# Reaction of Diphenyldiazomethane with Phosphorus Monothioacids

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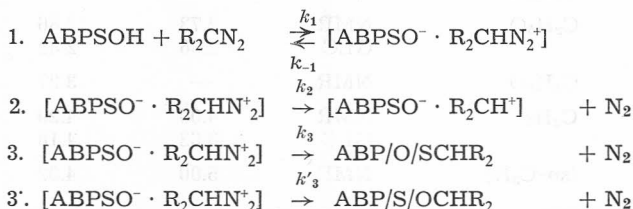
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The mechanism of the reaction of phosphorus monothioacids with diaryldiazomethanes was studied in different solvent systems at 20 °C. The thiolo to thiono product ratios were determined by $^1$H NMR spectroscopy and g.l.c. of the reaction mixtures. The results imply that the reaction involves two competing processes leading to the corresponding $S$- and $O$-isomeric esters.
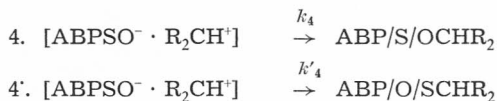
The alkylation of phosphorus monothioacids with aliphatic diazo compounds is a convenient model for studying the dual reactivity of the thiono-thiolo ambident triad, $[S .. P .. O^-]$. Unlike in reactions of metal salts of phosphorus monothioacids with alkyl halides, where the oxygen triad terminus is screened by a metal cation, the protonated diazoalkane molecule (that is, the attacking electrophile) itself acts as the counterion in the reaction under consideration. A detailed study[1-6] of the alkylation of phosphorus mono-thioacids with diazomethane[3], diazopropane[4a], and other aliphatic diazo compounds[4b] has shown that two isomeric esters, the products of the reaction at the sulphur and oxygen ambident triad termini, are formed in aprotic solvents:

$$ABPSOH + R_2CN_2 \rightarrow ABP(O)SCHR_2 + ABP(S)OCHR_2 + N_2$$
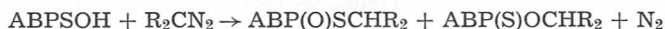
It has also been found that the product ratio $(Q_S/Q_O)$ of $S$- and $O$-esters depends on the properties of the substituents at phosphorus: a linear dependence of $\log(Q_S/Q_O)$ on $\Sigma \sigma^\Phi$, with a negative slope was observed[3,7].

The general scheme of the reaction mechanism may be written as follows:

1. $ABPSOH + R_2CN_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [ABPSO^- \cdot R_2CHN_2^+]$

2. $[ABPSO^- \cdot R_2CHN_2^+] \overset{k_2}{\rightarrow} [ABPSO^- \cdot R_2CH^+] \quad + N_2$

3. $[ABPSO^- \cdot R_2CHN_2^+] \overset{k_3}{\rightarrow} ABP/O/SCHR_2 \quad + N_2$

3'. $[ABPSO^- \cdot R_2CHN_2^+] \overset{k'_3}{\rightarrow} ABP/S/OCHR_2 \quad + N_2$

$$\text{4.} \quad [ABPSO^- \cdot R_2CH^+] \quad \overset{k_4}{\rightarrow} \quad ABP/S/OCHR_2$$

$$\text{4'.} \quad [ABPSO^- \cdot R_2CH^+] \quad \overset{k'_4}{\rightarrow} \quad ABP/O/SCHR_2$$

In agreement with this scheme, the first reaction step does not influence the product ratio. A kinetic analysis of Scheme 1 carried out previously[3] revealed that the following conditions should be met for the scheme to be consistent with the experimental linear dependence of $\log(Q_S/Q_O)$ on $\Sigma \sigma^\Phi$:

$$k_3 = 0, \ k'_3 = 0; \ Q_S/Q_O = k'_4/k_4 \qquad (1)$$

$$k_2 = 0; \ Q_S/Q_O = k_3/k'_3 \qquad (2)$$

$$k'_3 = 0; \ k'_4 = 0; \ Q_S/Q_O = k_3/k_2 \qquad (3)$$

We have already shown[3] that the negative slope of the dependence implies the dominating role of condition (3) in the reaction with diazomethane. That means that the corresponding $S$-methyl ester is formed by the attack of the ambident anion on the methyldiazonium cation (reaction 3) while the $O$-isomer is the product of the attack on the anion oxygen terminus by the carbocation (reaction 4).

Additional experimental evidence was needed to extend this mechanism to the reaction of phosphorus monothioacids with diphenyldiazomethane (DDM). In fact, the diphenylmethyl carbocation has a higher stability than its methyl analogue. As a result, the contributions from reactions 4 and 4' may increase to make condition (1) dominate the process. As for nontautomeric carboxylic acids, they were always believed to react with DDM via the carbocation intermediate.

This work summarises the results of our study on the dual reactivity of phosphorus monothioacids towards DDM, which led to the determination of the degree of participation of diphenylmethyl and diphenylmethyldiazonium cations in the $Q_S/Q_O$ ratio-determining stages.

TABLE I

*The Effect of the Initial Acid (ABPSOH) to DDM Molar Ratio on the Relative Yields, $Q_S/Q_O$.*

| A | B | Method | $Q_S/Q_O$ | | |
|---|---|---|---|---|---|
| | | | 3:1 | 1:1 | 1:3 |
| $C_2H_5O$ | $C_2H_5O$ | NMR | — | 2.28 | 2.33 |
| $CH_3$ | $C_2H_5O$ | NMR | 2.73 | 2.86 | 2.51 |
| | | GLC | 2.86 | 2.82 | 2.86 |
| $CH_3$ | $C_4H_9O$ | NMR | — | 3.27 | 3.29 |
| $C_2H_5$ | $C_2H_5$ | NMR | 4.00 | 4.29 | 3.72 |
| | | GLC | 3.63 | 4.18 | 3.69 |
| $Iso\text{-}C_3H_7$ | $iso\text{-}C_3H_7$ | NMR | 5.00 | 4.92 | — |

TABLE II

The Composition of the Products of the Reaction of Phosphorus Monothioacids
(ABPSOH) with DDM

| № | A | B | $\Sigma \sigma^{\ominus}$ | thiolo isomer $Q_S$, % | thiono isomer, $Q_O$, % | $Q_S/Q_O$ |
|---|---|---|---|---|---|---|
| 1. | $C_2H_5O$ | $C_2H_5O$ | −0.42 | 69.2 | 30.8 | 2.25 |
| 2. | $C_6H_5$ | $C_2H_5O$ | −0.69 | 73.2 | 26.8 | 2.73 |
| 3. | $CH_3$ | $C_2H_5O$ | −1.17 | 77.4 | 22.6 | 3.42 |
| 4. | $C_6H_5$ | $C_6H_5$ | −1.18 | 76.3 | 23.7 | 3.22 |
| 5. | $CH_3$ | $iso\text{-}C_3H_7O$ | −1.25 | 77.0 | 23.0 | 3.35 |
| 6. | $CH_3$ | $C_3H_7O$ | −1.28 | 76.5 | 23.5 | 3.26 |
| 7. | $CH_3$ | $cyclo\text{-}C_6H_{11}O$ | −1.31 | 76.3 | 23.7 | 3.22 |
| 8. | $CH_3$ | $C_4H_9O$ | −1.37 | 78.0 | 22.0 | 3.54 |
| 9. | $tert\text{-}C_4H_9$ | $CH_3O$ | −1.67 | 81.0 | 19.0 | 4.26 |
| 10. | $C_2H_5$ | $C_2H_5$ | −2.20 | 81.2 | 18.8 | 4.33 |
| 11. | $iso\text{-}C_3H_7$ | $iso\text{-}C_3H_7$ | −2.60 | 85.6 | 14.4 | 5.94 |
| 12. | $tert\text{-}C_4H_9$ | $tert\text{-}C_4H_9$ | −3.10 | 88.2 | 11.8 | 7.47 |

## EXPERIMENTAL

The phosphorus monothioacids, O,O-diethylthiophosphoric (b. p. 107—8 °C/2 mm Hg), O-ethylmethylthiophosphonic (b. p. 74—5 °C/1.5 mm), O-ethyl phenylthiophosphonic ($n^{20}_D$ 1.5736, neutralization equivalent 202.2), diphenylthiophosphinic (m. p. 140—142 °C), diisopropylthiophosphinic (m. p. 76—77.5 °C) and some other acids (see Table II) were synthesized by known procedures and had satisfactory characteristics[8-10].

DDM was prepared by the action of yellow mercury oxide on the hydrazone of benzophenone[11]; the latter compound was made from benzophenone and water-free hydrazine. Diaryldiazomethanes were synthesized by oxidation of the corresponding diarylhydrazones with yellow mercury oxide[11,13-16] or freshly prepared silver oxide[17-18] in ether in the presence of alcoholic alkali.

The solvents (ether, benzene, tetrahydrofuran, acetonitrile, nitromethane) were purified, dried and distilled as recommended in the literature[19].

The proton NMR spectra of the reaction mixtures were recorded on Varian-60 or Perkin-Elmer R 20 instruments at 60 MHz operating frequency with HMDS or TMS as internal references. Gas liquid chromatography was done with a Varian-200 chromatograph equipped with a sodium thermionic detector using 2m 3mm columns packed with Var-A-Port 100/120 mesh. Silicon SE-30 (3% of the carrier weight) was employed as the stationary phase. The conditions were: evaporator and column temperature 160 °C, carrier gas nitrogen, flow rate 24 ml/min.

## Reaction of Phosphorus Monothioacids with Diphenyldiazomethane and Diaryldiazomethanes (General Procedure)

Diaryldiazomethane (0.1 M solutions in ether, benzene, THF, acetonitrile, nitromethane) was added drop-wise to a magnetically stirred 0.1 M solution of an equimolar amount of phosphorus monothioacid in the same solvent. Nitrogen evolution and a change in colouration from deep-red to light-yellow was observed. The volume of nitrogen evolved during the reaction was near theoretical. The reaction rate depended on the acid strength; the reaction terminated in 5 to 8 hrs at 20 °C. The solvent was then removed, the residue dissolved in CCl₄ (c 1.0 M) and studied by proton NMR. In two cases, the product mixtures were chromatographed.

The amounts of *S*- and *O*-esters of phosphorus monothioesters in the product mixtures were determined from 2 or 3 independent experiments. The product ratios were obtained by measuring integral intensities of proton signals from the methyne groups attached to sulphur and oxygen. If satisfactory integral intensity curves could not be obtained because of the occurrence of phenyl proton signals in the vicinity of the CH—O doublet, the calculations were made with the higher-field doublet component. The accuracy of product ratio determinations was 2 to 3%.

The GLC patterns of the product mixtures from the reaction of DDM with *O*-ethylmethylthiophosphonic and diethylthiophosphinic acids contained two peaks corresponding to the *S*- and *O*-isomeric esters. The retention times for thiono esters were approximately two times smaller than for thiolo esters; for thiophosphonates and thiophosphinates studied, they were 17 and 30, 15 and 28 mins, respectively.

*Determination of Bimolecular Reaction Rates for the Reaction of DDM with Phosphorus Monothioacids*

The kinetic experiments were carried out in a cell placed in a Unicam SP-1200 colorimeter equipped with a 495—575 nm filter. The reactions were monitored colorimetrically by measuring the intensity of DDM colouration. The instrument was calibrated against DDM solutions in ether in the concentration range $1.65 \cdot 10^{-2}$ to $1.65 \cdot 10^{-3}$ M. In kinetic experiments, 2 ml quantities of monothioacid and DDM solutions of the same concentration ($1.06 \cdot 10^{-2}$ M) in absolute ether were placed into the cell. Measurements were taken at $20 \pm 2\,^{0}$C at 20 to 30 min intervals. The cell pathlength was 1 cm.

<div align="center">RESULTS AND DISCUSSION</div>

*The Influence of the Structure of the Phosphorus Monothioacid*

We studied the reactions of DDM with twelve phosphorus monothioacids in ether solutions at $20\,^{0}$C; the thioacids were chosen so that $\Sigma\,\sigma^{\Phi}$ of the phosphorus substituents varied in as wide a range as possible (—0.42 to —3.10). The reaction was found to yield a mixture of thiolo and thiono isomers in all cases:

$$ABPSOH + (C_6H_5)_2CN_2 \rightarrow ABP(O)SCH(C_6H_5)_2 + ABP(S)OCH(C_6H_5)_2 + N_2$$

A part of the proton NMR spectrum of the product mixture of the reaction with 0,0-diethylthiophosphoric acid is reproduced in Figure 1. The doublet signals of the protons of the methyne groups $SCH(C_6H_5)_2$ at 5.4—5.9 ppm ($J_{PSCH}$ 10.0 Hz) and $OCH(C_6H_5)_2$ at 6.2—6.7 ppm ($J_{POCH}$ 12.5 Hz) are shown. The GLC data of the reaction mixture containing isomeric *S*- and *O*-diphenyl-methyl-*O*-ethymethylthiophosphonate is given in Figure 2. It was shown earlier that the Pishchimuka rearrangement did not occur under the chromatographing conditions ($160\,^{0}$C).

In special experiments it was also found that the thiolo to thiono product ratio ($Q_S/Q_O$) was independent of the initial acid to DDM molar ratio (Table I) and thus independent of the total reaction yields.

The $Q_S$ and $Q_O$ values for various phosphorus monothioacids are summarized in Table II. These data show that the percentage of the *O*-isomer increases with the electron withdrawing power of the substituent. The $Q_S/Q_O$ ratio decreases approximately threefold on going from di-tert. butylthiophosphinic to *O,O*-diethylthiophosphoric acid. A linear dependence fitting the equation is observed in the $\log (Q_S/Q_O)$ vs. $\Sigma\,\sigma^{\Phi}$ coordinates.

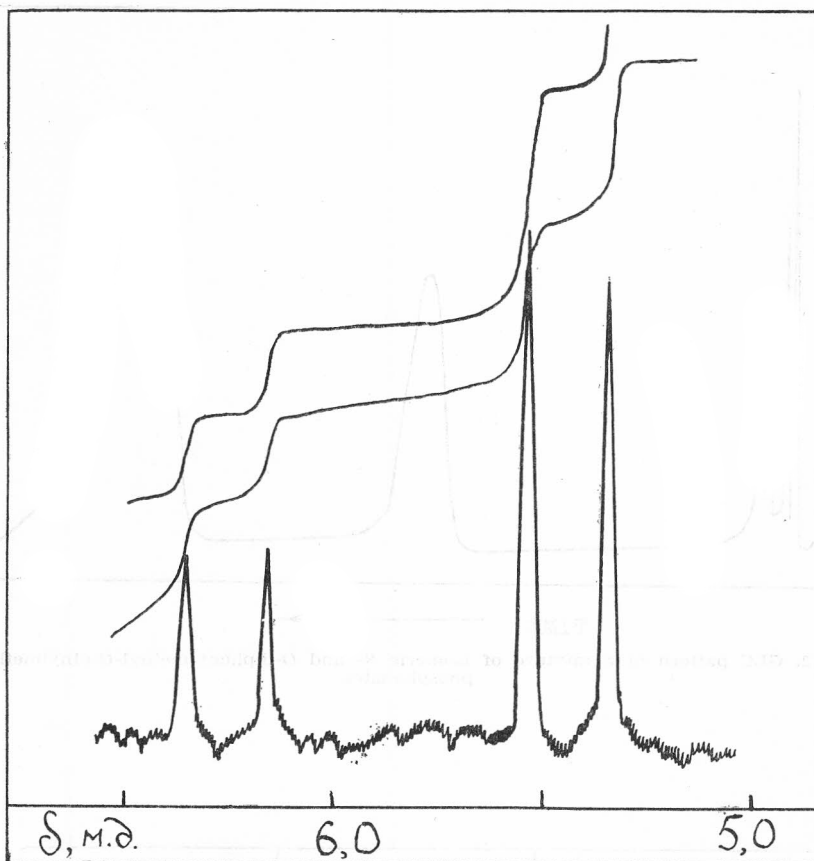$$\log (Q_S/Q_O) = 0.30 - 0.18\,\Sigma\,\sigma^{\Phi} \quad (r\ 0.984,\ S\ 0.03,\ S_\varrho\ 0.01).$$

Figure 1. Part of the proton NMR spectrum of a reaction mixture containing isomeric *S*- and *O*-diphenylmethyl esters of *O,O*-diethylthiophosphoric acid.

This finding (linear dependence with a negative slope) is inconsistent with the suggestion that the reaction proceeds via the carbocation intermediate only. If the product ratio depended on condition (1) the slope would be positive because it is known from the correlation analysis of organophosphorus compounds that, of two reactions of the same type, the reaction at oxygen is characterized by a larger negative slope than the reaction at sulphur[7]:

$$\varrho_{Q_S/Q_O} = \varrho_{4'} - \varrho_4 > 0$$

Conversely, the observed negative slope agrees with condition (3) which implies that *S*-alkylated derivatives are formed in an $S_N2$ reaction of the alkyldiazonium cation with the sulphur terminus of the ambident triad (step 3 of Scheme 1) whereas *O*-derivatives are products of the decomposition of the alkyldiazonium cation yielding the corresponding carbocation. The latter reaction proceeds by the $S_N1$ mechanism, and it is followed by the collapse of the thiophosphorus triad at oxygen (steps 2 and 4). All the reactions take place within ion pairs.
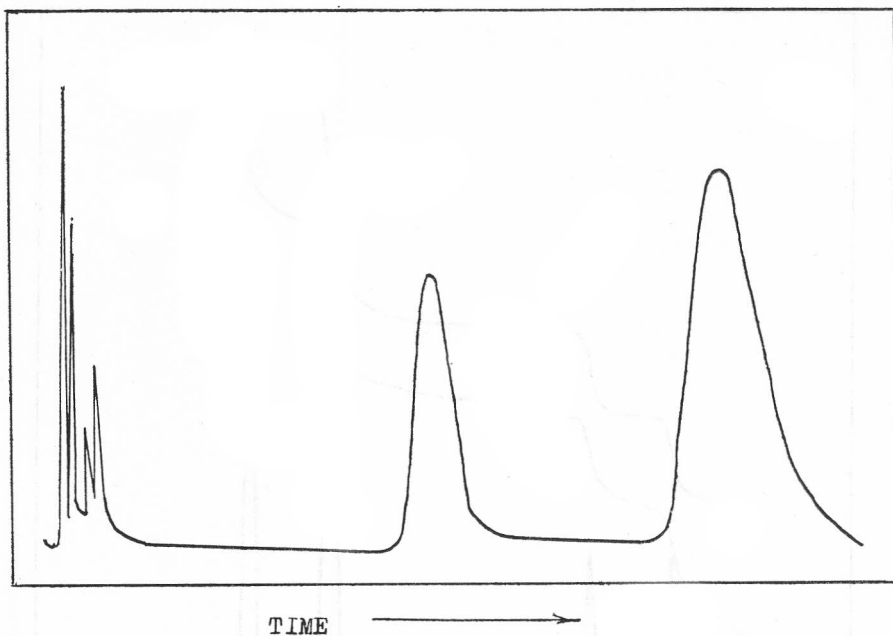
Figure 2. GLC pattern of a mixture of isomeric $S$- and $O$-diphenylmethyl-$O$-ethylmethylthio-phosphonates.
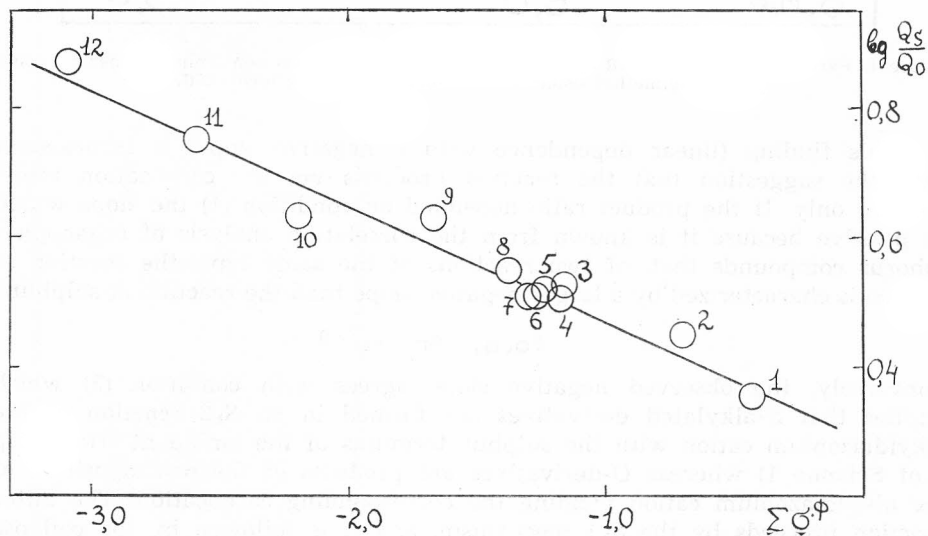


Figure 3. The log $(Q_S/Q_O)$ vs. $\Sigma \sigma^\Phi$ dependence for the reaction of phosphorus monothioacids with DDM. Numbering of points corresponds to that given in Table II.

As the reacting particles approach each other rather closely within the ion pair while the diphenyl group is bulk enough, the question of the dependence of the $Q_S/Q_O$ ratio on steric factors naturally arises. The introduction of sterically hindered groups into the monothioacid molecule might have a decelerating action on reactions of the alkyldiazonium cation (the $S_N2$ reaction) owing to an increase in the transition state energy caused by repulsions between radicals in the reagents. This might distort the $\log (Q_S/Q_O)$ vs. $\Sigma \sigma^\Phi$ linear dependence. The data given in Figure 3 show that the points corresponding to acids with bulky substituents do not fall out (points 4, 9, 11 and 12). The steric factor thus has no noticeable action on the product ratio in the reaction under consideration.

By analogy with carboxylic acids[20,21], the first reaction step-proton transfer in Scheme 1 was believed to be the rate determining one. To confirm this suggestion, we studied the kinetics of the reaction of phosphorus thioacids with DDM in ether by the colorimetric technique. The rate constants, $k_1$, were calculated from the bimolecular kinetics equation (4)

$$V = k_1 \, [\text{ABPSOH}] \, [\text{DDM}] \tag{4}$$

It is known from the literature[20] that in a number of cases, $k_1$ values show a concentration dependence in reactions of carboxylic acids with DDM in aprotic solvents. This observation was explained by the involvement of acid di-, tri- and even polymeric particles having different reactivities. It was shown earlier[22] that in a solvent of such low polarity as benzene, phosphorus monothioacids exist as trimeric species. We therefore had to check the applicability of equation (4). For that purpose, we studied the kinetics of the reaction of diethylthiophosphinic acid with DDM in benzene and nitromethane. After preliminary calibration, degrees of conversion were determined at regular time intervals. The results were plotted as $1/c$ vs. time (c is the concentration) (Figure 4). As the dependence was linear, it was concluded that the second-order kinetics (4) remained valid in the concentration range studied.

The kinetic data on the reaction of DDM with phosphorus monothioacids, ABPSOH, in ether are given in Table III. The reaction rate constant increases significantly with the electron withdrawing power of the substituent at phosphorus, i. e. with the acid strength. A linear dependence with positive slope is observed in a plot of $\log k_1$ vs. $\Sigma \sigma^\Phi$. These data agree with those on the reaction of DDM with carboxylic acids[23-25].

The reaction rate constant was also found to depend substantially on solvent nature in certain cases (see below).

TABLE III

*The Rate Constants, $k_1$, of Reactions of DDM with Phosphorus Monothioacids, ABPSOH, in Ether*

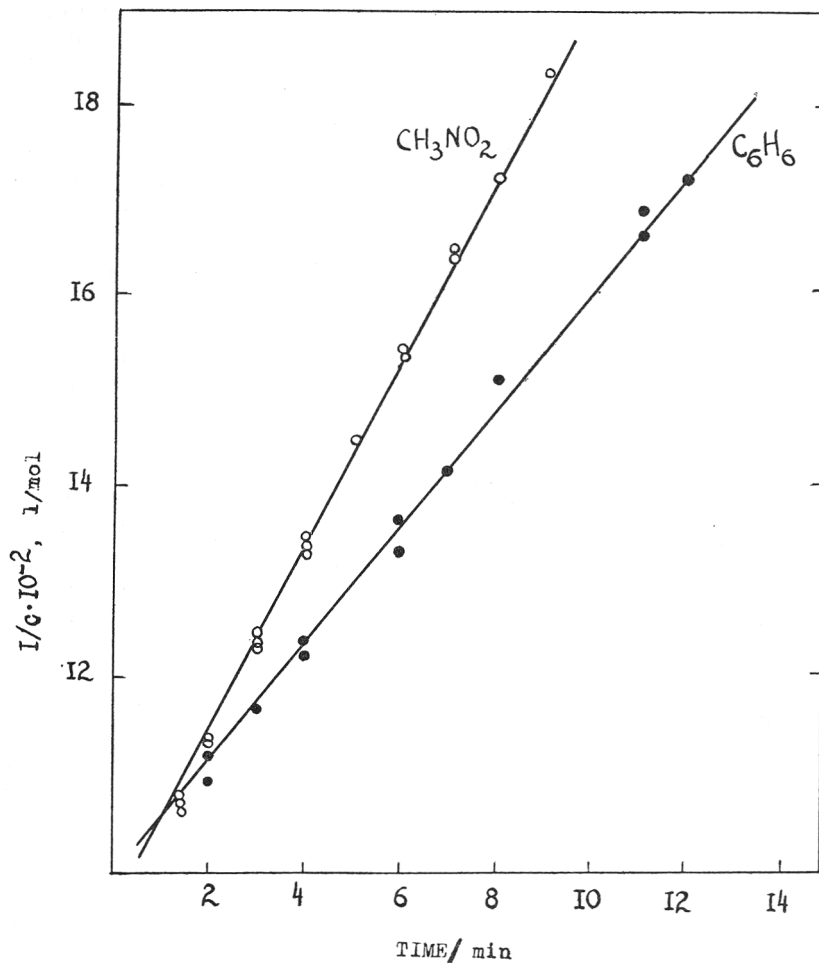| A | : | B | : | $k_1$ |
|---|---|---|---|---|
| $C_2H_5O$ | | $C_2H_5O$ | | 0.105 |
| $CH_3$ | | $C_2H_5O$ | | 0.058 |
| $C_2H_5$ | | $C_2H_5$ | | 0.020 |
| iso-$C_3H_7$ | | iso-$C_3H_7$ | | 0.012 |

Figure 4. Verification of the kinetic equation $V = k_1$ [ABPSOH] [DDM]. Time dependence of the reciprocal of DDM concentration.

It thus follows that the reaction of DDM with phosphorus monothioacids involves the same rate-determining step (proton transfer) as with carboxylic acid. Its specific features are revealed in the subsequent steps.

## The Effect of Substituents in Diphenyldiazomethane

Relative variations of the diarylmethylcarbonium cation stability should affect the contribution from the $S_N1$ reaction (through variation of $k_2$, see Scheme 1) and, therefore, the relative yield of the O-benzhydryl ester. This prompted us to investigate the effect of substituents in the phenyl nuclei of diaryldiazomethanes on the ratio of S- and O-benzhydryl esters of phosphorus monothioacids.

We studied the reactions of O,O-diethylthiophosphoric acid with p-methoxy, p,p'-dimethoxy-, p,p'-dichloro-, and p,p'-dibromodiphenyldiazomethanes

in ether. The product ratios of isomeric benzhydryl esters, $Q_S/Q_O$, obtained in these experiments are given in Table IV. In spite of only insignificant variations in $Q_S$ and $Q_O$ depending on $\Sigma \sigma_p$, the thiono isomer yield ($Q_O$) was found to increase on going to diaryldiazomethanes containing electron donor substituents R$'$ and R$''$. This observation is consistent with condition (3) of Scheme 1, $Q_S/Q_O = k_3 k_2$ according to which an increase in the stability of the diarylmethylcarbocation and the corresponding increase in $k_2$ should result in a decrease in $Q_S/Q_O$.

TABLE IV

*The Composition of the Products of the Reaction of O,O-diethylthiophosphoric Acid with Diaryldiazomethanes,* p-R$'$C$_6$H$_4$(p-R$''$C$_6$H$_4$)CN$_2$.

| № | R$'$ | R$''$ | $\Sigma \sigma_p$ | thiolo isomer, $Q_S$, % | thiono, isomer, $Q_O$, % | $Q_S/Q_O$ |
|---|---|---|---|---|---|---|
| 1. | CH$_3$O | CH$_3$O | — 0.54 | 65.1 | 34.9 | 1.87 |
| 2. | CH$_3$O | H | — 0.27 | 69.3 | 30.7 | 2.26 |
| 3. | H | H | 0 | 69.9 | 30.1 | 2.32 |
| 4. | Cl | Cl | 0.45 | 73.7 | 26.3 | 2.80 |
| 5. | Br | Br | 0.46 | 77.1 | 22.9 | 3.37 |

The dependence of $\log (Q_S/Q_O)$ on $\Sigma \sigma_p$ is linear (Figure 5):

$$\log (Q_S/Q_O) = 0.39 + 0.21 \Sigma \sigma_p \quad (r\ 0.946,\ S\ 0.04\ S_p\ 0.04)$$

The study of the effects of phosphorus monothioacid and diaryldiazomethane structures on the isomeric esters ratio thus enabled us to suggest that S-esters are formed in the reaction of the ambient triad sulphur terminus with arylmethyldiazonium cations while O-esters are the products of the collapse of diarylmethyl cations at the oxygen triad terminus.
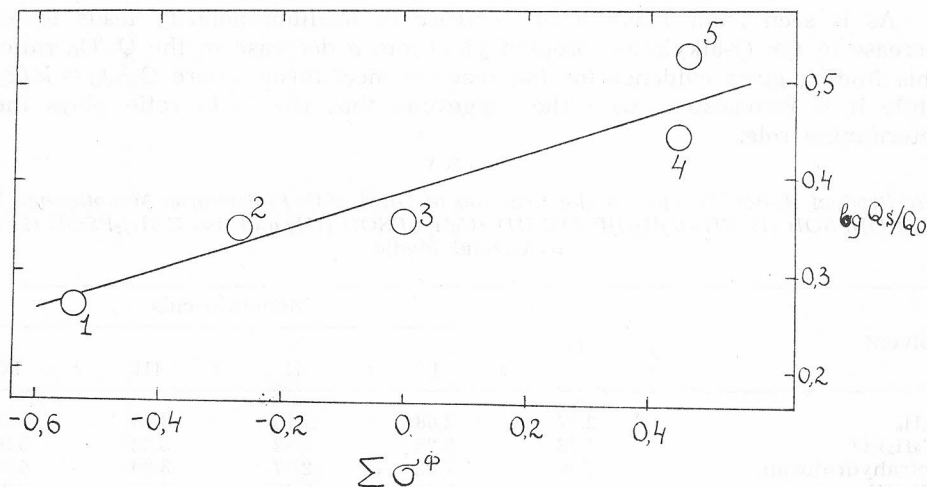


Figure 5. The $\log (Q_S/Q_O)$ vs. $\Sigma \sigma_p$ dependence for the reaction of O,O-diethylthiophosphoric acid with diaryldiazomethanes.

*Solvent Effects*

The study of solvent effects on the product ratio, $Q_S/Q_O$, yielded additional information about the reaction mechanism. The steps determining the $Q_S/Q_O$ ratio (Sheme 1), involve transition states characterized by different charge distributions between the reacting particles. According to Ingold[26], the rate of reaction (3) (Scheme 1) which is the $Y^- + RX^+ \to Y^{\delta-} .. R .. X^{\delta+} \to \to YR + X$-type reaction should decrease substantially with an increase in solvent polarity. The decomposition of the alkyldiazonium cation (reaction (2)) which is the $RX^+ \to R^{\delta+} .. X^{\delta+} \to R^+ + X$ type reaction should also decelerate in polar media, however, to a far lesser degree. The $k_3$ constant value should thus decrease greatly while $k_2$ only insignificantly. If the product ratio, $Q_S/Q_O$, is determined by the $k_3/k_2$ ratio, the net effect will be a decrease in that ratio on going to polar solvents. The transition states involved in competing recombinations going at rates $k_4'$ and $k_4$ are characterized by a substantial decrease in charges in the ion pair: $X^- + R^+ \to X^{\delta+} .. R^{\delta+} \to RX$. An increase in medium polarity should therefore decelerate these reactions strongly. Taking into account that charge density on oxygen is higher than that on sulphur, a relative charge decrease in the transition state should be greater in the O-reaction. An increase in medium polarity should, therefore, decelerate the O-reaction to a higher degree than the S-reaction. It thus follows that the $Q_S/Q_O$ ratio will increase or at least remain constant if $Q_S/Q_O = k_4'/k_4$.

It was shown earlier[5] that an increase in medium polarity results in a decrease in $Q_S/Q_O$ in reactions of phosphorus monothioacids with diazomethane, in agreement with the suggestion $Q_S/Q_O = k_3/k_2$.

We studied the effect of medium polarity on the $Q_S/Q_O$ ratio in reactions of O,O-diethylthiophosphoric (I), O-ethylmethylthiophosphonic (II), diphenylthiophosphinic (III) and diisopropylthiophosphinic (IV) acids with DDM. The experiments were carried out under standard conditions. Product mixtures were analysed by the proton NMR method. The results are given in Table V.

As is seen from Table V an increase in medium polarity leads to an increase in the O-alkylation product yield and a decrease in the $Q_S/Q_O$ ratio. This finding gives evidence for the reaction mechanism where $Q_S/Q_O = k_3/k_2$, while it is inconsistent with the suggestion that the $k_4'/k_4$ ratio plays the determining role.

TABLE V

*The Product Ratios, $Q_S/Q_O$, for the Reaction of DDM with Phosphorus Monothioacids, $(C_2H_5O)_2PSOH$ (I), $CH_3(C_2H_5O)PSOH$ (II), $(C_6H_5)_2PSOH$ (III) and $(iso\text{-}C_3H_7)_2PSOH$ (IV), in Various Media*

| Solvent | : | D | : | Monothioacids | | | | |
|---------|---|---|---|------|---|-----|---|-----|
| | : | | : | I | : | II | : | III | : | IV |
| $C_6H_6$ | | 2.27 | | 2.68 | | 4.18 | | 3.78 | | 7.20 |
| $(C_2H_5)_2O$ | | 4.33 | | 2.25 | | 3.42 | | 3.22 | | 5.94 |
| Tetrahydrofuran | | 7.40 | | 1.82 | | 2.77 | | 3.20 | | 5.58 |
| $CH_3CN$ | | 37.5 | | 1.43 | | 2.36 | | 2.39 | | 4.29 |
| $CH_3NO_2$ | | 38.6 | | 1.41 | | — | | — | | — |

TABLE VI

*The Parameters of the Linear Dependences log $(Q_S/Q_0)$ vs. $1/D$ for Reactions of DDM with Phosphorus Monothioacids, $(C_2H_5O)_2PSOH$ (I), $CH_3(C_2H_5O)PSOH$ (II), $(C_6H_5)_2PSOH$ (III) and $(iso\text{-}C_3H_7)_2PSOH$ (IV).*

| Correlation parameters | | Monothioacids | | | | | |
|---|---|---|---|---|---|---|---|
| | : | I | : | II | : | III | : | IV |
| lg( $Q_S/Q_0$)$_0$ | | 0.15 | | 0.37 | | 0.40 | | 0.65 |
| tg  α | | 0.69 | | 0.61 | | 0.43 | | 0.51 |
| r | | 0.972 | | 0.985 | | 0.912 | | 0.961 |
| S | | 0.03 | | 0.02 | | 0.04 | | 0.03 |
| $S_{tg\alpha}$ | | 0.10 | | 0.08 | | 0.14 | | 0.10 |
| n | | 5 | | 4 | | 4 | | 5 |

The plots of log $(Q_S/Q_0)$ vs. $1/D$ ($D$ is the medium dielectric permittivity) are straight lines with the parameters given in Table VI.

The data for solvents having substantially different polarities such as benzene and acetonitrile fit these linear dependences well which implies that the reaction mechanism remains the same in all the solvents studied. Since the reaction in benzene, probably occurs within ion pairs, ion pairs should also be involved in the reactions in acetonitrile and nitromethane where the ions may go out of the solvent cage (or at least, the dissociation of ion pairs should not affect the yields significantly).
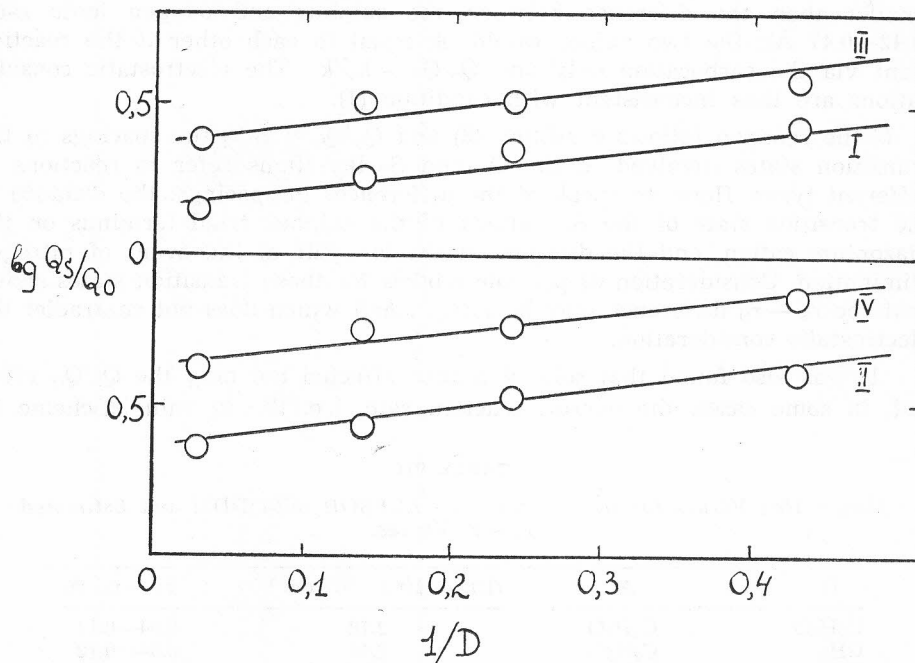


Figure 6. The log $(Q_S/Q_0)$ vs. $1/D$ dependence for reactions of DDM with phosphorus mono-thioacids (I—IV). Numbering of points corresponds to that given in Table V.

The linear dependences shown in Figure 6 are indicative of the importance of electrostatic interactions in the transition states of reactions at sulphur and oxygen. This enabled us to apply the Scatchard equation[27] modified by Emis[28] to choose between the two possible reaction directions with $Q_S/Q_O = k_3/k_2$ and $Q_S/Q_O = k_4'/k_4$. For the reaction under consideration, the Scatchard-Emis equation yields[5].

$$\log Q_S/Q_O = \log (Q_S/Q_O)_{D-\infty} + \frac{e^2}{2,3\,kTD} \left( \frac{1}{r_o} - \frac{1}{r_s} \right)$$

where $e$ is the electron charge, $k$ — the Boltzmann constant, $r_s$ and $r_o$ are ion spacings in the reactions at sulphur and oxygen, respectively.

As the experimental linear dependences (Table VI, Figure 6) fit this equation, their slopes are given by

$$\operatorname{tg} \alpha = \frac{e^2}{2,3\,kT} \left( \frac{1}{r_o} - \frac{1}{r_s} \right)$$

The tg $\alpha$ values were employed to calculate the differences $1/r_o - 1/r_s$. The $r_s - r_o$ values were estimated using the Hammond[29] postulate, viz. on the assumption that ion spacing in the transition states should differ only insignificantly from that in the initial ion pairs in reactions involving unstable intermediate diazonium and carbonium cations. The most probable values for the ion pairs are 4.0—7.0 Å. Using these estimates we have calculated the $r_s - r_o$ differences (Table VII). In all cases, these values are far smaller than the diference between the sulphur and oxygen ionic radii (0.42—0.47 Å); the two values would be equal to each other if the reaction went via the carbocation only and $Q_S/Q_O = k_4'/k_4$. The electrostatic considerations are thus inconsistent with condition (1).

If the reaction follows condition (3) and $Q_S/Q_O = k_3/k_2$ the spacings in the transition states involved in the O- and S-alkylations refer to reactions of different types. Here we speak of the differences in spacings: the distance in the transition state of the $S_N2$ attack of the sulphur triad terminus on the diazonium cation, and the distance in the ion pair at the event of nitrogen elimination. Consideration of possible models for those transition states shows that the $r_s - r_o$ difference may be fairly small which does not contradict the electrostatic consideration.

It was also found that solvent nature affected not only the $Q_S/Q_O$ value but, in some cases, the overall reaction rate, i. e. the $k_1$ value (Scheme 1).

TABLE VII

(1/$r_0$ — 1/$r_s$) Values for the Reactions of ABPSOH with DDM and Estimated $r_s - r_0$ Values.

| B | : | A | : | $(1/r_0 - 1/r_s) \cdot 10^{-5}$ cm$^{-1}$ | : | $r_s - r_0$, Å |
|---|---|---|---|---|---|---|
| $C_2H_5O$ | | $C_2H_5O$ | | 2.78 | | 0.04—0.14 |
| $CH_3$ | | $C_2H_5O$ | | 2.46 | | 0.04—0.12 |
| $C_6H_5$ | | $C_6H_5$ | | 1.73 | | 0.03—0.08 |
| iso-$C_3H_7$ | | iso-$C_3H_7$ | | 2.06 | | 0.03—0.10 |

For the reaction of diethylthiophosphinic acid with DDM, $k_1$ was shown to change only insignificantly on going from benzene to nitromethane ($k_1 = 1.035$ and 1.565 l/mol sec, respectively), while in ether, the reaction was far slower under the same conditions (Table III). It appears that, as with carboxylic acids[30], the overall reaction rate is determined by the solvent basicity rather than by its polar properties.

The overall experimental data obtained in this work enabled us to extend the mechanism of dual reactivity previously suggested by us for the reaction of phosphorus monothioacids with aliphatic diazocompounds[2,3] to the reaction with DDM. Unlike in the reactions of DDM with carboxylic acids, the reaction of DDM with phosphorus monothioacids involves two competing processes
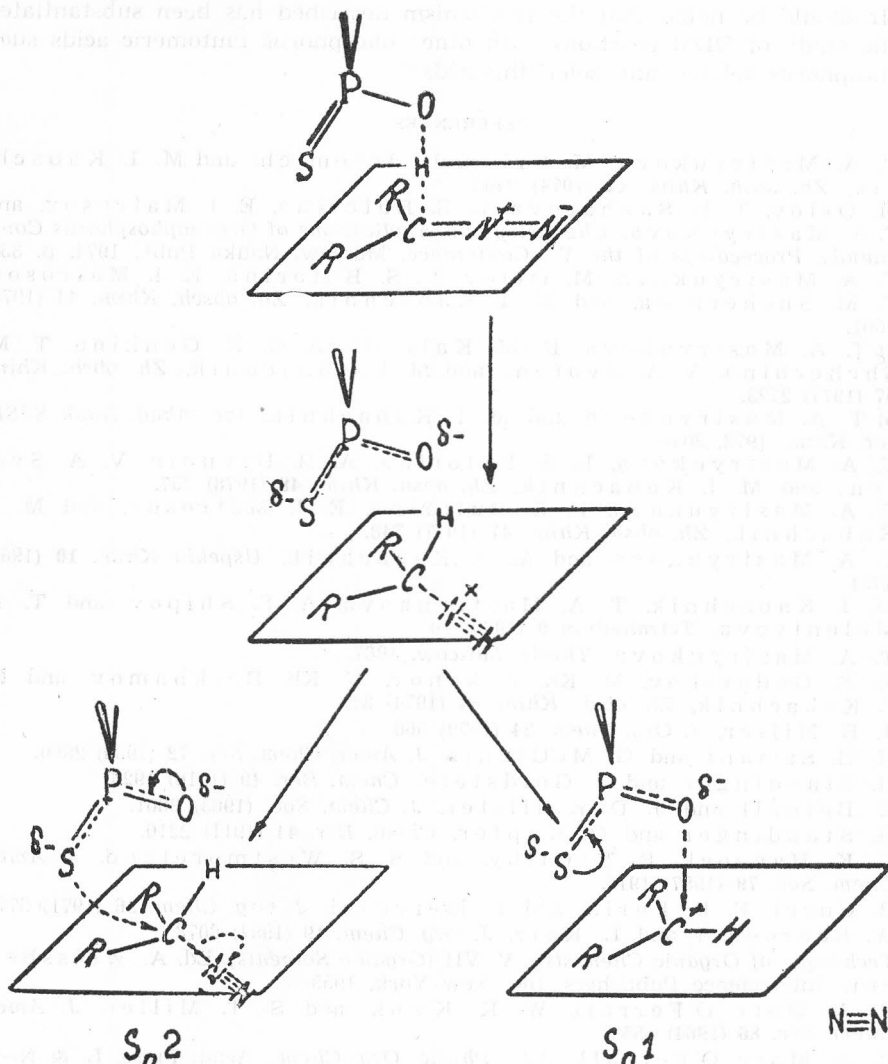


Figure 7. The transition state structure in the reaction of DDM with phosphorus monothioacids.

leading to $S$- and $O$-isomeric esters. The product ratio corresponds to the condition $Q_S/Q_O = k_3/k_2$ (see Scheme 1) which implies an $S_N2$-type interaction of the diphenylmethyldiazonium cation with the sulphur triad terminus and an $S_N1$-type decomposition of the diazonium cation to the corresponding carbonium cation followed by a collapse at oxygen.

Such a difference in mechanism may be explained by the difference in the geometries of carboxylic and tautomeric phosphorus acids[31]. The structure of the transition state (Figure 7) in reactions of DDM with phosphorus monothioacids is such that the sulphur atom may approach the central carbon atom of the diazonium cation and act as a nucleophile assisting in the elimination of the nitrogen molecule (by an $S_N2$-mechanism). This process is also facilitated by sulphur being a stronger nucleophile than oxygen.

It should be noted that the mechanism described has been substantiated by the study of DDM reactions with other phosphorus tautomeric acids such as phosphorus seleno- and selenothioacids[32].

REFERENCES

1. T. A. Mastryukova, M. Orlov, D. Jeremich, and M. I. Kabachnik, Zh. obsh. Khim. **44** (1974) 2403.
2. M. Orlov, T. B. Sakharova, L. S. Butorina, E. I. Matrosov, and T. A. Mastryukova, Chemistry and Applications of Organophosphorus Compounds, Proceedings of the $V^{th}$ Conference, Moscow, Nauka Publ., 1974, p. 358.
3. T. A. Mastryukova, M. Orlov, L. S. Butorina, E. I. Matrosov, T. M. Shcherbina, and M. I. Kabachnik, Zh. obsch. Khim. **44** (1974) 1001.
4. a) T. A. Mastryukova, R. M. Kalyanova, G. K. Genkina, T. M. Shcherbina, V. A. Svoren', and M. I. Kabachnik, Zh. obsh. Khim. **47** (1977) 2723.
   b) T. A. Mastryukova and M. I. Kabachnik, Izv. Akad. Nauk SSSR, ser. Khim. 1978, 2040.
5. T. A. Mastryukova, L. S. Butorina, A. B. Uryupin, V. A. Svoren', and M. I. Kabachnik, Zh. obsh. Khim. **48** (1978) 257.
6. T. A. Mastryukova, L. S. Butorina, E. I. Matrosov, and M. I. Kabachnik, Zh. obsh. Khim. **47** (1977) 748.
7. T. A. Mastryukova and M. I. Kabachnik, Uspekhi Khim. **10** (1969) 1751.
8. M. I. Kabachnik, T. A. Mastryukova, A. E. Shipov, and T. A. Melentyeva, Tetrahedron 9 (1960) 10.
9. T. A. Mastryukova, Thesis, Moscow, 1967.
10. N. N. Godovikov, M. Kh. Bekanov, M. Kh. Berkhamov, and M. I. Kabachnik, Zh. obsh. Khim. **44** (1974) 34.
11. J. B. Miller, J. Org. Chem. **24** (1959) 560.
12. H. H. Szmant and G. McGinnis, J. Amer. Chem. Soc. **72** (1950) 2890.
13. H. Staudinger and J. Goldstein, Chem. Ber. **49** (1916) 1926.
14. D. Bethell and J. D. Kallister, J. Chem. Soc. (1963) 3801.
15. H. Staudinger and O. Kupfer, Chem. Ber. **44** (1911) 2210.
16. C. K. Hancock, R. F. Gilby, and S. S. Westmoreland, J. Amer. Chem. Soc. **79** (1957) 1917.
17. R. Curci, F. D. Furia, and F. Mercuzzi, J. Org. Chem. **36** (1971) 3774.
18. W. Schroeder and L. Katz, J. Org. Chem. **19** (1954) 6078.
19. Technique of Organic Chemistry, V. VII (Organic Solvents). Ed. A. Weissberger, Interscience Publishers, Inc. New York, 1955.
20. R. A. More O'Ferrall, W. K. Kwok, and S. T. Miller, J. Amer. Chem. Soc. **86** (1964) 5553.
21. R. A. More O'Ferrall, Adv. Physic. Org. Chem., Acad. Press, L. & N.-Y. **5** (1967) 331.

22. V. K. Pogorelyi, I. I. Kukhtenko, L. S. Butorina, and T. A. Ma-
    stryukova, *Dokl. Akad. Nauk SSSR,* **214** (1974) 385.
23. J. Hine and W. C. Bailey, Jr., *J. Amer. Chem. Soc.* **81** (1959) 2075.
24. A. B. Hoefelmeyer, and C. K. Hancock, *J. Amer. Chem. Soc.* **77** (1955)
    4746.
25. J. D. Roberts and C. M. Regan, *J. Amer. Chem. Soc.* **76** (1954) 939.
26. C. K. Ingold, *Structure and mechanism in organic chemistry,* Cornell Univ.
    Press, Ithaca a. London, 1969.
27. G. Scatchard, *Chem. Revs.* **10** (1932) 229.
28. E. S. Amis, *Solvent effects on reaction rates and mechanisms,* Academic Press,
    New York a. London, 1966, ch. 1.
29. G. S. Hammond, *J. Amer. Chem. Soc.* **77** (1955) 334.
30. N. B. Chapman, M. R. J. Dack, D. J. Newman, J. Shorter, and
    R. Wilkinson, *J. Chem. Soc. Perkin II,* (1974) 971.
31. T. A. Mastrykova, *Phosphorus and Sulfur,* **1** (1976) 211.
32. T. A. Mastryukova, Y. Michalski, A. B. Uryupin, Z. Skrzyp-
    czynski, and M. I. Kabachnik, *Zh. obsh. Khim.* **48** (1978) 1447.

## SAŽETAK

### Reakcija difenildiazometana sa fosfor monotiokiselinama

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Studiran je mehanizam reakcije fosfor monotiokiselina sa diarildiazometanima
u različitim otapalima kod 20 °C, i odnos količina nastalih S- i O-izomernih estera
određivan je ¹H NMR spektroskopijom i plinskom kromatografijom. Dobiveni rezul-
tati kao i kinetička mjerenja pokazuju da reakcija uključuje dva konkurentna pro-
cesa od kojih jedan rezultira u tiolo produktu, a drugi u odgovarajućem tiono
izomeru.