (1H, H_α, $^3J_{\mathrm{HH}}$ 13.2 Hz, $^2J_{\mathrm{PH}}$ 25.3 Hz), 2.01 s, 1.99 s (6H, $\mathrm{Me_2C{=}}$). ^{31}P NMR spectrum, δ, ppm: 34.20 ($\mathrm{POCl_2}$, $^2J_{\mathrm{PH}}$ 25.3 Hz, $^3J_{\mathrm{PH}}$ 14.7 Hz). Found, %: C 27.37; H 4.22; Cl 32.39; N 5.82; P 14.07. $\mathrm{C_5H_8Cl_2NO_2P}$. Calculated, %: C 27.91; H 3.72; Cl 32.56; N 6.51; P 14.42.

Compound **II** was prepared analogously from 0.5 g of 3-methylbutan-2-one *O*-vinyloxime and 1.64 g of phosphorus pentachloride. A white fine powder hydrolyzing in air. Yield 1.5 g (75%). Treatment of a dispersion of 1 g of compound **II** in 5 ml of benzene with sulfur dioxide and subsequent evaporation of volatile products in a vacuum gave ca. 100% of compound **IV** as a light brown liquid. IR spectrum, ν, cm^{-1}: 540 (P–Cl), 1270 (P=O), 1590 (C=C), 1650 (C=N), 3060 (=C–H). ^{1}H NMR spectrum, δ, ppm: 7.74 d.d (1H, H_β, $^3J_{\mathrm{HH}}$ 13.2 Hz, $^3J_{\mathrm{PH}}$ 15.0 Hz), 5.78 d.d (1H, H_α, $^3J_{\mathrm{HH}}$ 13.2 Hz, $^2J_{\mathrm{PH}}$ 25.5 Hz), 2.60 m (1H, $\mathrm{Me_2CH}$, $^3J_{\mathrm{HH}}$ 6.9 Hz), 1.94 s (3H, MeC=), 1.13 d (6H, $\mathrm{Me_2CH}$, $^3J_{\mathrm{HH}}$ 6.9 Hz). ^{31}P NMR spectrum, δ, ppm: 34.25 ($\mathrm{POCl_2}$, $^2J_{\mathrm{PH}}$ 25.5 Hz, $^3J_{\mathrm{PH}}$ 15.0 Hz). Found, %; C 34.47; H 5.20; Cl 29.59; N 5.45; P 11.77. $\mathrm{C_7H_{12}Cl_2NO_2P}$. Calculated, %: C 34.57; H 4.94; Cl 28.81; N 5.76; P 12.76.

1070-3632/01/7106-0979 $25.00 ©2001 MAIK “Nauka/Interperiodica”

The IR spectrum was obtained on a Specord 75 IR spectrometer in KBr pellets. The ^{1}H and ^{31}P NMR spectra were measured in $CDCl_3$ solutions on a Bruker DPX 400 spectrometer at 400 and 161.98 MHz, respectively.

REFERENCES

1. Beckmann, E. and Sundel, K., *Justus Liebigs Ann. Chem.,* 1897, vol. 296, pp. 279–294.
2. Donaruma, L.J. and Heldt, W.Z., in *Organic Reactions,* Moscow: Mir, 1965, vol. 11, pp. 46–47.
3. Fridland, S.V. and Malkov, Yu.K., *Reakts. Metody Issled. Org. Soedin.,* 1986, pp. 106–149.