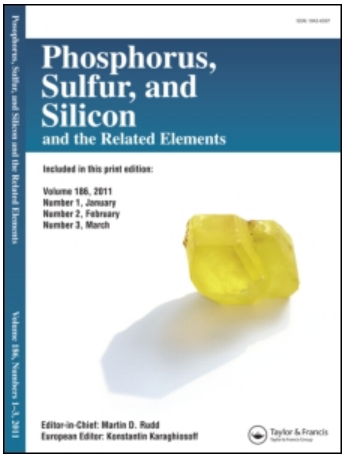

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MECHANISM OF THE CHLOROLYSIS REACTION OF P-S BOND IN PHOSPHORUS THIOLOESTERS. THE EFFECT OF THE SUBSTITUENT AT SULFUR ATOM ON THE STEREOCHEMISTRY

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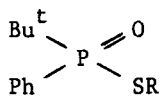
Abstract The effect of the substituent at sulfur atom on the stereochemistry of the chlorolysis reaction of P-S bond in phosphorus thioloesters was studied. It was found that the presence of the substituents lowering electron density at this atom reduces the reaction rate. Stereochemical aspects of this fact are discussed.

In our previous work[1], we have shown that the chlorolysis reaction of thioloesters of phosphorus acids involves the formation of two types of intermediates: chloro(phosphoryl)sulfonium salts, $RR'P(O)\overset{+}{S}(Cl)R''\ Cl^-$ and phosphoryloxyphosphonium salts, $RR'P(O)O\overset{+}{P}(SR'')RR'\ Cl^-$. This fact has apparently the important consequences for the reaction stereochemistry.

The present work is concerned with the investigation of the effect of substituent attached to the sulfur atom of phosphorus thioloester on the stereochemical course of the reaction. The interest in this problem arises from the early work from this Laboratory[2], which reports very strong effect of the substituent at sulfur atom on stereochemistry: the change of the S-ethyl group in O,S-diethyl ethylphosphonothioate for the S-2-chloroethyl inverses the stereochemistry. This fact has never been satisfactorily explained.

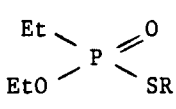
We supposed that the substituent at sulfur atom ought to influence the course of the reaction by the change of the nucleophilicity of sulfur atom. We expected that the observation of the ^{31}P NMR spectra of the reaction mixtures containing the esters with various S-substituents would allow to find differences in the contribution of the particular intermediates, what would allow to clarify the inexplicable stereochemical results.

As the models for our investigations, we have used the series of the S-methyl, S-2-chloroethyl and S-phenyl phosphoro-, phosphono- and phosphinothiolate, which were reacted with sulfuryl chloride. In order to simplify the discussion, the results obtained for two sets of models will be described below: esters of tert-butylphenylphosphinothioate, 1a-c and O-methyl ethylphosphonothioate 2a-b.



1

(a) R=Me
(b) R=CH_2CH_2Cl
(c) R=Ph



2

(a) R=Me
(b) R=CH_2CH_2Cl

The reaction of the chosen models with chlorinating agent was carried out in the temperature range 183-293 K in methylene chloride. The course of the reaction was observed by means of ^{31}P NMR, depending on the temperature and the time (Table I). The measurements had not the character of any precise kinetic studies. However, the application of the comparable conditions allows us to draw some semiquantitative conclusions concerning the differences in the reaction rates between the particular models.

TABLE I. ^{31}P NMR Analysis of the reaction of Et(EtO)P(O)SR with SO_2Cl_2 in CH_2Cl_2

No of compd.	Temp.(K)	Relative intensity of ^{31}P NMR signals (%)							
		198		203		243		273	
		(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)
(1)		48	85	15	75	6	16	-	14
(5)		21	7	35	12	-	-	-	-
(6)		25	8	44	13	76	56	84	57

(i): R=CH_3; (ii): R=CH_2CH_2Cl

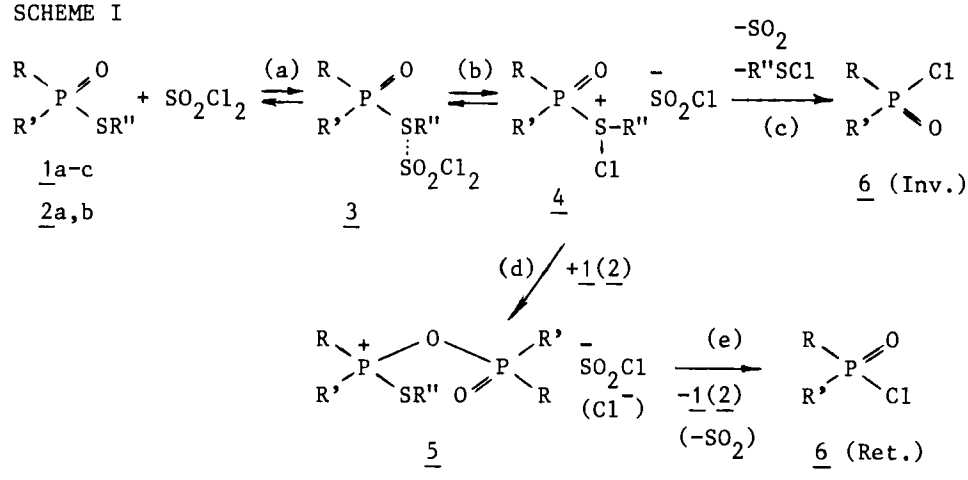
The results shown reveal, that thioloester which contains sulfur atom substituted with electron withdrawing group (R=CH_2CH_2Cl) reacts dramatically slower when compared to ester with S-methyl group. The same results have been obtained from the studies of the reactions of esters 1a-c. The differences in the rates of the reactions of these models are manifested in the fact, that at the room temperature, when the reaction of 1a was completed, the esters 1b and 1c were still un-

changed in 76% and 39%, respectively. Additionally, from the ^{31}P NMR spectra, it was found, that only in the case of the reaction of ester 1a the signal characteristic for intermediate 4 (or equilibrium 3 ⇄ 4) has been observed. Neither during the reaction of 1b, nor 1c the corresponding signals appeared. However, intermediates which contain two phosphorus atoms, i.e. phosphonium salts 5 were present in all studied reaction mixtures.

Stereochemical investigations of models 1a-c and the reinvestigation of 2a-b show, that the chlorolysis of all three esters 1a-c and ester 2b involves the retention of the configuration, while the ester 2a reacts with inversion. The data concerning esters 2a-b are in agreement with those described earlier.[2]

The experimental facts suggest that in the discussed examples the formation of chlorosulfonium salt 4 is the crucial step of the studied reaction. Due to the fact that this step is reversible, the introduction of the substituent, which lowers electron density at the sulfur atom either by the inductive effect (1b, 2b), or owing to the mesomeric effect (1c), results in the shifting of the equilibrium to favor the starting materials.

SCHEME I



If the sulfonium salt 4 is formed immediately and if it collapses relatively fast to give the reaction product 6 via path (c), the reaction will involve inversion of configuration, as in the case of the ester 2a. However, the presence of the intermediate 5, suggests some contribution from the second mechanism with retention of configuration.

It clarifies relatively low stereoselectivity observed in the reaction of ester 2a.[2]

Under the conditions when the formation of chlorosulfonium salt 4 is slower than its further reactions, the importance of the pathways (b), (d), (e) involving retention of configuration (by two inversions) is enhanced. It follows from the fact that in the reaction medium the high concentration of the uncomplexed starting ester is present. It is able to react as nucleophile, competing with chloride anion, which is present in rather low concentration. This is probably the case of the ester 2b, which reacts with retention of configuration. The low stereoselectivity observed for this reaction, results from the considerable contribution from the pathway (c).

In the case of models 1, we have additional effect of the bulky substituent at the phosphorus atom, which favors the reaction via pathways (d) → (e) with retention of configuration, even in the case of the ester 1a.

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REFERENCES

1. B. Krawiecka, J. Michalski, E. Wojna-Tadeusiak, J. Org. Chem., 51, 4201 (1986).
2. J. Michalski, A. Ratajczak, Roczniki Chem., 37, 1185 (1963).