Exchange reactions of tetrathiophosphates with thiophosphoryl chloride

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Exchange reactions of tetrathiophosphates with thiophosphoryl chloride were studied. The exchange of thiol groups between compounds with tetracoordinated phosphorus centers proceeds at 150–220 °C and results in the formation of dialkyl trithiochlorophosphates and alkyl(aryl) dithiodichlorophosphates or their mixtures depending on the ratio of the reagents.

Key words: trialkyl tetrathiophosphates, triaryl tetrathiophosphates, dialkyl trithioclorophosphates, alkyl dithiodichlorophosphates, aryl dithiodichlorophosphates, exchange reaction; thiophosphoryl chloride, isotope label ³²P.

Reactions of intermolecular exchange of thioalkyl and thioaryl groups for the P atom can be convenient methods for synthesis and are of theoretical interest for estimation of the reactivity and stability of phosphorussulfur-containing compounds.

The exchange of thioalkyl groups at the halogen atom in compounds of tricoordinated phosphorus was observed for the first time by M. I. Kabachnik and coworkers in 1948.¹ Later we studied the molecular exchange of thiol groups in compounds of tetracoordinated phosphorus.²⁻⁴ It has been established that exchange reactions of trialkyl and triaryl tetrathiophosphates with P(S)Br₃ proceed most readily. For example, redistribution of substituents in a mixture of tetrathiophosphates and $P(S)Br_3$ is completed within 5-8 h already on heating to 120 °C and results in the formation of alkyl(aryl) dithiodibromophosphates.² In this work, we studied the exchange reactions of tetrathiophosphates (1) with P(S)Cl₃. As should be expected, the reactions of tetrathiophosphates with P(S)Cl₃ occur at higher temperatures than those with $P(S)Br_3$, and they can be completed on heating in a steel tube at 180-220 °C; at temperatures >250 °C, partial resinification of the reaction mixture is observed. It was also revealed that the exchange of thiol groups of tetrathiophosphates can occur stepwise, and at the molar ratio $1 : P(S)Cl_3 = 2 : 1$, dialkyl trithiochlorophosphates (2) are predominantly formed and isolated in 52-78% yields (Eq. (1), Table 1). At the 1:1 molar ratio of the starting reagents, mixtures of dialkyl trithiochlorophosphates 2 and alkyl dithiodichlorophosphates (3) are formed (Eq. (2)). Dialkyl trithiochlorophosphates 2 are also formed in the reactions of trialkyl tetrathiophosphates 1 with alkyl dithiodichlorophosphates 3 at 180-200 °C (Eq. (3)). Under the same conditions, the use of two or

more moles of $P(S)Cl_3$ per mole of tetrathiophosphate results predominantly in the formation of alkyl(aryl) dithiodichlorophosphates **3** (Eq. (4)).

$$2 (RS)_3 PS + P(S)CI_3 \longrightarrow 3 (RS)_2 P(S)CI \qquad (1)$$

1a-e 2a-e

 $(RS)_3PS + P(S)CI_3 \longrightarrow (RS)_2P(S)CI + RSP(S)CI_2 (2)$ 1a-e 2a-e 3a-e

$$(RS)_3PS + RSP(S)CI_2 \longrightarrow 2 (RS)_2P(S)CI \qquad (3)$$

$$(RS)_3PS + 2 P(S)CI_3 \longrightarrow 3 RSP(S)CI_2$$
(4)
1a-i 3a-i

Dialkyl trithiochlorophosphates 2 also enter the exchange reactions with $P(S)Cl_3$ to give alkyl dithiodichlorophosphates 3 (Eq. (5)). In fact, reactions (1)-(5) are in equilibrium: when an excess of $P(S)Cl_3$ is used, the equilibrium in reactions (2), (4), and (5) is shifted toward the formation of dithiodichlorophosphates. It is of interest that the equilibrium can be shifted to the opposite direction: for example, heating of methyl dithiodichlorophosphates with distillation off of P(S)Cl₃ gave $(MeS)_3PS$ (see Eq. (4), R = Me). The mobility of thiol groups in alkyl dithiodichlorophosphates was confirmed by the radioactive label ³²P (Eq. (6)). For example, on heating of a mixture of MeSP(S)Cl₂ and radioactive [32P]P(S)Cl₃ at 170-220 °C, the exchange of phosphorus isotopes ³¹P ----- ³²P was observed, and the degree of exchange reaches 57% of the equilibrium value within 5 h at 220 °C.5

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| Com- pound | R | x | Yield (%) | B.p./°C (p/Torr)ª | n _D ²⁰ a | d4 ²⁰ a | Found (%) Calculated | | | Molecular formula |
|---------------|--------------------------------|---------------------------------|--------------|------------------------------|--------------------------------|--------------------|-------------------------|-----------------------|-----------------------|--|
| | | | | | | | Cl | Р | S | |
| 2a | Me | SMe | 64 | 92-93 (2) [92-94 (2)] | 1.6505 [1.6525] | 1.4153 [1.4085] | ~ | | | |
| 2b | Et | SEt | 76 | 108—110 (1.5) [92 (0.01)] | 1.6104 [1.6096] | 1.2908 | - | | | |
| 2c | Pr" | SPr" | 63 | 120—122 (1) [118—120(1)] | 1.5680 [1.5690] | 1.1750 [1.1761] | | | | |
| 2d | Bu" | SBu ⁿ | 73 | 144—145 (1) | 1.5682 | 1.1611 | <u>12.70</u> 12.86 | <u>11.03</u> 11.21 | <u>34.40</u> 34.72 | C ₈ H ₁₈ CIPS ₃ |
| 2e | C ₆ H ₁₃ | SC ₆ H ₁₃ | 52 | 179-180 (1) | 1.5474 | 1.1496 | <u>10.27</u> 10.67 | <u>9.07</u> 9.32 | <u>28.11</u> 28.24 | C ₁₂ H ₂₆ CIPS ₃ |
| 3a | Me | Cl | 76 | 91—92 (20) [50 (0.1)] | 1.6130 [1.6090] | 1.5309 [1.5258] | - | — | - | |
| 3b | Et | Cl | 69 | 53—54 (1.5) [54—55 (0.1)] | 1.5870 [1.5910] | 1.4264 [1.4240] | | | - | |
| 3c | Pr ⁿ | Cl | 72 | 60—61 (1.5) [60—61 (0.1)] | 1.5747 [1.5772] | 1.3653 [1.3626] | | | - | |
| 3d | Bun | Cl | 89 | 80—81 (1.5) [80—82 (0.1)] | 1.5681 [1.5680] | 1.3142 [1.3227] | - | | | |
| 3e | C ₅ H ₁₁ | Cl | 70 | 89-90 (1) | 1.5530 | 1.2609 | <u>30.00</u> 29.96 | <u>13.52</u> 13.08 | <u>27.06</u> 27.00 | C ₅ H ₁₁ Cl ₂ PS ₂ |
| 3f | C ₆ H ₁₃ | CI | 68 | 121-122 (1) | 1.5522 | 1.2359 | <u>28.25</u> 28.29 | <u>12.30</u> 12.35 | <u>25.49</u> 25.49 | $C_6H_{13}CI_2PS_2$ |
| 3g | C7H15 | Cl | 67 | 104-108 (0.5) | 1.5487 | 1.2100 | <u>26.90</u> 26.79 | <u>11.70</u> 11.69 | <u>23.80</u> 24.15 | C ₇ H ₁₅ Cl ₂ PS ₂ |
| 3h | C ₈ H ₁₇ | Cl | 67 | 114-116 (0.5) | 1.5452 | 1.1841 | <u>25.11</u> 25.44 | <u>10.90</u> 11.11 | <u>23.07</u> 22.93 | C ₈ H ₁₇ Cl ₂ PS ₂ |
| 3i | Ph | Cl | 69 | 116 - 118(1) [120(4)] | 1.6577 | 1.4490 | | | | |

Table 1. Yields and physicochemical constants of compounds RS - P(S) - Cl (2, 3)

^a The published data for compounds 2a,⁷ 2b,⁸ 2c,⁷ 3a-d,⁹ and 3i ¹⁰ are given in brackets.

$$(RS)_2 P(S)CI + P(S)CI_3 \implies 2 RSP(S)CI_2$$
(5)
2a-e 3a-e (5)

$$MeSP(S)Cl_{2} + [^{32}P]P(S)Cl_{3} =$$
3a

$$[^{32}P]MeSP(S)Cl_{2} + P(S)Cl_{3} = (6)$$

$$[^{32}P]3a$$

Note that tetrathiophosphates I can be obtained by the reactions of mercaptans (thiophenols) with $P(S)Cl_3$ in the catalysis with pyridine and, thus, they are easily accessible compounds.⁶ The results presented indicate that the reactions of these compounds with $P(S)Cl_3$ can be used for the synthesis of both dialkyl trithiodichlorophosphates and alkyl(aryl) dithiodichlorophosphates. The use of the reactions of triaryl tetrathiophosphates with $P(S)Cl_3$ for preparing diaryl trithiochlorophosphates, which have not yet been described, is restricted by the difficult purification of the latter because of their instability (disproportionation) during vacuum distillation.

Experimental

³¹P NMR were recorded on a Bruker AC-80 spectrometer (32.4 MHz) using 85% H₃PO₄ as the external standard. The starting trialkyl(triaryl) tetrathiophosphates were synthesized according to the procedure developed previously⁶ from mercaptans and P(S)Cl₃ (Merck). Radioactive [³²P]P(S)Cl₃ was obtained from the Izotop Company and used after dilution with nonradioactive P(S)Cl₃ until the specific radioactivity of 10-30 kBq mL⁻¹ was achieved. Radioactivity of solutions was measured by the scintillation method on an SL-4000 spectrometer (France) in potassium-free glass vials containing 10 mL of a scintillation solution. Toluene containing 2,5-diphenyloxazole (PPO) (5 g L⁻¹) and 1,4-di(5-phenyl-2-oxazolyl)benzene (POPOP) (0.1 g L⁻¹) was used as the scintillation solution. Chromatograms were radioscanned by

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the measurement of radioactivity at each cm of the chromatogram using a PP-8 radiometer by a T-25 BFL end-window counter with a 10-mm slit.

Dimethyl trithiochlorophosphate (2a) (typical procedure). A. A mixture of trimethyl tetrathiophosphate 1a (20.4 g, 0.1 mol) and $P(S)Cl_3$ (8.4 g, 0.05 mol) was heated in a closed steel tube at 180–190 °C for 8 h, then the tube was cooled, and dimethyl trithiochlorophosphate (18.7 g) was isolated by vacuum distillation.

B. A mixture of trimethyl tetrathiophosphate (1a) (20.4 g, 0.1 mol) and methyl dithiochlorophosphate (18.1 g, 0.1 mol) was heated in a steel tube at 190–195 °C for 8 h, then the tube was cooled, and compound 2a was isolated by vacuum distillation in 70% yield (27.5 g).

The yields and physicochemical parameters of other dialkyl trithiochlorophosphates obtained under conditions described above (procedure A) are presented in Table 1.

Methyl dithiodichlorophosphate (3a) (typical procedure). A. A mixture of trimethyl tetrathiophosphate (1a) (20.4 g, 0.1 mol) and P(S)Cl₃ (50 g, 0.3 mol) was heated in a steel tube at 180–190 °C for 6 h, then the tube was cooled, and an excess of P(S)Cl₃ was distilled off. Compound 3a was isolated in 76% yield (41 g) by vacuum distillation of the residue ³¹F NMR, δ : +71.6.

C. A mixture of trimethyl tetrathiophosphate (1a) (20.4 g, 0.1 mol) and $P(S)Cl_3$ (16.9 g, 0.1 mol) was heated in a steel tube at 180-190 °C for 6 h; compound 2a (10.6 g, 54%) and product 3a (4.9 g, 21%) were isolated.

The yields and physicochemical constants of other alkyl(aryl) dithiodichlorophosphates obtained under the conditions indicated above (procedure A) are presented in Table 1.

Trimethyl tetrathiophosphate (1a). Methyl dithiodichlorophosphate (3a) (18.1 g) was heated in a Claisen flask at 199– 200 °C for 8 h until $P(S)Cl_3$ ceased to be distilled off. Trimethyl tetrathiophosphate 1a (5 g, 70%) was isolated by vacuum distillation, m.p. 24 °C. ³¹P NMR, δ : +90.3.

Isotope exchange between methyl dithiodichlorophosphate (3a) and radioactive $[^{32}P]P(S)Cl_3$. A mixture of radioactive $[^{32}P]P(S)Cl_3$ (1.5 mmol) and methyl dithiodichlorophosphate

(1.5 mmol) was scaled in a glass tube, which was placed in a steel tube containing nonradioactive $P(S)Cl_3$ to equalize the pressure between the tube walls, and the steel tube was scaled and heated for 120-220 °C for 1-5 h. Then the steel tube was cooled, the tube was opened, $P(S)Cl_3$ was distilled off *in vacuo*, and nonradioactive $P(S)Cl_3$ (1.5 mmol) was added to the residue and distilled off again. The residue and distillate were dissolved in CHCl₃, and radioactivities of the solutions were measured by the scintillation method. To identify the exchange products, a drop of the solution in CHCl₃ was applied onto a Silufol plate and chromatographed in a hexane-CHCl₃ (9 : 1) mixture. The radioactive spot with $R_f 0.49$ was identified on the chromatograms. The mobility of this spot is identical to that of the nonradioactive methyl dithiodichlorophosphate (3a).

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