# Reactions of some acid phosphites and thiophosphites with thiocyanatoalcohols

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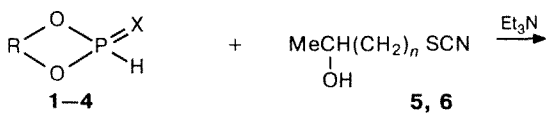
Thiocyanatoalcohols react with some acid alkylene glycol phosphites and thiophosphites in the presence of $Et_3N$ to give the corresponding hydroxyalkyl alkylene glycol thiophosphates or hydroxyalkyl dithiophosphates. The structure of the latter compounds determines their subsequent conversions.

**Key words**: alkylene glycol phosphites, thiophosphites, thiocyanatoalcohols, reactions.

In a continuation of studies on the interaction of aromatic derivatives of phosphorus-containing acids with thiocyanatoalcohols,[1–5] we carried out reactions of the latter with some acid phosphites and thiophosphites (**1**—**4**).

In the absence of a base ($Et_3N$), compounds **1**—**4** react with thiocyanatoalcohols only on refluxing in benzene for a period of several days. However, this reaction is completed in 15—30 min in the presence of an equimolar amount of $Et_3N$.

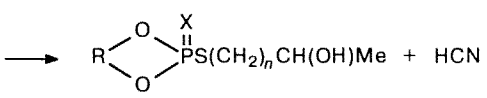
It is known[6] that the interaction of dialkylphosphites or their metal salts with alkylthiocyanates affords the corresponding $P^{IV}$ thiol esters. Judging from the results obtained, the first step of the interaction of compounds **1**—**4** with thiocyanatoalcohols **5** and **6** also occurs at the thiocyanate group with the formation of thioesters **7**—**11**.



**1**—**4** **5, 6**

**1**: X = O, R = $MeCHCH_2CH_2$
**2**: X = S, R = $MeCHCH_2CH_2$
**3**: X = O, R = MeCHCHMe
**4**: X = S, R = MeCHCHMe

$n$ = 1 (**5**), 2 (**6**)

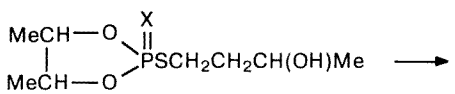


**7**—**11**

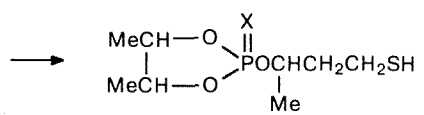
**7**: X = O, R = $MeCHCH_2CH_2$, $n$ = 2
**8**: X = S, R = $MeCHCH_2CH_2$, $n$ = 2
**9**: X = O, R = MeCHCHMe, $n$ = 2
**10**: X = S, R = MeCHCHMe, $n$ = 2
**11**: X = S, R = MeCHCHMe, $n$ = 1

The subsequent transformations of thioesters **7**—**11** possibly involve their hydroxyl group. Distillation of isolated compounds **7** and **8** results in the hydroxy-thiol rearrangement of the former compound,[7] whereas the latter one does not change.

We failed to isolate compounds **9** and **10**, probably due to their isomerization to *O*-esters **12** and **13**.



**9, 10**

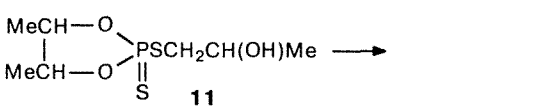


**12, 13**

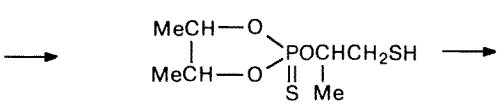
X = O (**12**), X = S (**13**)

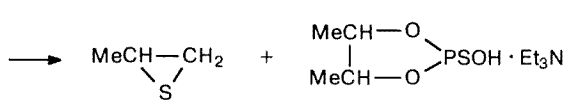
The isomerization of *S*-ester **10** into *O*-ester **13** is the first example of hydroxy-thiol rearrangement in the series of 3-hydroxyalkyl alkylene glycol dithiophosphates.

The reaction of thiophosphite **4** with thiocyanatoalcohol **6** resulted in triethylammonium 2,3-butylene glycol thiophosphate (**14**). The reaction probably proceeds as an $S \rightarrow O$-rearrangement with the elimination of α-propylene sulfide.



**11**





**14**

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## Experimental

$^{31}P$ NMR spectra were obtained on a KGU-4 spectrometer (10.2 MHz) with 85 % $H_3PO_4$ as the standard without any solvent.

**Reactions of compounds 1—4 with thiocyanatoalcohols (general procedure).** An equimolar amount of thiocyanatoalcohol **5** or **6** was added to a solution of equimolar amounts of $Et_3N$ and phosphite or thiophosphite **1—4** in boiling benzene. The reaction mixture was usually observed to boil up violently. After mixing the reagents, the reaction mixture was refluxed for 15—30 min, and then the solvent and all volatile compounds were distilled off *in vacuo* (10—0.1 Torr) at ~60 °C. In most cases, the residue was analyzed without distillation. Compounds **7**, **8**, **12**, and **13** were obtained in quantitative yields.

**2-Oxo-2-(3-hydroxybutylthio)-4-methyl-1,3,2-dioxaphosphorinane (7).** $n_D^{20}$ 1.4980. $^{31}P$ NMR, δ: +20 (s). IR, ν/cm$^{-1}$: 3430 (OH) (*cf.* Ref. 7).

**2-Thiono-2-(3-hydroxybutylthio)-4-methyl-1,3,2-dioxaphosphorinane (8).** B.p. 145—147 °C (0.08 Torr), $d_4^{20}$ 1.2251, $n_D^{20}$ 1.5350. Found (%): C, 37.15; H, 6.74; P, 11.76. $C_8H_{17}O_3PS_2$. Calculated (%): C, 37.50; H, 6.64; P, 12.10. $^{31}P$ NMR, δ: +94 (s). IR, ν/cm$^{-1}$: 3420 (OH).

**2-Oxo-2-(1-methyl-3-mercaptopropoxy)-4,5-dimethyl-1,3,2-dioxaphospholane (12).** $d_4^{20}$ 1.1886, $n_D^{20}$ 1.4740. $^{31}P$ NMR, δ: +12 (s). IR, ν/cm$^{-1}$: 2550 (SH) (*cf.* Ref. 8).

**2-Thiono-2-(1-methyl-3-mercaptopropoxy)-4,5-dimethyl-1,3,2-dioxaphospholane (13).** $n_D^{20}$ 1.5010. Found (%): P, 12.39. $C_8H_{17}O_3PS_2$. Calculated (%): P, 12.10. $^{31}P$ NMR, δ: +79 (s). IR, ν/cm$^{-1}$: 2545 (SH).

The reaction of thiophosphite **4** (1.52 g), thiocyanatoalcohol **6** (1.17 g), and $Et_3N$ (1.01 g) in benzene (10 mL) afforded 2.65 g of salt **14**, $n_D^{20}$ 1.4960 (very viscous liquid). Found (%): C, 44.47; H, 8.70; P, 11.41. $C_{10}H_{24}NO_3PS$. Calculated (%): C, 44.60; H, 8.92; P, 11.52. $^{31}P$ NMR, δ: +68 (s).

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