Synthesis and isomerization of several thioallyl esters of P^{III} acids

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S-Allyl diphenylthiophosphinite and S,S-diallyl phenyldithiophosphonite have been obtained for the first time. Molecular oxygen has been found to catalyze the isomerization of thioallyl esters of P^{III} acids. Possible schemes for the isomerization have been proposed.

Key words: thioallyl esters of P^{III} acids; molecular oxygen; monoelectron transfer; isomerization; radical cations.

Earlier¹⁻³ we reported the synthesis of some thiobenzyl esters of P^{III} acids by the reaction of the corresponding P^{III} acid chlorides with benzyl trimethylsilyl sulfide. The compounds obtained appeared to be extremely unstable due to their sensitivity to air oxygen.^{1,2} The reaction with oxygen was inhibited by spin traps, indicating the involvement of radicals in this reaction.² However, an attempt to prepare thiobenzyl and thioallyl esters of diphenylphosphinous acid resulted in the corresponding phosphine sulfides.⁴ It was concluded on the basis of these data that both of these compounds readily undergo isomerization at ~20 °C. However, a number of more recent works^{5,6} reported thioallyl esters of P^{III} acids with other substituents at the phosphorus atom. In the opinion of the authors of refs. 5 and 6, the driving force of the spontaneous isomerization of thioallyl esters of P^{III} acids is the nucleophilic attack of the lone electron pair of the phosphorus atom on the double bond of the allyl system. Allyl phosphites are known⁷ to be rather stable and undergo isomerization only under drastic conditions, although the nucleophilicity of the phosphorus atom in these compounds is higher than that in the corresponding thio-analogs. When we compared thiobenzyl and thioallyl esters of PIII acids, we assumed that in this case the instability of the substances under consideration may be also due to the presence of molecular oxygen, which is a good electron acceptor. As a consequence, the radical cation of the substrate and the superoxide anion are present in the system. In our opinion, the isomerization mechanism of thicallyl esters of P^{III} acids may involve a monoelectron transfer step.

We were the first to obtain the thioallyl esters of P^{III} acids by the interaction of chlorodiphenyl- and dichlorophenyl phosphines with allyl trimethylsilyl sulfide in dry argon. After being kept in an argon atmosphere for several hours, *S*-allyl diphenylthiophosphinite (1) and

S,S-diallyl phenyldithiophosphonite (2) are completely transformed into the corresponding isomerization products, the process proceeding faster in the case of compound 2. It was interesting to study the stability of thioallyl esters of P^{III} acids in an oxygen atmosphere.

When molecular oxygen was passed through thioester 1 at -10 °C for 10 min, S-allyl diphenylthiophosphinite was completely converted into S-allyl diphenyl phosphine sulfide (3) ($\delta^{31}P$ 42.05). The reaction was monitored by ³¹P NMR spectra. The degree of isomerization of compound 1 that was not in contact with oxygen (sealed in an ampoule) over that same time interval was only 15 % at -10 °C. The structure and composition of phosphine sulfide 3 were confirmed by the elemental analysis and ¹H and ³¹P NMR spectroscopic data.

Similar experiments were carried out with phenylphosphonite 2 ($\delta^{31}P$ 76). In this case the isomerization in the absence of oxygen proceeded even more slowly: 15 % over 1 h. When oxygen was passed for 15 min, strong heating of the mixture was observed, and the ³¹P NMR spectrum contained one signal at $\delta^{31}P$ 68 corresponding to allyl allylphenyldithiophophinate (4).

Compound 4 was isolated and characterized by spectral methods.

As was shown previously,¹⁻⁻³ the interaction of a series of thiobenzyl esters of P^{III} acids with molecular oxygen usually afforded, along with the isomerization products, the products of sulfur addition as well as the products of replacement of the phenyl radical with a thiobenzyl fragment. Thioallyl esters of P^{III} acids do not



enter reactions that lead to the formation of dithio and trithio products.

On the basis of the experimental data obtained, one can propose two reaction pathways for the isomerization of thioallyl esters of P^{III} acids (Schemes 1 and 2).

Thus, according to Scheme 1, an adduct of P^{III} thioester with molecular oxygen is initially formed, followed by monoelectron transfer. The attack of the terminal carbon atom on the electrophilic phosphorus atom of the radical cation **A** results in the intermolecular isomerization of the P^{III} thioester, which affords intermediate **B**. In our opinion, in the absence of oxygen in the reaction mixture (see Scheme 2), intramolecular monoelectron transfer with the formation of radical cation **C** may take place. Subsequent rearrangement according to the cyclic mechanism affords the reaction products.

The P-S bond is known to be more polarized than the P-O bond. Therefore, we consider the monoelectron transfer in P^{III} thioesters to proceed more readily. In our opinion, this determines the higher stability of oxygen analogs of the phosphorus-based thioallyl esters.

The data presented in ref. 9 also testify that the isomerization proceeds according to the one-electron transfer scheme. Thus, photoexcitation of allyl phosphites results in the formation of 1,3-biradicals which then undergo cyclization and transformation into isomerization products.

Thus, one can conclude from the data presented that in an inert atmosphere the reaction proceeds according to Scheme 2 with intramolecular one-electron transfer. However, in the presence of molecular oxygen the trans-

Scheme 2



fer of an electron from the P^{III} thioester to oxygen occurs, followed by the rearrangement of the thioester radical cation. But it is practically impossible to remove all the molecular oxygen from the system, so both schemes probably occur during the isomerization of thioallyl esters of P^{III} acids.

Experimental

³¹P NMR spectra were recorded on a Bruker CXP-100 instrument at a working frequency of 36.47 MHz. ¹H NMR spectra were recorded on a Varian T-60 spectrometer at a working frequency of 60 MHz.

Thioallyl esters of P^{III} acids were synthesized according to the procedure described in refs. 1 and 2 by the interaction of the corresponding P^{III} acid chlorides with allyl trimethylsilyl sulfide on cooling to -15 °C.

S-Allyl diphenylthiophosphinite (1) was obtained according to the general procedure from 4.4 g (0.02 mol) of chlorodiphenylphosphine and 2.92 g (0.02 mol) of allyl trimethylsilyl sulfide at -15 °C. ³¹P NMR, δ : 28.47. ¹H NMR in a capillary, δ : 3.55 (td, ³J_{PH} = 10.99 Hz, PSCH₂CH=CH₂); 5.35 (m, PSCH₂CH=CH₂); 5.95 (m, PSCH₂CH=CH₂); 7.65 (m, C₆H₅).

S,*Š*-Diallyl phenyldithiophosphonite (2) was obtained according to the general procedure from 3.58 g (0.02 mol) of dichlorophenyl phosphine and 6.84 g (0.04 mol) of allyl trimethylsilyl sulfide at -15 °C. ³¹P NMR, δ : 76. ¹H NMR in a capillary, δ : 3.66 (td, ³*J*_{PH} = 10.99 Hz, PSCH₂CH=CH₂); 5.47 (m, PSCH₂CH=CH₂); 5.98 (m, PSCH₂CH=CH₂); 7.60 (m, C₆H₅).

The interaction of compound 1 with molecular oxygen. Oxygen was passed for 20 min through thioester 1 prepared according to the general procedure and cooled to -20 °C. After the removal of chlorotrimethylsilane, fractionation under a water-jet pump vacuum afforded 4.12 g (80 %) allyldiphenylphosphine sulfide (3), b.p. 171 °C (0.02 Torr). ³¹P NMR, δ : 42.25. ¹H NMR in a capillary, δ : 3.42 (dd, ²J_{PH} = 14.04 Hz, PSCH₂CHCH₂); 5.33 (m, PSCH₂CHCH₂); 5.91 (m, PSCH₂CHCH₂); 7.50 (m, C₆H₅). Found (%): C, 69.30; H, 5.36; P, 12.01; S, 12.05. C₁₅H₁₅PS₂. Calculated (%): C, 69.76; H, 5.81; P, 12.15; S, 13.02.

The interaction of compound 2 with molecular oxygen. Oxygen was passed for 30 min through thioester 2 prepared according to the general procedure and cooled to -20 °C. After the removal of chlorotrimethylsilane, fractionation under a water-jet pump vacuum afforded 2.31 g (75 %) *S*-allyl allylphenyldithiophosphinate (**4**), b.p. 153 °C (0.02 Torr). ³¹P NMR, δ : 68. ¹H NMR in a capillary, δ : 3.72 (dd, ²*J*_{PH} = 15.47 Hz, PSCH₂CHCH₂); 5.27 (m, PSCH₂CHCH₂); 5.98 (m, PSCH₂CHCH₂); 7.78 (m, C₆H₅). Found (%): P, 12.24; S, 25.16. C₁₂H₁₅PS₂. Calculated (%): P, 12.20; S, 25.20.

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A study of the effect of the nature of the solvent and temperature on the route of the reaction of thiobenzyl esters of P^{III} acids with molecular oxygen

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The effects of the nature of the solvents, the degree of dilution, the duration of the process, and the temperature on the ratio of the products obtained in the reactions of S-benzyl diphenylthiophosphinite or S, S-dibenzyl phenyldithiophosphonite with molecular oxygen have been studied. Possible reaction schemes are discussed.

Key words: thiobenzyl esters of P^{III} acids; solvents; degree of dilution; isomerization; phosphoranyl radicals, radical ions; complexes.

We have previously reported¹⁻³ the synthesis of some thiobenzyl esters of P^{III} acids by the reaction of the corresponding chlorides of P^{III} acids with benzyl trimethylsilyl sulfide. It has been shown^{1,2} that the resulting compounds are extremely unstable owing to their sensitivity to atmospheric oxygen; the fact that the reaction with oxygen is inhibited by spin traps attests to a radical mechanism of the reaction.² This has made it possible to suggest that the reaction of thiobenzyl esters of P^{III} acids with molecular oxygen involves phosphoranyl radicals. It has been shown previously^{4,5} that β -decomposition of phosphoranyl radicals prevails in their solutions in polar solvents at high temperatures, otherwise it competes with α -splitting. These regularities serve as a criterion for determining if a reaction proceeds via phosphoranyl radicals.^{4,5} At the same time the reaction of molecular oxygen with organic compounds according to the one-electron transfer mechanism involving the formation of a substrate radical cation and a superoxide anion is also possible.⁶

It is known that the effect of a solvent on the reaction rate may be due to the decrease in the concentration of the reacting compounds and, consequently, a decrease in the rate of the intermolecular processes, on the one hand, and by an increase in the solubility of molecular oxygen on the other hand. There are also indications⁷ that organic solvents form molecular complexes with oxygen. It is suggested that the absorption of

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