

STEREOCHEMISTRY OF SILVER-ION-ASSISTED SOLVOLYSIS OF *tert*-BUTYLPHENYLPHOSPHINOTHIOIC IODIDATE. PHOSPHATHIACYLIUM CATION FORMATION

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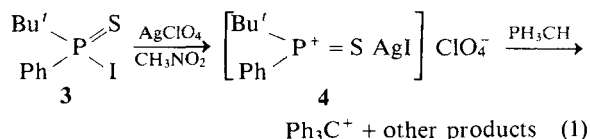
Studies on the stereochemistry of silver-ion-assisted solvolysis of a new optically active *tert*-butylphenylphosphinothioic iodidate demonstrated that the reaction proceeds with inversion of configuration at the phosphorus atom. Evidence for phosphathiacylium cation formation as a reactive intermediate is presented.

INTRODUCTION AND RESULTS

Although processes leading to the formation of acylium cations (RCO^+) are well known,¹ reactions leading to their phosphaanalogues ($\text{R}'\text{R}''\text{P}^+=\text{X}$, $\text{X}=\text{O}, \text{S}$) are rare. Only the synthesis of the nitrogen-stabilized analogues ($\text{R}_2\text{N})_2\text{P}^+=\text{X}$ ($\text{X}=\text{O}, \text{S}$) have been reported.² Chemical evidence for the formation of the phosphathiacylium cation $\text{BuPhP}^+=\text{S}$ as a reaction intermediate in the solvolysis of *tert*-butylphenylphosphinothioic-*O*-trifluoromethanesulphonate **2** in solvents of high ionizing power was recently obtained.³ In search for dissociative displacement reactions proceeding with the formation of phosphacylium cations, $\text{RR}'\text{P}^+=\text{X}$ ($\text{X}=\text{O}, \text{S}$), silver-ion-assisted solvolysis of organophosphorus substrates were studied.⁴ It was found that the presence of silver ions caused a sharp increase in the rate of solvolysis of organophosphorous acid halides, thiolates and selenoates.^{4a} An $\text{S}_{\text{N}}1(\text{P})$ mechanism of this reaction and the formation of phosphacylium cation $\text{RR}'\text{P}^+=\text{X}$ ($\text{X}=\text{O}, \text{S}$) were rejected on the basis of stereochemical results. It was assumed^{4a} that heterolytic bond cleavage between phosphorus and the leaving group, occurring under the influence of silver ions, should lead to the formation of racemic reaction products or products of retained configuration. The inversion of configuration which was observed was explained as the result of an associative $\text{S}_{\text{N}}2(\text{P})$ mechanism of substitution at the phosphorus atom with the formation of a pentacoordinated transition state (or intermediate) in which the leaving group is coordinated to the silver ion and occupies an axial position.

Our recent synthesis^{3,5} of the optically active *tert*-butylphenylphosphinothioic iodidate **3** opened up the possibility of the study of the silver-ion-assisted

solvolysis of organophosphorus compounds. The weakness of the $\text{P}-\text{I}$ bond⁶ suggested that under the influence of silver ions it can be heterolytically cleaved with the formation of the positively charged species **1**. Indeed, it was found that whereas the chloride $\text{Bu}'\text{PhP}(\text{S})\text{Cl}$ was stable in the presence of silver ions in nitromethane solution, the iodidate **3** under the same reaction conditions reacted with the production of a complex mixture of phosphorus compounds. When the reaction of **3** (6×10^{-5} mol) with silver perchlorate (6×10^{-5} mol) was performed in a nitromethane solution (10 ml) of triphenylmethane (1.4×10^{-4} mol), the reaction mixture turned intense orange. After centrifugation of the precipitated silver iodide, the UV spectrum of the resulting solution exhibited strong absorption at 405 nm (absorbance = 1.0) and 430 nm (absorbance = 0.98), with a shape characteristic of the triphenylmethyl cation, Ph_3C^+ .^{*} The formation of the triphenylmethylcation in the above reaction can be explained as a result of the hydride shift[†] from triphenylmethane to the very reactive cationic species generated from the iodidate **3** under the influence of silver ions [equation (1)].

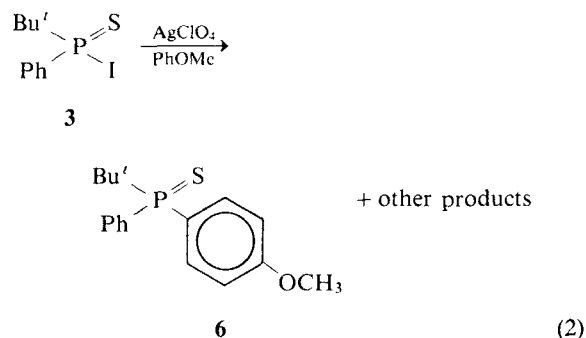


* It was found that Ph_3C^+ was not formed as a result of the reaction of Ph_3CH with silver perchlorate. For the UV investigation of Ph_3C^+ , see Ref. 7.

† Recently reactions involving hydride shifts were used in the study of silylenium cation, R_3Si^+ , formation.⁸

The ^{31}P NMR spectrum of the resulting reaction mixture showed that among many organophosphorus products, the sulphide $\text{Bu}'\text{PHP}(\text{S})\text{H}$ (**5**) was not present. Probably, if **5** was formed as a reaction product, it underwent further reactions or formed complexes with silver perchlorate.

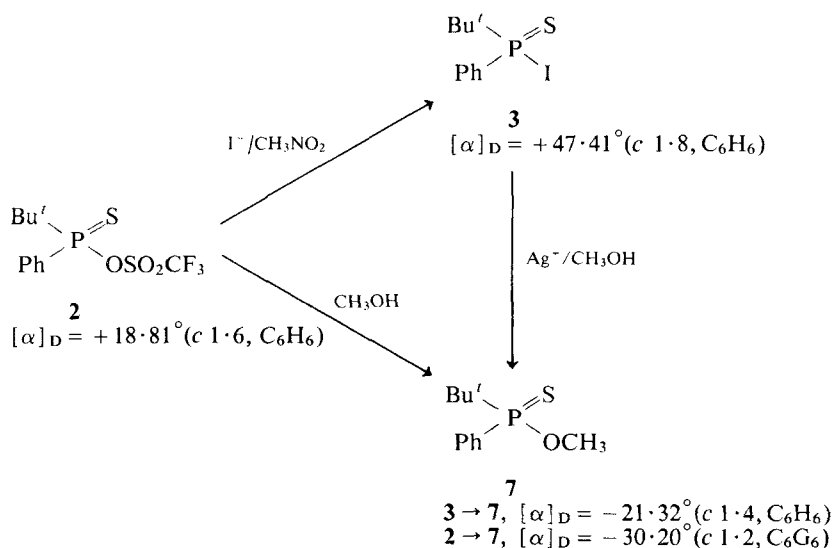
Chemical evidence for the generation of the cation **1** from the iodidate **3** under the influence of silver ions was supplied by the reaction performed in anisole as a solvent. When 0.063 g (0.002 mol) of **3** dissolved in anisole (1 ml) was treated with a nitromethane solution (0.7 ml) of silver perchlorate (0.06 g, 0.000203 mol), a complex mixture of products was formed. ^{31}P NMR and gas chromatographic-mass spectrometric analysis of the reaction mixture revealed the presence of the phosphine sulphide **6**, formed as a product of an electrophilic attack of the cation **1** on the aromatic ring of anisole [equation (2)].



The sulphide **6** was formed in a very low yield (4% by ^{31}P NMR) and was not isolated from the complex reaction mixture. Nevertheless, the chromatographic properties (TLC, GLC), m/z values and the mass spectrum of the compound found in the reaction mixture were identical with those of phosphine sulphide (**6**) synthesized independently.³

The complexity of the reaction mixture is not surprising. Heterolytic bond cleavage between phosphorus and iodide led to the formation of a positively charged organophosphorus intermediate, which can exist as part of differently constituted ion pairs.⁹ In the absence of nucleophilic reagents which can react with phosphorous atom, decomposition of the cation **1** leads to a variety of products.

The ionic character of the P—I bond breaking that occurred under the influence of silver ions and the availability of **3** in an optically active form created a unique opportunity for studying the stereochemical course of silver-ion-assisted solvolysis reactions. It was found that the iodide **3** dissolved in methanol was solvolytically stable and was not converted into the corresponding ester **7**. Addition of silver perchlorate to a methanolic solution of **3** caused immediate precipitation of silver iodide and the formation of the reaction product (**7**). When the optically active iodidate (+)-**3** was used as a substrate, the reaction led to the formation of optically active *O*-methyl ester (–)-**7**. The stereochemical course of this reaction was established on the basis of the stereochemical cycle presented in Scheme 1.



Scheme 1

Two of the three reactions in the stereochemical cycle are of known stereochemistry. It was found earlier that the conversion of the anhydride **2** into the iodide **3** proceeds with retention of configuration at the phosphorus atom.³ Inversion of configuration was found³ for the methanolysis of the anhydride **2**, leading to the ester **7**. Based on these results, it can be deduced from Scheme 1 that silver-ion-assisted solvolysis of **3** leads to the product **7** with inversion of configuration at the phosphorus atom. Ester **7** formed via the route **2** → **3** → **7** is of lower optical purity than the product formed via **2** → **7**. This can be attributed to the low stereoselectivity of the conversion **3** → **7**, but is also due to the relatively low stereoselectivity of the reaction **2** → **3**, as shown earlier.³

CONCLUSIONS

In previous work, silver-ion-assisted solvolysis of organophosphorus compounds was studied in search for a phosphacylium cation as reaction intermediate.⁴ It was expected^{4a} that the products formed in such a reaction would be racemic or have retained configuration. The results presented here illustrate conditions under which the phosphorus—iodide bond is heterolytically cleaved and a phosphathiacylium cation is produced. The stereochemical study of this reaction showed that previous assumptions were not correct and the inversion of configuration at the phosphorus atom dominates as the stereochemical reaction course.

EXPERIMENTAL

NMR spectra were recorded on JEOL JNM-FX6FT (24.3 MHz, ³¹P) and Bruker MSL-300 spectrometers. Products were identified with an LKB MNodel 2091 gas chromatograph—mass spectrometer. UV spectra were recorded on Specord-M40 instrument. Quartz cells of 0.1 mm were used. Optical rotations were measured at 589 nm at 20 ± 2 °C on a Perkin—Elmer 141 polarimeter. Thin-layer chromatography was performed on Merck silica gel 60F₂₅₄ sheets of 0.25 mm thickness. Column chromatography was performed on Merck silica gel (100–200 mesh). Optically active **3** was synthesized as described earlier.³

Silver-ion-assisted methanolysis of 3. To a solution of 0.083 g (0.0004 mol) of silver percholate in 8 ml of dry methanol, a solution of 0.065 g (0.000205 mol) of **3** in 1 ml of benzene was added. After the reaction was completed, precipitated silver iodide was filtered off. The filtrate was concentrated under reduced pressure and subjected to column chromatography (100–200-mesh silica gel, benzene). The isolated ester **7** was found to be identical with an authentic specimen.³

ACKNOWLEDGEMENT

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