

SHORT
COMMUNICATIONS

Phosphoryl-containing α -Thiocyanatoaldehydes

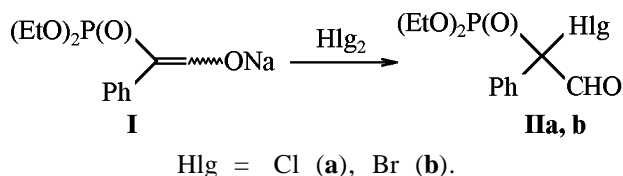
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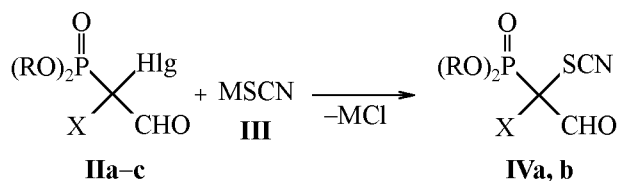
α -Thiocyanatoamides and -ketones as synthetic equivalent of two-carbon electrophilic synthons are used in the synthesis of heterocyclic structures [1–3] some of which possess useful properties [4, 5]. Unlike these carbonyl compounds the procedures for preparation and chemical properties of α -thiocyanatoaldehydes are poorly known.

Aiming at the synthesis of previously unknown α -thiocyanatoaldehydes we studied reactions of phosphorylated α -haloaldehydes (**II**) with alkali metals thiocyanates (**III**). The initial haloaldehydes **IIa, b** were obtained by reaction of enolate **I** with halogens in CH_2Cl_2 at 30–40°C.



In the IR spectra of compounds **IIa, b** the aldehyde group appears as an absorption band in the region 1770–1780 cm^{-1} , and in the ^1H NMR spectra at 9.59–9.65 ppm as an intense doublet with $^3J_{\text{PH}} 6.25$ Hz.

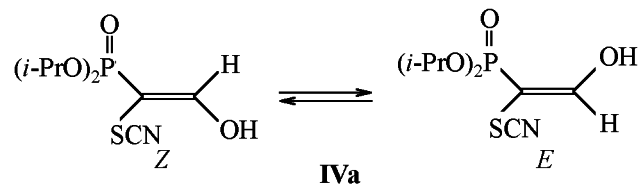
The reaction of halocarbonyl compounds **IIa, b** with nucleophilic reagents **III** proceeded in boiling acetone for 6–7 h giving rise to α -thiocyanatoaldehydes **IVa, b** in 75–80% yield.



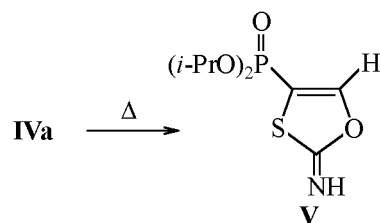
II, Hlg = Cl (**a, c**), Br (**b**); R = Et (**a, b**), *i*-Pr (**c**);
X = Ph (**a, b**), H (**c**); **IV**, R = *i*-Pr, X = H (**a**);
R = Et, X = Ph (**b**); M = Na, K.

Thiocyanatoaldehydes **IVa, b** are colorless crystalline substances; their structure was proved by IR, ^1H and ^{31}P NMR spectroscopy.

Aldehyde **IVa** exists in solution exclusively as enol in a mixture of *cis*- and *trans*-isomers in 1:2 ratio. Therewith the methylene protons give in the ^1H NMR spectrum doublet signals at 7.63 and 7.43 ppm with $^3J_{\text{PH}} 5$ Hz. Basing on data from [6] the doublet at 7.63 ppm was assigned to the *trans*-isomer, and that at 7.43 ppm to the *cis*-isomer.



Heating of compound **IVa** or its treating with bases results in formation of *O,O*-diisopropyl(2-imino-1,3-oxathiol-4-yl)phosphonate (**V**).



The heterocyclization is confirmed by the ^1H NMR data. In the spectrum of compound **V** appears only one doublet of methylene protons at 7.35 ppm ($^3J_{\text{PH}} 5$ Hz), the signal of imine group is observed as a singlet at 7.40 ppm.

α -(Diethoxyphosphoryl)phenylchloroacetaldehyde (**IIa**). Through a suspension of 139 g (0.5 mol) of enolate **I** in 500 ml of dichloromethane at room temperature while stirring was passed gaseous

chlorine till the solution turned yellow, and heat evolution stopped. Then the reaction mixture was heated to 40°C, and chlorine was passed for 2 h more. The precipitate was filtered off, the solvent was removed, and fractional distillation of the residue furnished aldehyde **IIa**, yield 135 g (93%), bp 115–116°C (0.05 mm Hg), n_D^{20} 1.5133. IR spectrum, ν , cm^{-1} : 1260 (P=O), 1750 (CHO). ^1H NMR spectrum [$(\text{CD}_3)_2\text{CO}$], δ , ppm: 1.15 d.t (6H, 2CH₃), 4.05 m (4H, 2OCH₂), 7.35 m (3H, Ph), 7.50 m (2H, Ph), 9.65 d (1H, CHO, J 6.25 Hz). ^{31}P NMR spectrum: δ 8.0 ppm

α -(Diethoxyphosphoryl)bromophenylacet-aldehyde (IIb). To a suspension of 83.4 g (0.3 mol) of enolate **I** in 300 ml of dichloromethane at room temperature was added dropwise 0.3 mol of bromine. The reaction mixture was heated to 40°C for 2 h, the precipitate was filtered off, the solvent was removed, and fractional distillation of the residue furnished aldehyde **IIb**, yield 90 g (90%), bp 129–130°C (0.05 mm Hg), n_D^{20} 1.5131. IR spectrum, ν , cm^{-1} : 1260 (P=O), 1750 (CHO). ^1H NMR spectrum [$(\text{CD}_3)_2\text{CO}$], δ , ppm: 1.20 d.t (6H, 2CH₃); 4.01 m (4H, 2OCH₂); 7.30 m (3H, Ph); 7.65 m (2H, Ph); 9.50 d (1H, CHO, J 6.25 Hz). ^{31}P NMR spectrum: δ 8.2 ppm.

α -Diisopropoxyphosphoryl- α -thiocyanatoacet-aldehyde (IVa). A mixture of 0.02 mol of aldehyde **IIc** [7] and 0.02 mol of sodium or potassium thiocyanate in 30 ml of acetone was boiled for 6 h. The separated precipitate was filtered off, the filtrate was evaporated. To the oily substance obtained was added a mixture acetone–ethyl ether (1:2). The separated crystalline aldehyde **IVa** was filtered off and recrystallized from 2-propanol, yield 80%, mp 172–173°C. IR spectrum, ν , cm^{-1} : 1251 (P=O), 1736 (CHO), 2154 (C \equiv N). ^1H NMR spectrum [$(\text{CD}_3)_2\text{CO}$], δ , ppm: 1.20 d.t (12H, 4CH₃); 4.25 q (1H, OH); 4.60 m (2H, 2OCH); 7.43, 7.63 d (1H, =CH, J 7.5 Hz). ^{31}P NMR spectrum: δ 10.00 ppm Found, %: N 5.24; P 11.78; S 11.98. C₉H₁₆NO₄PS. Calculated, %: N 5.28; P 11.7; S 12.07.

α -Diethoxyphosphoryl- α -thiocyanatoacet-aldehyde (IVb) was prepared under similar conditions from aldehyde **IIa** or **IIb** and potassium thio-

cyanate, yield 76%, mp 178–180°C. IR spectrum, ν , cm^{-1} : 1250 (P=O), 1660 (C=C), 2130 (C \equiv N), 3160 (OH). ^1H NMR spectrum [$(\text{CD}_3)_2\text{SO}$], δ , ppm: 1.10 d.t (6H, 2CH₃); 4.0 m (4H, 2OCH₂); 7.35 m (3H, Ph); 7.75 m (2H, Ph); 9.8 s (1H, CHO). ^{31}P NMR spectrum: δ 6.59 m.d. Found, %: N 4.54; P 9.81; S 10.14. C₁₃H₁₆NO₄PS. Calculated, %: N 4.47; P 9.90; S 10.22.

***O,O*-diisopropyl(2-imino-1,3-oxathiol-4-yl)phosphonate (V)**. In 15 ml of 2-propanol 2.65 g (0.01 mol) of aldehyde **IVa** was boiled for 8 h. The reaction mixture was filtered, the filtrate was evaporated by 60% and left overnight in a refrigerator. The precipitated crystals of compound **V** were filtered off, washed with ethyl ether, and dried. Yield 1.9 g (72%), mp 169–170°C. IR spectrum, ν , cm^{-1} : 1280 (P=O), 1620 (C=C), 2500 (=NH). ^1H NMR spectrum [$(\text{CD}_3)_2\text{SO}$], δ , ppm: 1.20 t (12H, 4CH₃); 4.50 m (2H, 2OCH); 7.35 d (1H, =CH, J 5 Hz); 7.40 s (1H, =NH). ^{31}P NMR spectrum: δ 10.00 ppm Found, %: N 5.22; P 11.64; S 12.16. C₁₉H₁₆NO₄PS. Calculated, %: N 5.28; P 11.70; S 12.07.

IR spectra were recorded on spectrophotometer UR-20. ^1H NMR spectra were measured on spectrometer Tesla BW-567 (100 MHz), reference HMDS. ^{31}P NMR spectra were registered on spectrometer Bruker WP-80 (32.38 MHz), reference % H₃PO₄.

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