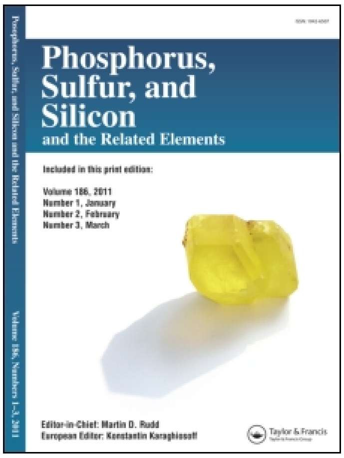

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REACTIONS OF PHOSPHORUS MONOTHIO ACIDS WITH ALIPHATIC DIAZO COMPOUNDS †

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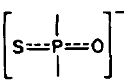
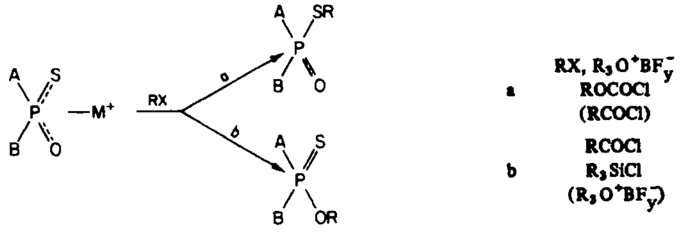
Reactions of phosphorus monothio acids with diazomethane, diazoacetone, diphenyldiazomethane, and diazofluorene have been studied. The ratio of the yields of the S- and O-derivatives Q_S/Q_O has been found to be dependent on three factors: (i) the nature of substituents at phosphorus – with electron-donor substituents raising the O-derivative yield and the quantity log (Q_S/Q_O) varying as $\Sigma\sigma^\Phi$ of the substituents; (ii) stability of alkyldiazonium and carbocation – with Q_O increasing with the carbocation stability; and (iii) polarity of the medium – the O-derivative yield rises with dielectric permeability of the medium and Q_S/Q_O has been found to be a linear function of $1/D$. The most probable mechanism has been established as proton transfer from the acid to the diazocompound followed be formation of the S-derivative and the O-derivative. The former results from an S_N2 reaction of the alkyldiazonium cation with the thiol-thione anion within the ion pair. The O-derivative arises from the thiol-thion anion and the carbocation; the latter resulting from decomposition of the alkyldiazonium cation within the ion pair.

INTRODUCTION

Reactivity of the thiophosphorus triad  $\left[S{=}P{=}O\right]^-$ is an attractive problem of organophosphorus chemistry. It pertains also to a general problem of reactivity of ambident anions. Synthetically the triad SPO is a crossroad for many preparative routes in organophosphorus chemistry.

We have been studying the action of electrophiles on organophosphorus thione-thiol acid anions and, primarily, alkylation and acylation of phosphorus monothio acid salts.[1-6]



It has been found that the direction of the reaction depends on various factors such as the nature of the electrophile, the substituents at phosphorus, solvent, and so on. Alkyl halides attack the sulfur end of the triad preferentially, if not exclusively, and yield the thiol esters. The highly electrophilic acyl halides and chlorosilanes predominantly attack the oxygen end. The most electrophilic aklylating agents such as triethyloxonium tetrafluoroborate attack both the sulfur and the oxygen, byt prefer sulfur.[7]

Solvent effects and the nature of the cation have been studied infrequently. Last year we found however that bipolar solvents active in solvating cations may facilitate the O-reactions. The O-esters accompanied by the S-esters form isopropyl or isobutyl bromides when acted upon by sodium diethyl monothiophosphate in dimethylformamide or hexamethylphosphorotriamidate. *n*-butyl or isobutyl tosylates in these solvents give the O-esters in yields as high as 20%, or even higher.

Kornblum's rule[8] probably operates in the general case, that is, a transition state of the S_N2 type (with respect to the electropihile carbon) favors the reaction at sulfur (the soft-soft interaction according to Hudson[9]), and a transition state of the S_N1 type favors the reaction at oxygen (the hard-hard interaction).

In media of low dielectric constant ion pairs play an important part. In these solvents, the cation probably has nothing to seize but the oxygen end, the site of the highest electron density.[10-14] Consequently the

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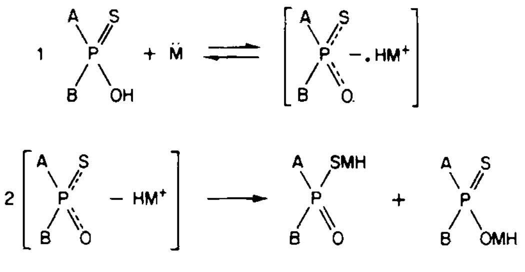
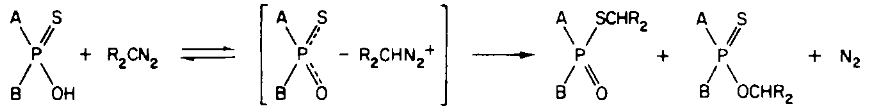
electrophilic attack on sulfur is facilitated. Bipolar solvents favor the O-reaction because they solvate the cation, remove it from the oxygen end, and thus make the site more open to electrophilic attack.

On the whole the problem is very complicated. To solve it some simplifications are necessary. One approach consists in using the reactions where the attacking electrophile is the counterion of the salt. In this way the electrophile/cation interaction problem, or the shielding problem, is eliminated. Further, solvents of small dissociating ability may be used to force the process into ion pairs which produces first-order reactions in all cases. Reactions of this kind should embrace various known or assumed processes for phosphorus monothio acids in which the proton leaves the acid for the base that will become an electrophile.



Examples are the alkylation of phosphorus monothio acids with diazo alkanes,[15-18]

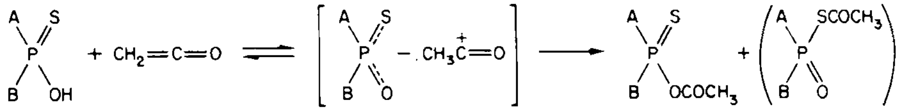


which are similar to the alkylation of carboxylic acids[19]

$$RCOOH + R_2CN_2 \rightleftharpoons [RCOO^-.R_2CHN_2^+] \longrightarrow RCOOCHR_2 + N_2$$

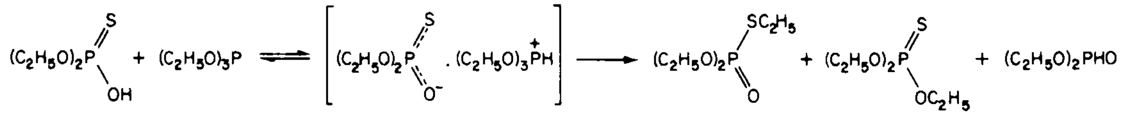
and acylations with ketene.[20]

The latter reaction resembles formation of acetic anhydride from ketene and acetic acid.

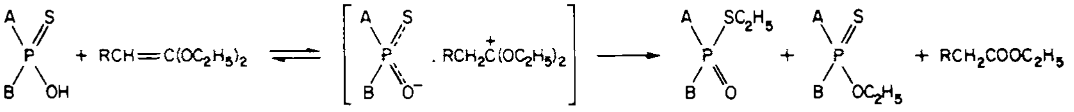


$$CH_3COOH + CH_2{=}C{=}O \rightleftharpoons [CH_3COO^-.CH_3\overset{+}{C}{=}O] \longrightarrow (CH_3CO)_2O$$

Another example is a reaction of diethyl thiophosphate with triethyl phosphite.[21]

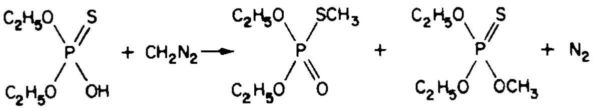


Another case is the reaction with ketene acetals:[22]



Reactions with ethylene oxide or carbodiimides may also be relevant. Unfortunately none of these reactions have been studied quantitatively in any depth.

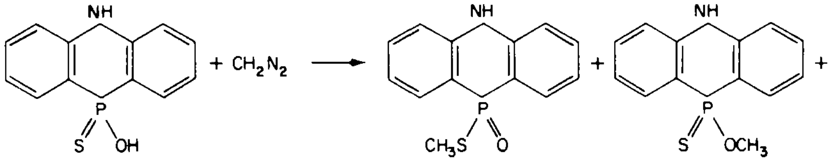
In this article I will speak of the results obtained in our recent study of reactions of phosphorus monothio acids with diazo alkanes or other aliphatic diazo compounds. More than ten years ago, we found[15] that phosphorus monothio acids, when alkylated with diazomethane, yielded both the S- and the O-methyl esters.

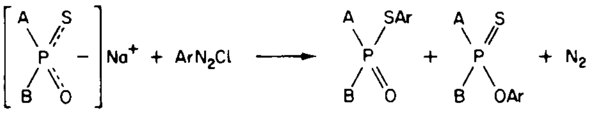


The S/O yield ratio depended on the substituents attached to the phosphorus.[15,16,23] For instance, the O-derivative yield decreased across the series

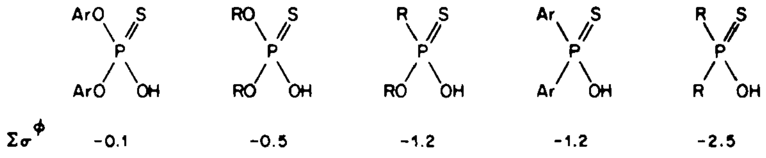
$$(RO)_2PSOH > R(RO)PSOH > R_2PSOH$$

Formation of isomeric S- and O-esters in reactions of phosphorus thio acids with diazo compounds was published later by other authors.[24,25]

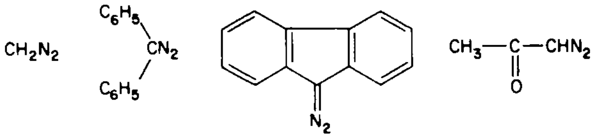




We have thoroughly studied reactions of phosphorus monothio acids with aliphatic diazo compounds. Various monothio acids were subjected to the alkylation.



Substituents at the phosphorus were selected so that the sum of the polar constants $\Sigma\sigma^{\Phi}$ would vary over a wide range, as indicated under the formulae. Thus the strength of the acids and hence the nucleophilicity of the anions varied greatly. Reactions with various diazo alkanes were studied.



The diazo alkanes were selected to provide the widest possible variation in the stability of both the diazo compound proper and the resulting diazonium and carbonium cations.[19] Aprotic media were used throughout to avoid any reaction with the solvent. Maximum possible variation in the range of solvent polarity was employed.

GENERAL EXPERIMENTAL PROCEDURE

In all cases a phosphorus monothio acid in a selected solvent was allowed to react with a diazo compound by merely mixing the solutions at room temperature, sometimes followed by heating the mixture. The reaction time depended strongly on the reactivity of the diazo compound and the strength of the acid. After nitrogen evolution ceased, the reaction mixture was analyzed for the O- and S-isomer content. The yield ratio Q_S/Q_O was a characteristic of the reaction pattern. The analysis employed ir, pmr, and glc methods. To test the procedures and plot the ir and glc calibration curves, esters of known structures were synthesized and used to prepare test mixtures. Thiol esters were synthesized by alkylating a salt of the respective monothio acid with halogen compounds[1-6]

$$\mathrm{ABPSONa} + \mathrm{RX} \longrightarrow \mathrm{ABP(O)SR} + \mathrm{NaX}$$

and thione esters by a reaction of the respective alkoxide with the thione acid chloride.[26]

$$\mathrm{ABP(S)Cl} + \mathrm{NaOR} \longrightarrow \mathrm{ABP(S)OR} + \mathrm{NaCl}$$

In some cases the reference compounds were synthesized from a monothio acid and a diazo compound. As a matter of course the syntheses were carried out on a preparative scale. The resulting S- and O-derivatives were separated, purified, and structures assigned in an appropriate way.

Ir analyses were carried out using the P = O band intensities (at 1190 to 1280 cm^{-1}) for thiol esters, the P–O–C band intensities (at 800 to 1000 cm^{-1}) for thione esters. pmr analyses were based on the ratio of intensities of the protons attached to sulfur and the protons attached to oxygen. The signals were usually resolved fairly well (Fig. 1).

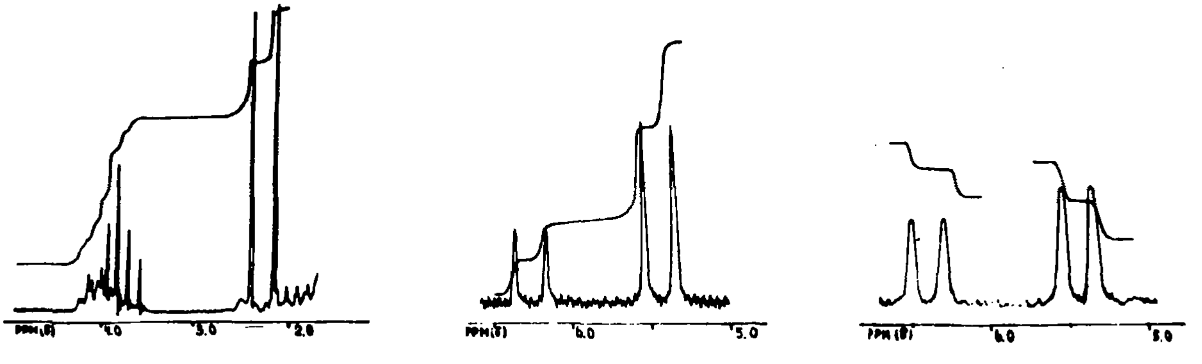


FIGURE 1 ^{1}H-nmr spectra of the reaction mixtures: (a) $(C_4H_9O)_2PSOH + CH_2N_2$; (b) $(C_2H_5O)CH_3PSOH + (C_6H_5)_2CN_2$; (c) $(C_2H_5O)_2PSOH + (o\text{-}C_6H_4)_2CN_2$.

In some cases the CH signal was too close to the intense aromatic proton signal. Consequently only one of the doublet components was used for the integration. Sometimes however the overlapping made any analysis impossible. Internal reference compounds were used in our glc analyses. Retention times are lower for thione esters than thiol esters; therefore the peaks were readily assignable. Chromotographic conditions were selected to avoid any thione-thiol rearrangement. Table I compares analytical results obtained *via* various techniques.

Table I

The S/O ester yield ratio in the reaction of acids ABPSOH with diazo compounds (DM-diazomethane, DDM-diphenyldiazomethane, DF-diazofluorene) as determined by ir, pmr and glc techniques.

Diazo	Tho acid			Method	
compound	A	B	ir	pmr	glc
DM	C_6H_5O	C_6H_5O	$\frac{82.3}{17.6}$	$\frac{82.5}{17.5}$	...
DM	C_2H_5O	C_2H_5O	$\frac{80.5}{19.6}$	...	$\frac{81.3}{18.7}$
DM	CH_3	C_2H_5O	$\frac{86.6}{12.9}$	$\frac{87.0}{13.0}$	$\frac{86.0}{14.0}$
DDM	CH_3	C_2H_5O	...	$\frac{74.5}{25.5}$	$\frac{73.8}{26.2}$
DDM	C_2H_5	C_2H_5	...	$\frac{81.1}{18.9}$	$\frac{79.8}{20.2}$
DF	C_2H_5	C_2H_5	$\frac{58.0}{42.0}$	$\frac{59.0}{41.0}$	...
DF	i–C_3H_7	i–C_3H_7	$\frac{59.4}{40.6}$	$\frac{61.0}{39.0}$	...

GENERAL CONSIDERATION

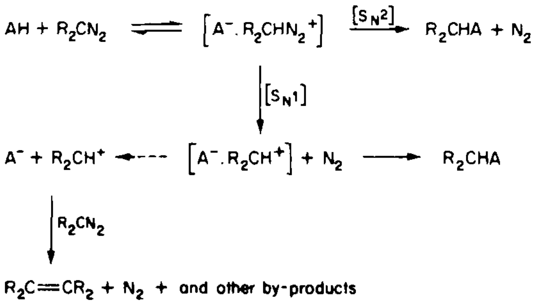
Before coming to the results and discussion, let us consider the kinetics and mechanism of reactions of aliphatic diazo compounds with acids. Diphenyldiazomethane is a favorite choice of researchers. It is easy to treat and allows one to follow the kinetics readily by spectrophotometry. Many contributions were made by Roberts and his team,[27,28] Chapman and his coworkers,[29-33] and More O'Ferrall with his group.[34] Many other workers have also made essential contributions to this problem.[19,35]

Kinetic studies by Roberts, Regan and Allen,[36] Lane and Feller,[37] and others[19] clarified the mechanism of the diazoacetic ester reactions. With diazomethane and its homologs, kinetic studies appear very difficult. Other methods were used. For instance, comparative isomerizations of alkyl groups in reactions of diazo alkanes with acids, in decomposition of nitrosoalkyl acyl amines, or in reactions of alkyl amines with nitrous acid. They shed some light on the mechanism (see, for example, papers by Huisgen and coworkers[38]).

A conventional point of view is that the first step of a reaction of a diazo alkane or another aliphatic diazo compound with an acid is proton transfer from the acid to the diazo alkane. The next steps are matters of controversy. Perhaps the most general scheme was put forward by Gompper,[39] as he suggests, the mechanism in an aprotic medium may be written as follows (Scheme 1).

The first step is proton transfer resulting in an ion pair that includes the anion of the acid and the diazonium cation. It may be reversible and fast (the pre-equilibrium case) or practically irreversible and slow. Nitrogen evolution may occur directly in the ion pair and result in the ester. This is an S_N2 reaction where the carboxylate anion is an attacking electrophile while nitrogen is the leaving group. The reaction proceeds within the ion pair, hence its first-order kinetics.

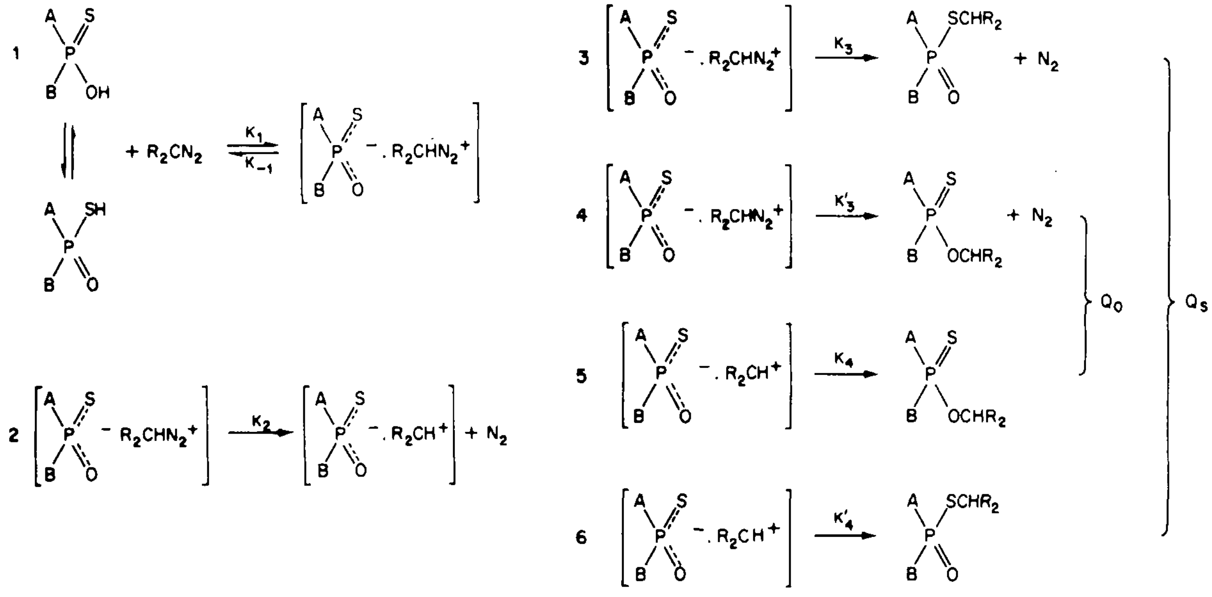
The other possibility is cleavage of the diazonium cation within the ion pair resulting in evolution of nitrogen and formation of a new ion pair comprising a carboxylate anion and a carbocation. This is an S_N1 reaction with respect to the diazonium cation. The reaction is, of course, of the first order. Finally, the new species couple within the pair and yield the ester. Again we have a first order reaction. In an alcohol medium the process is complicated by the fact that the diazonium cation and/or the carbocation escape from the cage and react with the solvent. This results in an ether.



Scheme 1

$$A^- + R_2CH^+ + ROH \longrightarrow AH + R_2CHOR$$

The escape however is possible in aprotic media as well. The lone electrophilic cation reacts with the starting diazo molecule serving as a nucleophile and this leads to byproducts. When applied to phosphorus monothio acids the pattern is complicated since the acid is tautometric and the thiol-thione anion is ambidental (Scheme 2).



Scheme 2

The diazonium cation may give both the S- and the O-esters (3 and 4) *via* the S_N2 type reaction. The carbocation may also couple with the thiol-thione anion at either the oxygen or the sulfur (5 and 6). The processes occurring within the ion pair obey first-order kinetics.

If the proton transfer is the rate-controlling, slowest step and the constant k_1 is much lower than the other constants, then all the ion pairs may be considered very unstable species and the stationary-state method may be applied. Then the ratio of rates may be expressed as follows:

$$\frac{V_S}{V_O} = \frac{k_3(k_4 + k_4') + k_4 k_4'}{k_3'(k_4 + k_4') + k_4 k_4} \tag{1}$$

The rate ratio for the formation of the thiol and thione isomers V_S/V_O turns out to be a constant that does not depend on either concentration or the total rate constant k_1. A possible conclusion is that V_S/V_O does not depend on the extent of conversion. Patterns of this kind were discussed by Exner[40] who showed that the rate ratio was equal to the yield ratio at any conversion.

$$\frac{V_S}{V_O} = \frac{Q_S}{Q_O} \tag{2}$$

In some cases the pre-equilibrium becomes important and nitrogen evolution is the rate-controlling step. The equilibration is fast; therefore we may write equation (3)

$$[\mathrm{ABPSO^-.R_2CHN_2^+}] = K_{eq}\,[\mathrm{ABPSOH}]\,[\mathrm{R_2CN_2}] \tag{3}$$

where K_{eq} is the equilibrium constant whereas the stationary-state method may be applied only to reactions 5 and 6. In this case the ratio of rates leads us to the relation (1) derived above. It is rather striking that the law which governs the isomer ratio does not depend on the rate-controlling step. On the other hand this is not completely unexpected. Expression (1) may be derived without referring to the kinetic equations. Figure 2 shows the reaction fluxes whose powers are proportional to the respective constants (all reactions are of the first order).

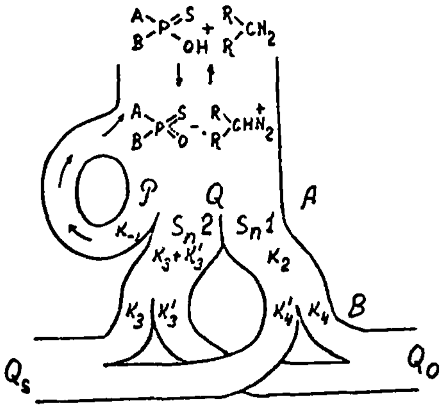


FIGURE 2 The reaction fluxes in the reaction of phosphorus monothio acids with diazo compounds.

At level A, the total flux associated with the interaction of a diazo compound with an acid may be divided into two currents, the retrocycle P (k_{-1}) and the direct current Q. The retrocycle does not affect the ratio Q_S/Q_O and is, therefore, not discussed further. The monomolecular cleavage of the diazonium cation creates two subfluxes, S_N1 and S_N2. It is clear that the right-hand subflux power $Q_{(S_N1)}$ may be written in the form of (4), the left-hand power $Q_{(S_N2)}$ in the form of (5).

$$Q_{S_N1} = \frac{k_2}{k_2 + k_3 + k_3'} Q \tag{4}$$

$$Q_{S_N2} = \frac{k_3 + k_3'}{k_2 + k_3 + k_3'} Q \tag{5}$$

The S_N1 subflux carries carbocations and the S_N2 subflux the diazonium cation. At level B, the carbocation subflux is again divided into two streams proportionally to k_4 and k_4'. The stream k_4 enters the storage term Q_O, the stream k_4' the storage term Q_S. In exactly the same way the S_N2 subflux is divided into two streams: the stream k_3' entering into Q_O and k_3 into Q_S. It is clear that we have to solve an elementary problem and calculate the amount received by the storage terms Q_O and Q_S. Again we come to formula (1). We see that the yield ratio Q_S/Q_O is in fact independent of whether the material enters the direct current slowly or rapidly and whether the retrocycle plays a role.

RESULTS AND DISCUSSION

1. *Diazomethane*[17]

Table II

The yield ratio for the S- and O-reactions (Q_S/Q_O) of phosphorus monothio acids ABPSOH with diazomethane in ether.

No.	A	B	$\Sigma\sigma^{\phi}$	Q_S/Q_O
1	C_6H_5O	C_6H_5O	−0.12	4.68
2	C_2H_5O	C_2H_5O	−0.42	4.31
3	C_4H_9O	C_4H_9O	−0.82	5.05
4	CH_3	C_2H_5O	−1.17	6.24
5	C_6H_5	C_6H_5	−1.18	6.94
6	C_6H_5	i–C_3H_7	−1.78	7.85
7	C_2H_5	C_2H_5	−2.20	10.57
8	i–C_3H_7	i–C_3H_7	−2.60	17.19
9	t–C_4H_9	t–C_4H_9	−3.10	20.74

The most extensive studies were carried out in ether. Table II shows that the highest amounts of O-derivative are formed when diaryl and dialkyl thiophosphates are methylated. Note that the reaction rate decreases in a qualitatively significant way in passing from thiophosphates to thiophosphonates and further to thiophosphinic acids. It is well know that the acidities decrease in the same order. Consequently the total reaction rate falls while the relative S-derivative yield rises, with a decrease in the acidity. The lower rates found for the reactions of weaker acids are quite natural and fit well with known[41] regularities. On the other hand the increase in the relative S-derivative yield requires special discussion.

To employ the kinetic considerations derived above we have to test whether the relation $Q_S/Q_O = V_S/V_O$ is applicable. Table III gives a positive answer.

Table III
Effect of concentrations of $(C_6H_5O)_2PSOH$ and CH_2N_2 on the yield ratio of S- and O-methyl esters (the concentration of 0.05 mol/l is arbitratily taken as unity)

$(C_6H_5O)_2PSOH$ / CH_2N_2	Q_S/Q_O
1/1	4.68
1/2	4.53
1/4	4.77
4/4	4.73

To find how substituents at the phosphorus affect the yield ratio, we have plotted the Hammet correlation using the constants σ^{Φ}.[42]

$$\log (Q_S/Q_O) = \log (Q_S/Q_O)^0 + \rho \Sigma \sigma^{\Phi} \tag{6}$$

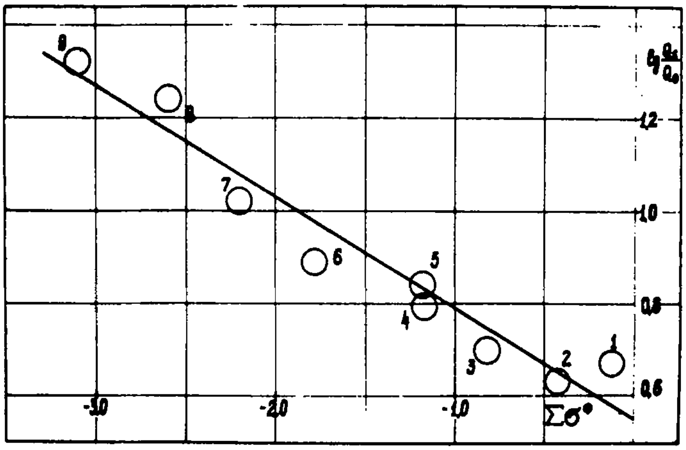


FIGURE 3 Plot of log Q_S/Q_O vs $\Sigma\sigma^{\Phi}$ for the reactions of ABPSOH with CH_2N_2. The circles are numbered with respect to compound numbers in Table II.

Figure 3 presents the plot obtained. The parameters are log $(Q_S/Q_O)^0 = 0.55$, $\rho = -0.24$, $r = 0.971$, $s = 0.006$, $s_\rho = 0.02$. The negative slope suggests that at the yield-ratio controlling stage (or stages) the acid anion is attacked by an electrophile.

Combination of equations (1) and (6) results in the following:

$$\log \frac{k_3(k_4 + k_4') + k_2 k'_4}{k_3(k_4 + k_4') + k_2 k_4} = \rho \Sigma \sigma^{\Phi} + \text{const} \tag{7}$$

Any of the partial rate constants k_i, when considered separately, must obey the Hammett equation because it is expressed through σ^{Φ} as follows:

$$\log k_i = \log k_i^0 + \rho_i \Sigma \sigma^{\Phi} \quad . \tag{8}$$

The linearity of equation (7) will hold if the second derivative is zero.

$$\frac{d^2[\log(Q_S/Q_O)]}{d[\Sigma\sigma^{\phi}]^2} = 0\,. \qquad (9)$$

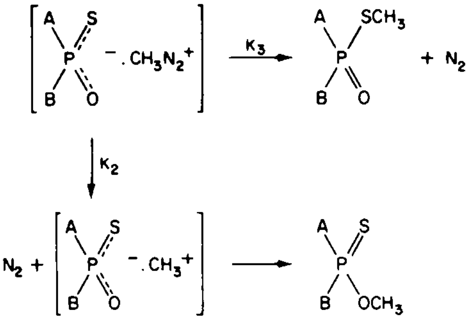
To satisfy this requirement several other requirements should be met. The most probable situation is that k_3' and k_4' are zero. Then we have,

$$\frac{Q_S}{Q_O} = \frac{k_3}{k_2} \qquad (10)$$

The second probable case is $k_3 = 0, k_3' = 0$. The result can be expressed as:

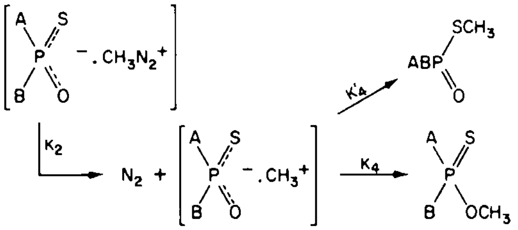
$$\frac{Q_S}{Q_O} = \frac{k_4'}{k_4} \qquad (11)$$

Let us consider both equations from the point of view of the mechanism (Scheme 3).



Scheme 3

The first condition means that the methyldiazonium cation reacts with the thiol-thione anion within the ion pair to form the S-methyl ester *via* an S_N2 reaction of the soft-soft type. Sulfur, the more nucleophilic end of the triad, is attacked. the O-derivative is formed *via* pre-decomposition of the methyldiazonium cation giving the methyl cation which couples to yield only the O-derivative(the hard-hard case). The second condition (Scheme 4) means that the methyldiazonium cation does not enter the S_N2 reaction at all and decomposes completely to give solely the methyl cation.



Scheme 4

The yield ratio Q_S/Q_O is governed by the ratio of the collapse rates with sulfur and oxygen. We will show that this is probable in the reaction of diphenyldiazomethane where the carbocation is stable since the diazonium cation decomposition energy is low (cf. Ref. 19). Decomposition of the methyldiazonium cation leads to a very unstable ion (methyl cation). This should raise the methyldiazonium decomposition barrier higher than the S_N2 reaction barrier. Consequently the methyldiazonium cation S_N2 reaction cannot be ruled out and the first condition is preferred with respect to diazomethane.

The monomolecular cleavage of the methyldiazonium cation does not depend on the constant σ^{Φ}; therefore the entire effect exerted by substituents at the phosphorus on Q_S/Q_O is transmitted by k_3 and we may write

$$\log(Q_S/Q_O) = \log k_3^0 - 0.24\,\Sigma\sigma^{\Phi} \tag{12}$$

This agrees both with the negative ρ due to the S_N2 type reaction (the methyldiazonium cation attack on the thiol-thione anion) and with the low absolute magnitude of the constant ρ. Low values of this kind were often observed for reactions affecting sulfur in the S–P–O and S–P–S triads.[42] If our conclusion is correct higher solvent polarities will accelerate the monomolecular decomposition of the methyldiazonium cation whereas the S_N2 type reaction will be affected just slightly. We have studied solvent effect on Q_S/Q_O for the reaction of diethyl thiophosphate with diazomethane. Table IV and Figure 4 present the results. It is apparent that an increase in the dielectric constant of the medium does favor the O-methylation (Q_S/Q_O decreases) which agrees with our assumption.

Table IV

Solvent effect on the yield ratio Q_S/Q_O) for the reaction of diethyl thiophosphate with diazomethane.

Solvent	D	Q_S/Q_O
Hexane	1.89	7.30
Benzene	2.27	5.93
Ether	4.33	4.56
THF	7.40	3.29
Methylene bromide	7.70	4.00
Acetonitrile	37.5	3.55

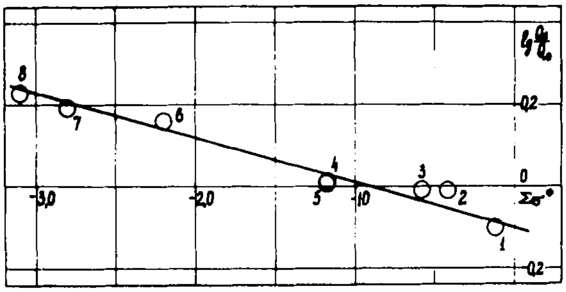


FIGURE 4 Plot of log (Q_S/Q_O) vs 1/D for the reaction of $(C_2H_5O)_2PSOH$ with CH_2N_2 (slope + 0.60; r 0.994; s 0.02).

2. *Diphenyldiazomethane*[18]

It has already been mentioned that reactions of diphenyldiazomethane with acids differ from the diazomethane reactions in that proton transfer is the rate-determining step and the diphenyldiazonium cation is much more susceptible to S_N1 decomposition because its carbocation is more stable. One should expect therefore that higher amounts of the O-derivative will form.

Indeed, the Q_S/Q_O values are lower than in the experiments with diazomethane (Table V, cf. Table II). They decrease with an increase in electron acceptor effect of substituents at the phosphorus. The linear correlation $\log(Q_S/Q_O) = 0.29 - 0.18\,\Sigma\sigma^{\phi}$; ($r$, 0.969; s, 0.04; s_ρ, 0.02) has been observed (Figure 5). The absolute magnitude of the slope ρ (−0.18) is lower than that found for the diazomethane reactions. It is plausible to assume that the S/O yield ratio is governed by the ratio of rate constants k_3/k_2 and that the S-derivative should be formed *via* the S_N2 reaction. It has never been proven that nitrogen evolution occurs under conditions of nucleophilic assistance in any reaction of diphenyldiazomethane with acids. We have therefore to allow the S_N1 reaction and then Q_S/Q_O is equal to k'_4/k_4. In other words the benzhydryl cation may attack both ends of the triad. However this assumption does not explain why the reaction at sulfur is faster than the one at oxygen.

Table V
The yield ratio for S- and O-benzhydryl esters for the reaction of ABP (S) OH with diaphenyldiazomethane in ether.

No.	A	B	$\Sigma\sigma^{\phi}$	Q_S/Q_O
1	C_2H_5O	C_2H_5O	−0.42	2.28
2	CH_3	C_2H_5O	−1.17	2.92
3	C_6H_5	C_6H_5	−1.18	3.83
4	CH_3	i−C_3H_7O	−1.25	3.35
5	CH_3	C_3H_7O	−1.28	3.26
6	CH_3	c−$C_6H_{11}O$	−1.31	3.22
7	CH_3	C_4H_9O	−1.37	3.54
8	C_2H_5	C_2H_5	−2.20	4.29
9	i−C_3H_7	i−C_3H_7	−2.60	5.57
10	t−C_4H_9	t−C_4H_9	−3.10	7.47

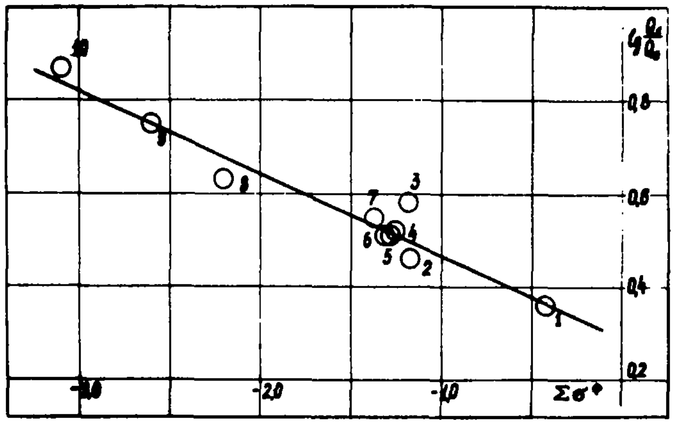


FIGURE 5 Plot of $\log(Q_S/Q_O)$ vs $\Sigma\sigma^{\phi}$ for the reaction of ABPSOH with $(C_6H_5)_2CN_2$. The circles are numbered with respect to compound numbers in Table V.

Table VI
Rate constants for the reaction of diphenyldiazomethane with phosphorus monothio acids ABP (S) OH in ether at 20°.

No.	A	B	k_1 l/mole sec.
1	C_2H_5O	C_2H_5O	0.105
2	CH_3	C_2H_5O	0.058
3	C_2H_5	C_2H_5	0.020
4	i–C_3H_7	i–C_3H_7	0.012

Diphenyldiazomethane reacts with acids rather slowly and the total rate, hence the constant k_1, may be determined. The experiments were carried out in ether using a photocolorimetry technique. Table VI lists the resulting bimolecular rate constants. The constant rises, as expected, with increasing electron withdrawing effect of the substituents; in other words, with acidity.The plot of log k_1 vs $\Sigma\sigma^{\Phi}$ is a straight line with a slope of 0.4 (Figure 6).

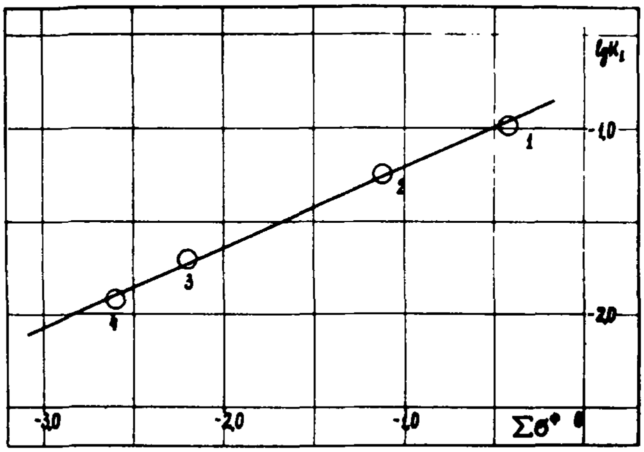


FIGURE 6 Plot of log k_1 vs $\Sigma\sigma^{\Phi}$ for the reactions of ABPSOH with $(C_6H_5)_2CN_2$. The circles are numbered with respect to compound numbers in Table VI.

3. *Diazofluorene*

The diazofluorene carbonium ion is approximately as stable as the benzhydryl cation. On the other hand some 9-substituted fluorenes can react *via* an S_N2 mechanism[43] which is nearly unknown for diphenylmethane derivatives.

The experiments were carried out in acetonitrile. Table VII and Figure 7 show the results obtained and the correlation with the constants σ^{Φ} based on the equation $\log(Q_S/Q_O) = -0.10 - 0.11\ \Sigma\sigma^{\Phi}$ (r, 0.995; s, 0.01; s_ρ, 0.004). The correlations found for diazofluorene, diphenyldiazomethane, and diazomethane are evidently identical. The slope is a small negative value in all these cases.

Table VII
The yield ratio for S- and O-fluorenyl esters for the reaction of ABP (S) OH with diazofluorene in acetonitrile at room temperature

No.	A	B	$\Sigma\sigma^{\Phi}$	Q_S/Q_O
1	C_6H_5O	C_6H_5O	-0.12	0.80
2	C_2H_5O	C_2H_5O	-0.42	0.89
3	i-C_3H_7O	i-C_3H_7O	-0.58	0.89
4	CH_3	C_2H_5O	-1.17	1.08
5	C_6H_5	C_6H_5	-1.18	1.04
6	C_2H_5	C_2H_5	-2.20	1.44
7	i-C_3H_7	i-C_3H_7	-2.60	1.56
8	t-C_4H_9	t-C_4H_9	-3.10	1.70

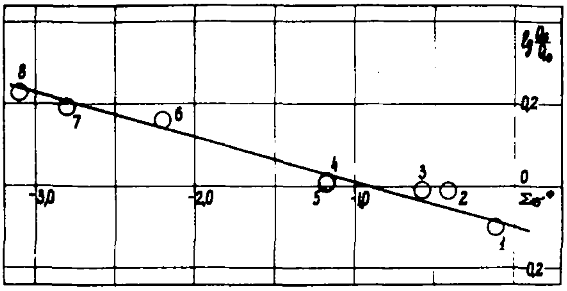
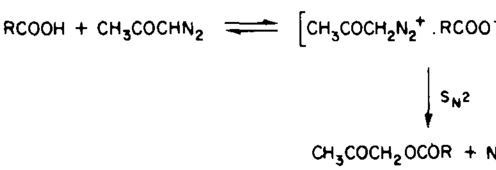


FIGURE 7 Plot of log (Q_S/Q_O) vs $\Sigma\sigma^{\Phi}$ for the reactions of phosphorus monothio acids with diazofluorene. The circles are numbered with respect to acid numbers in Table VII.

4. *Diazoacetone*[44]

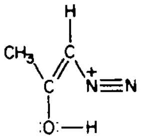
In the diazoacetone reactions with carboxylic acids, the proton transfer is a fast equilibrium step.[19,37] Nitrogen removal from the acetonyldiazonium ion requires conditions of nucleophilic assistance (Scheme 5).



$$RCOOH + CH_3COCHN_2 \rightleftharpoons [CH_3COCH_2N_2^+ . RCOO^-] \xrightarrow{S_N2} CH_3COCH_2OCOR + N_2$$

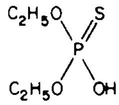
Scheme 5

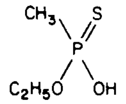
The acetonyldiazonium cation is more stable than other diazonium cations considered in this work. It is enolized and stabilized by conjugation in contrast with all other cases.[51]

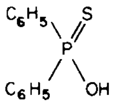


The acetonyl carbocation is very unstable. In any case the acetonyldiazonium cation is known to undergo S_N2 not S_N1 reactions in all cases. If this is correct, the our dual reactivity pattern of thiol-thione anions and diazo compounds requires that the reaction with diazoacetone yield nothing but the S-derivative. This is indeed the case.

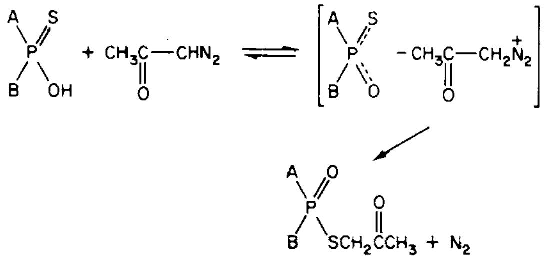
All the acids shown







give only the thiol derivatives when they react with diazoacetone in all solvents tested.



The reaction rate is low; it requires two hours heating at 50°.

5. *Solvent Effect*

The solvent effect is also informative. We have studied the Q_S/Q_O ratio as a function of dielectric constant of the medium. The data for diazomethane have already been shown. A good linear relationship has been found for log (Q_S/Q_O) vs 1/D. Figures 8 and 9 show the results obtained for diphenyldiazomethane and diazofluorene. The curves are linear in all cases; the slopes depend both on the nature of the diazo compound and the thio acid. This is more clearly shown in Table VIII.

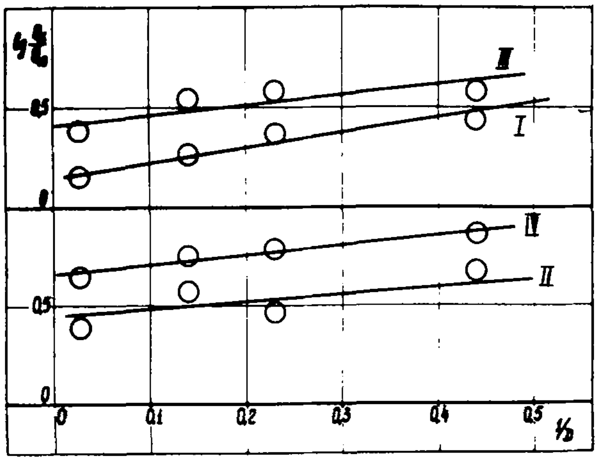


FIGURE 8 Plots of log (Q_S/Q_O) vs 1/D for the reactions of phosphorus monothio acids with diphenyldiazomethane. The acids are I $(C_2H_5O)_2PSOH$; II $(C_2H_5O)\ CH_3PSOH$; III $(C_6H_5)_2PSOH$; IV $(i\text{–}C_3H_7)_2PSOH$. The solvents are benzene, ether, THF, acetonitrile.

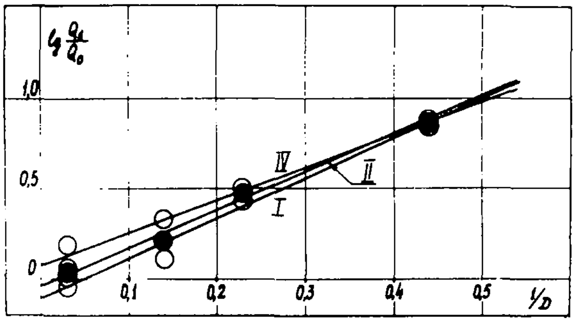


FIGURE 9 Plots of log (Q_S/Q_O) vs 1/D for the reactions of phosphorus monothio acids with diazofluorene. The acids are: I $(C_2H_5O)_2PSOH$; II $(C_2H_5O)\,CH_3PSOH$; IV $(i\text{-}C_3H_7)_2PSOH$. The solvents are benzene, ether, THF, acetonitrile.

Table VIII
Parameters of the lg (Q_S/Q_O) vs. 1/D straight line for reactions of APBSOH with diazo compounds.

Thio acid		DM		DDM		DF	
A	B	lg $(Q_S/Q_O)_0$	tgd	lg $(Q_S/Q_O)_0$	tgα	lg $(Q_S/Q_O)_0$	tgα
C_2H_5O	C_2H_5O	0.52	0.60	0.15	0.71	−0.11	2.19
CH_3	C_2H_5O	...	...	0.39	0.61	−0.04	2.10
$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	...	...	0.65	0.50	0.08	1.78

The linearity of the dependence shows that there is an important contribution of electrostatic interactions in the formation of transition states of the S- and O-reactions. We have used the Scatchard-Laidler-Eyring-Amis equation to estimate the contribution.[45-49] The constant of an ionic reaction depends on the dielectric constant of the medium as follows:

$$\ln K = \ln K_{D\to\infty} - \frac{Z_A Z_B e^2}{KTrD} \tag{13}$$

where Z_A and Z_B are the ionic charges (in our case, $Z_A = Z_B = 1$), e is the electron charge and r is the reaction distance in the transition state.

For reactions of phosphorus monothio acids with diazonium compounds, we have equations (10) and (11) and from them we derived equation (14).

$$\log\frac{Q_S}{Q_O} = \log_{D\to\infty}\frac{Q_S}{Q_O} + \frac{e^2}{2.3kTD}\left(\frac{1}{r_O} - \frac{1}{r_S}\right) \tag{14}$$

where r_O and r_S are distances associated with the transition states of the S- and O-reactions. Hence we obtain the slope

$$tg\alpha = \frac{e^2}{2.3kT}\left(\frac{1}{r_O} - \frac{1}{r_S}\right) \tag{15}$$

which readily gives the quantities $1/r_O - 1/r_S$ shown in Table IX.

Table IX
Values of $(1/r_0 - 1/r_s)$ for reactions of ABPSOH with aliphatic diazo compounds

A	B	$(1/r_0 - 1/r_s)\ 10^{-5}$		
		DM	DDM	DF
C_2H_5O	C_2H_5O	2.46	2.87	8.97
CH_3	C_2H_5O	–	2.50	8.60
$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	–	2.05	7.21

The differences are positive and r_S is higher than r_O. Starting from the most probable distances in the ion pairs, 4.5 to 7.0 Å, we may estimate the differences $(r_S - r_O)$ (Table X). Except for the last value they are lower than the difference between the oxygen and sulfur radii. This hardly fits with the assumption that the carbocation attacks the thiol-thione anion, i.e. the assumption that equation (11) is correct. Consequently it is more probable that $Q_S/Q_O = k_3/k_2$(Eq. 10).

Table X
Values of $(r_s - r_o)$ for reactions for ABPSOH with diazo compounds.

Diazo compound	$(r_s - r_o)$ distance, Å
DM	0.05 to 0.12
DDM	0.05 to 0.14
DF	0.15 to 0.46

Now let us summarize the results obtained. A study of dual reactivity of phosphorus monothio acids in their reactions with diazoacetone, diazomethane, diphenyldiazomethane, and diazofluorene has shown that the mechanism depends on the nature of the diazo compound. With diazoacetone and diazomethane, the data show that pre-equilibrium takes place and nitrogen evolution is a rate-determining step. With diphenyldiazomethane and diazofluorene, proton transfer is the rate-controlling step. These conclusions agree totally with the data obtained earlier for non-tautomeric acids.

The situation is different when we consider the yield-controlling steps. Our data show that for all the diazo compounds these steps have a common mechanism. Namely the O-derivatives arise *via* the carbocations; the S-derivatives are formed *via* nitrogen elimination with nucleophilic assistance provided by the sulfur end of the triad. The literature reports that nucleophilic assistance has been proved for diazoacetone and is quite probable for diazomethane. With diphenyldiazomethane, in its reaction with non-tautomeric acids, nucleophilic assistance has been refuted.

Our conclusion is that nucleophilic assistance also operates in the case of diphenyldiazomethane. The resulting contradiction may be resolved as follows. Of course cation stability plays a decisive part. Other factors however are also worth considering. During acid attack (Fig.10) the proton may move along the perpendicular to the diazo group plane while sulfur tends to range as far as possible from the negatively polarized nitrogen end of the diad. This schematic may be a representation of the most favorable transition structure for the proton transfer. Following this, the diazo group carbon leaves its sp^2 state for the sp^3 state, the diazo group dips below the plane, and the sulfur is thus situated near the carbon and on the side opposite to the diazo group. Nucleophilic assistance is effective; that is to say that an S_N2 type reaction occurs. It is favored by the tetrahedral geometry of phosphorus. This contrasts with carboxylic acids where the second oxygen lies further away and the diphenylmethyldiazonium cation loses nitrogen before the assisted attack takes place. This is, of course, just a model, but it seems to be quite realistic.

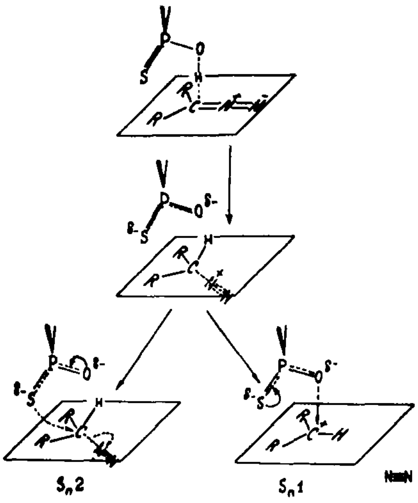


FIGURE 10 Intermediate and transition states for the S- and O-reaction of phosphorus monothio acids with diazo alkanes.

It should also be remembered that in aprotic media carboxylic acids are dimerized to give eight-membered cycles with hydrogen bonds. On the other hand the monothio molecules were shown by us in cooperation with Pogorelyi and others[50] to be trimerized only at their hydroxyls leaving the sulfur free. Consequently in the reactions of diphenyldiazomethane, nucleophilic assistance is possible with phosphorus monothio acids, but not with carboxylic acids.

To sum up, a reasonable assumption in the reactions studied is that the S-alkylation is a nucleophilic S_N2 type of attack of the thiol-thione anion on the diazonium cation, proceeding within the ion pair, whereas the O-reaction is an S_N1 cleavage of the diazonium cation, again within the ion pair, followed by collapse of the carbocation with the thiol-thione anion.

This work was carried out in cooperation with M. Orlov (Belgrade), L. S. Butorina and A. B. Uryupin.

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