Brief Communications

Effect of iodine on the reaction of tetraphosphorus decasulfide with dialkyl disulfides

I. S. Nizamov,* G. G. Garifzyanova, and E. S. Batyeva

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Scientific Center of the Russian Academy of Sciences, 8 ul. Akad. Arbuzova, 420083 Kazan', Russian Federation. Fax: +7 (843 2) 75 2253

Elemental iodine decreases the temperature of the reaction of P_4S_{10} with disulfides, which results in the formation of trialkyl tetrathiolothionophosphates, from 100–110 °C to 20–60 °C. The latter decompose to trialkyl tetrathiophosphates.

Key words: tetraphosphorus decasulfide, dialkyl disulfides, reaction; iodine; trialkyl tetrathiolothionophosphate; trialkyl tetrathiophosphates.

Earlier, it has been shown that tetraphosphorus decasulfide decomposes under the action of dialkyl disulfides in drastic conditions (100-110 °C) to give trialkyl tetrathiolothionophosphates, which are transformed to trialkyl tetrathiophosphates on heating.^{1,2} In this work, we attempted to chemically initiate this reaction. It is known that tetraphosphorus trisulfide (P_4S_3) reacts smoothly with elemental iodine at 20 °C in benzene or CS₂ to give an adduct, β -diiodotetraphosphorus trisulfide.³⁻⁵ We assumed that the reactivity of other phosphorus sulfides, e.g., P_4S_{10} (1), can be increased if iodine participates in their interaction with sulfur-containing organic compounds. In fact, we found that sulfide 1 reacted with dialkyl disulfides **2a**,**b** in the presence of elemental iodine in anhydrous benzene at 20-60 °C to give trialkyl tetrathiolothionophosphates **3a**,**b** (Scheme 1).

Pentathiophosphates **3a,b** were identified in the reaction mixtures from their ³¹P NMR spectra (δ 100 (**3a**) and 94.8 (**3b**); *cf.* Ref. 2 for **3b**: δ 94.8) as well as on the

Scheme 1

basis of their decomposition into trialkyl tetrathiophosphates 5a,b in the course of distillation; the latter are formed in higher yields than in the absence of iodine. The other decomposition products, alkylsulfenyl iodides 4a,b, were not isolated, owing to their instability under the experimental conditions.⁶ However, their formation

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was confirmed by chemical-ionization mass spectra of the crude reaction mixtures (for example, the molecular ion $[PrSI+H]^+$ with $m/z \ 203$, $I_{rel} = 60 \%$).

Experimental

 31 P NMR spectra were recorded on a Bruker CXP-100 spectrometer (36.5 MHz) in benzene (with 85 % H₃PO₄ as the external standard). Mass spectra (CI, isobutane, 100 eV) were obtained with a Hitachi M80-B chromatomass spectrometer.

Tripropyl tetrathiophosphate (5a). Crystalline iodine (1.5 g, 5.9 mmol) was added portionwise with stirring at 20 °C to a solution of disulfide **2a** (6.4 g, 42.6 mmol) in 10 mL of benzene, followed by the addition of P_4S_{10} (2.7 g, 6.1 mmol). The mixture was stirred at 60 °C for 4 h. The precipitate was filtered off, and the filtrate was diluted with 30 mL of benzene and washed with a saturated aqueous solution of sodium thiosulfate and then with water. The benzene layer was separated and dried with MgSO₄. The dessicant was filtered off, and the filtrate was kept *in vacuo* (0.1 and 0.02 Torr). Distillation of the residue gave 1.7 g (25 %) of tetrathiophosphate **5a**, b.p. 126–128 °C (0.03 Torr), n_D^{20} 1.5890. ³¹P NMR, δ : 92.6. MS, m/z (I_{rel} (%)): 289 [M+H]⁺ (18) (cf. Ref. 7: b.p. 131–132 °C (0.5 Torr), n_D^{20} 1.5885; ³¹P NMR, δ : 92.5).

Triisopropyl tetrathiophosphate (5b). Analogously, 2.1 g (27 %) of tetrathiophosphate 5b were obtained from P_4S_{10}

(3.0 g, 6.8 mmol), disulfide **2b** (7.1 g, 47.3 mmol), and iodine (1.7 g, 6.7 mmol) (20 °C, 4 h), b.p. 110 °C (0.02 Torr), n_D^{20} 1.5663. ³¹P NMR, δ : 87.1. MS, m/z (I_{rel} (%)): 288 [M]⁺ (30) (cf. Ref. 2: yield 11 %; Ref. 7: b.p. 123–125 °C (0.3 Torr)).

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Isomerization processes in the synthesis of asymmetric allyl chalcogenides

E. N. Deryagina^{*} and N. A. Korchevin

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 1 ul. Favorskogo, 664033 Irkutsk, Russian Federation. Fax: +7 (395 2) 46 0331

Allyl-propenyl rearrangement (prototropic isomerization) occurs in the synthesis of allyl organyl chalcogenides in a hydrazine hydrate—KOH system with a 6–10-fold molar excess of KOH. Specificities of the rearrangement that depend on the nature of the chalcogen were studied.

Key words: allyl chalcogenides, isomerization; hydrazine hydrate-KOH system.

Asymmetric dialkyl chalcogenides are obtained by the reduction of diorganyl dichalcogenides in a hydrazine hydrate—KOH system followed by alkylation of the thus formed chalcogenide anions with alkyl halides.¹

We have found that the allyl-propenyl rearrangement (Scheme 1) occurs in the course of the synthesis of asymmetric allyl chalcogenides from diorganyl dichalcogenides as the concentration of alkali in a hydrazine hydrate—KOH system (the molar ratio of R_2Y_2 : KOH = 1 : (6–10)) and the alkylation temperature increase (90–110 °C).

The ratio of isomers 1 and 2 formed depends on the nature of element Y; the degree of isomerization (2:1) decreases in the following order: S (95:5) > Se (53:47)

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