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LETTERS TO THE EDITOR

Recyclization of Acylation Products of 2-Aryl-5-hydrazino-4-(dialkoxyphosphoryl)oxazoles

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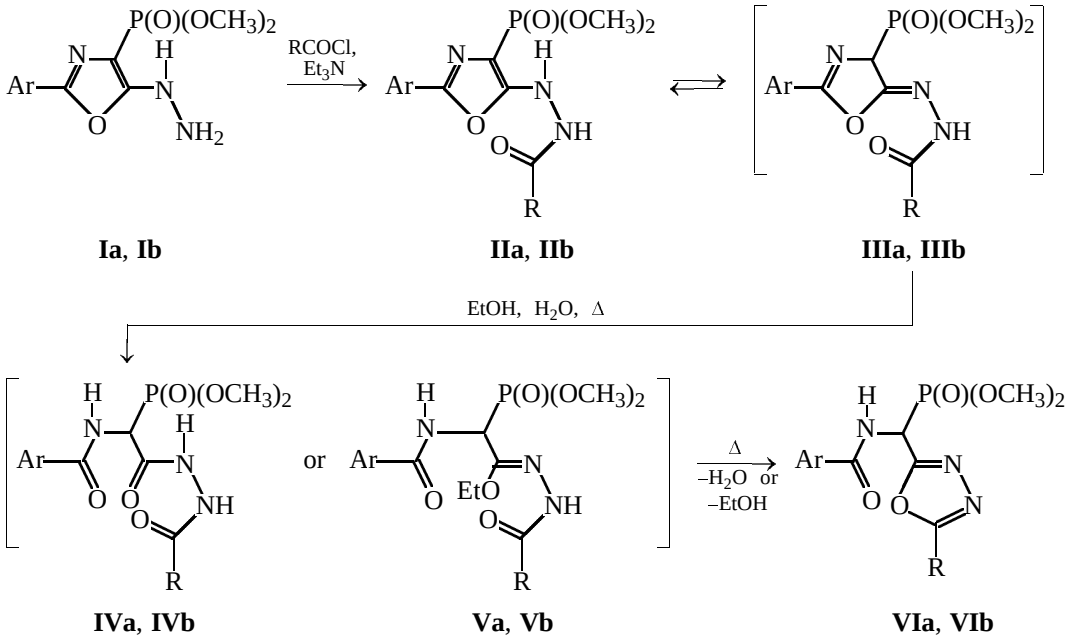
We found recently that phosphorus-containing enamides of the general formula

$$Cl_2C{=}C(NHCOR)P(O)(OAlk)_2$$

readily react with excess hydrazine hydrate to give 4-phosphorylated derivatives of 2-alkyl(aryl)-5-hydrazinooxazoles **I** [1]. Here we report that compounds **I** can be converted by easy reactions (see scheme) to 2,5-disubstituted 1,3,4-oxadiazoles containing the $CH(NHCOR)P(O)(OAlk)_2$ group in the side chain.



Ar = C_6H_5, R = 4-$CH_3C_6H_4$ (**a**); Ar = 4-ClC_6H_4, R = 4-$CH_3C_6H_4$ (**b**).

Probably, the reacting species in recyclization are not the aromatic oxazole derivatives **II** but their prototropic tautomers **III** containing the 2-oxazoline ring, because this ring can be cleaved under mild conditions with water or ethanol to form intermediates **IV** or **V** capable of intramolecular cyclocondensation. The transformation **IV** → **VI** resembles the cyclization of many other *N*,*N*'-diacyl derivatives of hydrazine [2]. The IR and ^1H and ^{13}C NMR data are consistent with the structure of the final products of recyclization **II** → **VI**.

For example, in the ^1H NMR spectra of compounds **VIa** and **VIb** the doublet of doublets at δ 6.25–6.35 ppm can be assigned to the methine proton of the –NH–CH–P(O)< group. Also, the ^{13}C NMR spectrum of **VIb** contains two downfield signals (δ > 164 ppm) of the C^2 and C^5 atoms of the electron-deficient 1,3,4-oxadiazole ring. The other evidences of structure **VI** and possible applications of the new recyclization will be discussed in subsequent papers.

4-Dimethoxyphosphoryl-5-(2-*p*-toluylhydrazino)-2-phenyloxazole IIa. To a solution of 4 mmol of **Ia**

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[1] in 10 ml of acetonitrile we added 4.4 mmol of triethylamine and 4 mmol of *p*-toluyl chloride. The resulting mixture was left for 24 h at 20–25°C, and the precipitate was filtered off, washed with water, combined with the product obtained from filtrate, and used for subsequent syntheses without additional purification. Yield 80%, mp 165–166°C. Found, %: N 10.35; P 7.60. $C_{19}H_{20}N_3O_5P$. Calculated, %: N 10.47; P 7.72.

4-Dimethoxyphosphoryl-5-(2-*p*-toluylhydrazino)-2-*p*-chlorophenyloxazole IIb was prepared similarly. Yield 83%, mp 170–171°C. ^{1}H NMR spectrum, δ, ppm: 2.38 s (3H, CH_3), 3.67 d (6H, $2CH_3O$, $^3J_{HP}$ 12.0 Hz), 7.30–7.80 m (8H, $2C_6H_4$), 8.77 br.s (1H, NH), 10.75 br.s (1H, NHCO). Found, %: Cl 8.05; P 6.99. $C_{19}H_{19}ClN_3O_5P$. Calculated, %: Cl 8.14; P 7.11.

2-[Dimethoxyphosphoryl(benzoylamino)]methyl-5-*p*-tolyl-1,3,4-oxadiazole VIa. A solution of 1 mmol of **IIa** in 10 ml of 80% aqueous ethanol was refluxed for 0.5 h, and the precipitate was filtered off and recrystallized from aqueous ethanol. Yield 80%, mp 132–133°C. ^{1}H NMR spectrum, δ, ppm: 2.40 s (3H, CH_3), 3.82 m (6H, $2CH_3O$), 6.35 d.d (1H, NCHP, $^3J_{HH}$ 8.6 Hz, $^2J_{HP}$ 21.4 Hz), 7.20– 8.00 (9H, C_6H_4, C_6H_5), 9.71 d (1H, NH, $^3J_{HH}$ 8.6 Hz). Found, %: C 56.55; H 4.95; N 10.30; P 7.62. $C_{19}H_{20}N_3O_5P$. Calculated, %: C 56.86; H 5.02; N 10.47; P 7.72.

2-[Dimethoxyphosphoryl(*p*-chlorobenzoylamino)]methyl-5-*p*-tolyl-1,3,4-oxadiazole VIb was prepared under the same conditions as **VIa**. Yield 86%, mp 150–151°C. ^{1}H NMR spectrum, δ, ppm: 2.40 s (3H, CH_3), 3.82 m (6H, $2CH_3O$), 6.27 d.d (1H, NCHP, $^3J_{HH}$ 8.6 Hz, $^2J_{HP}$ 21.4 Hz), 7.40–8.00 m (8H, $2C_6H_4$), 9.68 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 21.11 (CH_3), 43.79 (CH), 53.90, 54.19 ($2CH_3O$), 120.17, 131.61, 136.85, 142.49 ($C_{i,p}$, Ph), 126.55, 128.44, 129.88, 130.03 ($C_{o,m}$, Ph), 161.05 (C=O), 164.82, 165.60 (C^2=N, C^5=N). Found, %: Cl 8.05; N 9.72; P 7.02. $C_{19}H_{19}ClN_3O_5P$. Calculated, %: Cl 8.14; N 9.64; P 7.11.

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer in DMSO-d_6 relative to TMS.

REFERENCES

1. Brovarets, V.S., Vydzhak, R.N., Pil'o, S.G., Zyuz', K.V., and Drach, B.S., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 11, pp. 1822–1824.
2. *The Chemistry of Heterocyclic Compounds*, vol. 17: *Five- and Six-Membered Compounds with Nitrogen and Oxygen*, Weissberger, A. and Wiley, R.H., Eds., New York: Wiley, 1962, pp. 263–282.