WITH CARBONYL COMPOUNDS

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The reactions of S-acetylcyanophosphites with carbonyl compounds proceeds with the formation of the corresponding 1-acetoxycyanothiophosphonates.

S-Acetyl cyanides of trivalent phosphorus acids have not been studied. On the other hand, we might expect that such mixed acylcyanophosphites would react with involvement of either the S-acetyl or CN group [1-5].

S-Aacetylcyanophosphites react with ethyl pyruvate, chloral, benzaldehyde, and metafluorobenzaldehyde in the presence of catalytic amounts of boron trifluoride etherate with the involvement of the S-acetyl group to form diastereomeric 1-acetoxycyanothiophosphonates (IIa)-(IId) in 66-82% yield.



The structures of products (IIa)-(IId) were confirmed by spectral methods and their composition was supported by elemental analysis. The IR spectra of these compounds have characteristic bands at 1750-1780 (C=O), 2190-2200 (C=N), and 620-630 cm⁻¹ (P=S).

EXPERIMENTAL

The ³¹P NMR spectra were taken on a KGU-4 spectrometer at 10.2 MHz relative to 85 H_3PO_4 . The IR spectra were taken on a UR-20 spectrometer. The PMR spectra were taken on a Varian T-60 spectrometer with TMS as the internal standard.

<u>Reaction of 0-Ethyl-S-acetylcyanophosphite (I) with Ethyl Pyruvate</u>. A sample of 5.8 g ester was added to 8.8 g (I) in the presence of $BF_3 \cdot Et_2O$. The reaction mixture was main-tained for three days at 20°C. Distillation gave 11.8 g (82%) 0-ethyl-(1-acetoxy-1-ethoxy-carbonylmethyl)cyanothiophosphonate (IIa) with bp 145-146°C (0.06 mm), n_D^{20} 1.4665, d_4^{20} 1.0930. Found: C, 40.36; H, 4.91; N, 4.99%. Calculated for $C_{10}H_{16}NO_3PS$: C, 40.95; H, 5.46; N, 4.77%. ³¹P NMR spectrum (δ , ppm): 54.

Reaction of (I) with Chloral. A sample of 7.4 g chloral was added dropwise to 8.8 g (I) in the presence of a catalytic amount of $BF_3 \cdot Et_20$ with cooling to 0°C. Distillation gave 13.6 g (84%) 0-ethyl-(1-acetoxy-2,2,2-trichloroethyl)cyanothiophosphonate (IIb) with bp 139-141°C (0.06 mm), n_D^{20} 1.5076, d_4^{20} 1.4060. Found: C, 25.35; H, 3.11; P, 9.25%. Calculated for $C_7H_9NO_3PCl_3S$: C, 25.89; H, 2.77; P, 9.55%. ³¹P NMR spectrum (δ , ppm): 42-40. PMR spectrum in CCl₄ (δ , ppm, J, Hz): 1.9 t (³J_{HH} = 7.0) and 1.88 t (³J_{HH} = 7.0) (CH₃C, 3H), 2.75 s (CH₃CO, 3H), 6.3 d (²J_{HP} = 6.0) and 6.3 d (²J_{HP} = 4.5) (CHP, 1H).

<u>Reaction of (Ia) with Benzaldehyde</u>. A sample of 5.3 g benzaldehyde was added dropwise to 8.8 g (Ia) in the presence of a catalytic amount of $BF_3 \cdot Et_20$. Distillation gave 9.3 g (66%) 0-ethyl-(l-acetylbenzyl)cyanothiophosphonate (IId) with bp 147-148°C (0.06 mm), n_D^{20}

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1.5295, d²⁰_b 1.1604. Found: C, 50.69; H, 5.04; P, 10.15%. Calculated for C₁₂H₁₄NO₃PS: C, 50.88; H, 4.94; P, 10.95%. ³¹P NMR spectrum (δ, ppm): 51. PMR spectrum in CCl₄ (δ, ppm, J, Hz): 1.37 t (CH₃C, 3H, ${}^{3}J_{HH} = 7.0$), 2.42 s (CH₃CO, 3H), 6.4 d (${}^{2}J_{HP} = 5.0$), and 6.5 d (${}^{2}J_{HP} = 5.0$) 8.0) (CHP, 1H).

Reaction of (I) with meta-Fluorobenzaldehyde. A sample of 6.2 g aldehyde was added to 8.8 g (I) in the presence of a catalytic amount of $BF_3 \cdot Et_20$ upon cooling to 0-5°C. Distillation gave 10.5 g (70%) 0-ethyl-(1-acetoxy-meta-fluorophenylmethyl)cyanothiophosphonate (IIc) with bp 139-140°C (0.06 mm), n_D²⁰ 1.5185, d₄²⁰ 1.2475. Found: C, 47.62; H, 3.51; P, 10.08%. Calculated for $C_{12}H_{10}NO_3PSF$: C, 47.84; H, 3.32; P, 10.29%. ³¹P NMR spectrum (δ , ppm): 50. PMR spectrum in CCl₄ (δ , ppm, J, Hz): 1.8 t (${}^{3}J_{HH} = 7.0$, CH₃C, 3H), 2.66 s (CH₃CO, 3H), 6.60 d (${}^{2}J_{HP} = 4.0$) and 6.63 d (${}^{2}J_{HP} = 8.0$) (CHP, 1H).

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REACTION OF FLUORINE-CONTAINING 1,4,2-OXAZAPHOSPHOLINE

WITH OH-NUCLEOPHILES

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1,4,2-Oxazaphospholine (I) decomposes upon the action of OH-nucleophiles with the formation of phosphonate esters (II).

The synthesis and properties of 1,4,2-oxazaphospholines with a pentacoordinated P^{V} phosphorus atom have been studied rather extensively [1-3]. On the other hand, the information on the synthesis of 1, 4, 2-oxazaphospholanes with a tetracoordinated P^V atom is extremely limited and there are no data on their reactivity. In this regard, we undertook a study of the reaction of 1,4,2-oxazaphospholine (I) [4] with OH-nucleophiles, which opens, in our opinion, broad synthetic possibilities for the introduction of fluorine-containing a-aminoalkylphosphoryl fragments into OH-containing molecules.

The ring in (I) is virtually quantitatively opened by water and alcohols at the P-O bond with the formation of the corresponding phosphonic acid and its esters (IIa)-(IIg).

> $Me \xrightarrow{O} CF_{3} OEt + ROH \xrightarrow{Me} OCF_{3} O$ $H \xrightarrow{\parallel} P \xrightarrow{P} CF_{3} CF_{3}$ (IIa-g) R = H(a), Me(b), Et(c), n-Pr(d), n-Bu(e), n-Am(f), n-Hex(g).

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