Photosolvolysis of *O,O,S*-Trimethyl Phosphorodithioate. Evidence for an $S_N1(P)$ Mechanism[1]

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Summary Irradiation (254 nm) of $(MeO)_2P(S)SMe$ in ROH yields mainly (66%, R = Pr^i) the ionic photosolvolysis product $(MeO)_2P(S)OR$ with the very low capture ratio 1·9 ± 0·4 for R = Me *vs.* R = Pr^i under competitive photosolvolysis conditions, whereas irradiation in *e.g.* tetrahydrofuran and CH_2Cl_2 gives free-radical products, suggesting that the photoreactions proceed by way of an 'intimate radical-ion pair.'

In earlier photochemical investigations of organophosphate model compounds for pesticides, we found[2] that irradiation (254 nm) of EtO(Ph)P(O)SPr^n in EtOH leads mainly to photoreduction of the P–S and S–C bonds, whereas photosolvolysis to $(EtO)_2Ph(P)O$ is a minor reaction pathway. We now report that upon irradiation (254 nm(of $(MeO)_2$-P(S)SMe [(**1**), λ_{max} 202 nm, ϵ_{254} 83 ± 2 l mol^{-1},Pr^{i}OH] in Pr^{i}OH the photosolvolysis product $(MeO)_2P(S)OPr^i$ (**2**) (Scheme 1) becomes the major reaction product (66%).†

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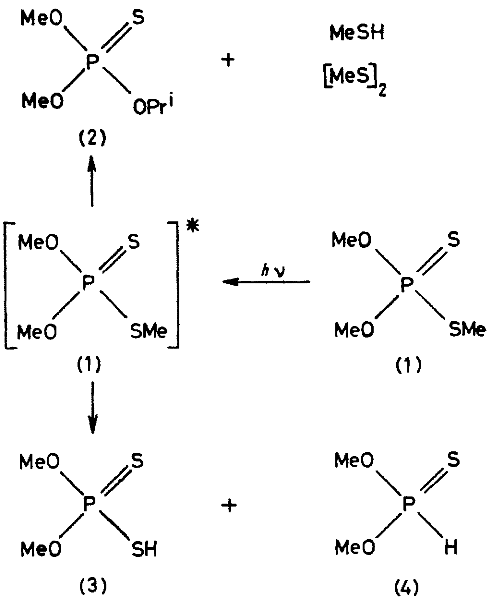
† Pesticides with the general structure $(MeO)_2P(S)SR$, *e.g.* malathion [R = $[CH(CO_2Et)CH_2(CO_2Et)]$ and dimethoate [R = CH_2-C(O)NHMe], show qualitatively the same photochemistry as the title compound (R = Me).

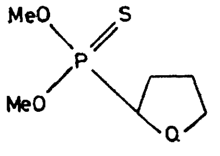
The photoreduction products (**3**) and (**4**) are formed to a minor extent ($<6\%$).



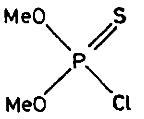
Scheme 1

A priori, several reaction mechanisms can be considered for the formation of (**2**): (i) bimolecular reaction of a singlet or triplet excited state of (**1**) with Pr^{i}OH, (ii) photosolvolysis *via* the radical cation $[(\text{MeO})_2\text{P(S)SMe}]^{\cdot +}$, (iii) direct photoionization of the P–S bond, and (iv) homolysis of the P–S bond, followed by electron transfer in the radical pair. When the photosolvolysis of (**1**) is carried out in acetonitrile with various concentrations of Pr^{i}OH (0·019—0·31 M), a linear relationship is observed between the reciprocal value of the quantum yield for the formation of (**2**) and the reciprocal Pr^{i}OH concentration. At high concentrations of Pr^{i}OH ($\geqslant 0·4$ M), this quantum yield has reached a maximum value (Φ 0·10). These results show that (**2**) is formed by bimolecular reaction either with excited (**1**) or with a reactive intermediate. From competitive photosolvolysis experiments in the presence of various molar ratios of MeOH and Pr^{i}OH (MeOH/Pr^{i}OH = 0·8—4·0), we have calculated a capture ratio for MeOH *vs*. Pr^{i}OH of $1·9 \pm 0·4$. This low ratio, similar to that for reactions of these alcohols with carbenium ions,[3] strongly indicates a reaction with highly reactive intermediates, rather than with excited (**1**). In the latter case, much higher capture ratios (*ca*. 7, *cf*. ref. 4) should be expected, owing to steric interactions of five ligands at phosphorus in the transition state of the reaction.

Photosolvolysis *via* the radical-cation $[(\text{MeO})_2\text{P(S)SMe}]^{\cdot +}$ is also ruled out, since the lowest ionization energy of (**1**), as measured from its photoelectron spectrum, is 8·97 eV (206·8 kcal).‡ Even when the approximate solvation energy of the free electron[5] and of the radical-cation[6] in acetonitrile is taken into account, this is probably above the possible range of the excitation energy of (**1**). Moreover, photosolvolysis of (**1**) in H_2O–MeOH, in the presence of N_2O, does not yield nitrogen, indicating that solvated electrons are not involved[7] in the photoreactions of (**1**).

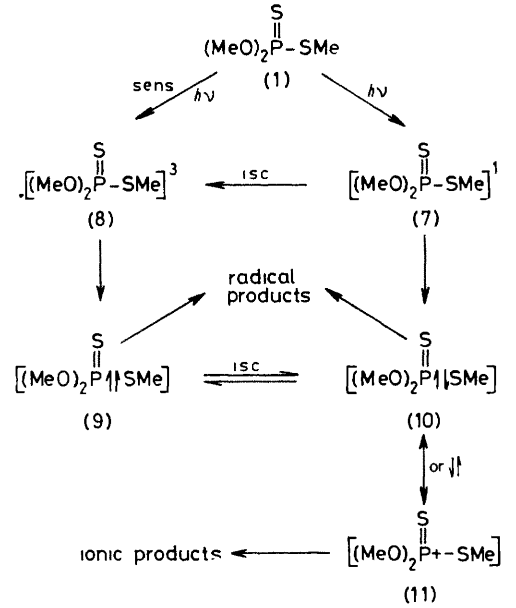


(5)



(6)

Thus, we propose that the photosolvolysis of (**1**) proceeds *via* an S_N1(P)-mechanism with the thiophosphorylium ion $(\text{MeO})_2\overset{+}{\text{P}}(\text{S})$ as an intermediate. The latter species might be formed either directly from the excited state or *via* primary homolysis of the P–S bond, followed by electron transfer. Our results do not permit a choice between these two pathways, which may also interchange *e.g.* with the polarity of the solvent. However, the following evidence indicates that the radical $(\text{MeO})_2\text{P(S)}\cdot$ can be involved in our reactions. (a) Irradiation of (**1**) in tetrahydrofuran (THF) yields *O,O*-dimethyl 2-tetrahydrofuranylphosphonothioate (**5**) as the major reaction product, whereas irradiation of (**1**) in CH_2Cl_2 yields *O,O*-dimethyl phosphorochloridothionate (**6**) as the major reaction product. (b) Irradiation of (**1**), either in Pr^{i}OH or in benzene, in the presence of the spin trap *N*-benzylidene-t-butylamine-*N*-oxide leads to the observation of the e.s.r. spectrum of the adduct of a P-centred radical to the trap, probably $(\text{MeO})_2\text{P(S)–CH(Ph)–N(O}\cdot)\text{Bu}^t$ [in benzene: $a(\text{P}) = 2·54$, $a(\text{N}) = 1·43$, $a(\text{H}) = 0·28$ mT; *cf*. Brunton *et al.*[8]].



Scheme 2

The irradiations in THF and in CH_2Cl_2 give end products which are evidently derived from radical-type reactions, whereas the e.s.r. evidence also shows that the radical $(\text{MeO})_2\text{P(S)}\cdot$ is formed. Tentatively, we suggest (Scheme 2) that (**2**) is formed *via* the 'intimate radical-ion pair' intermediates (**10**) and (**11**), similar to those in the photoreactions of benzyl and alkyl halides[9,10] and of bicyclic halides.[11,12]

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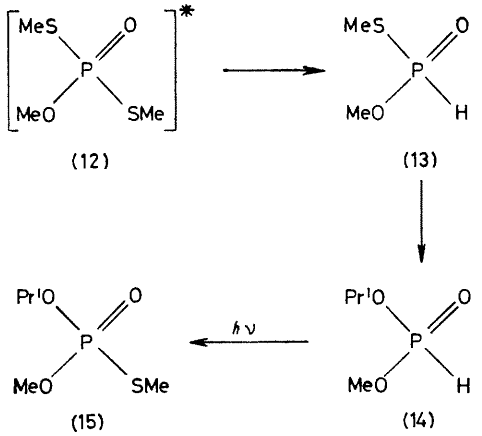
‡ Additional ionization energies were observed at 9·71 and 10·69 eV.

The alternative formation of (**2**) *via* direct addition of the radical $(MeO)_2\dot{P}(S)$ to Pr^iOH yielding the intermediate $(MeO)_2\dot{P}(S^-)$–$O^+(H)$–Pr^i by analogy with the suggestion of Emoto *et al*[13] for the formation of $(Ph)_2P(S)OMe$ during irradiation of $[(Ph)_2P(S)–]_2$ in $MeOH–CH_2Cl_2$ seems very improbable Our results show that their product can be formed *via* $(Ph)_2P(S)Cl$ [*cf* (**6**)]

The photosolvolysis of (**1**) in Pr^iOH is sensitized by high energy triplet sensitizers ($E_T > 80$ kcal/mol) such as benzene diphenyl ether anisole and *p* xylene but not by sensitizers with $E_T < 80$ kcal/mol (*e g* benzonitrile E_T 77 kcal/mol) These results indicate that photosolvolysis of (**1**) may proceed by way of a high energy triplet state (**8**) although reaction *via* the singlet state (**7**) cannot be ruled out The possible involvement of (**8**) has led to the introduction into Scheme 2 of an intersystem crossing between the initially formed triplet radical pair (**9**) and the subsequently formed intimate (singlet) radical ion pair (**10–11**)

The next major photolysis product (19%) of the irradiation of (**1**) in Pr^iOH *i e* $MeO(MeS)P(O)OPr^i$ (**15** Scheme 3) may have been formed *via* initial thiono thiolo isomerization of (**1**) Therefore we have irradiated (254 nm) the isomer $(MeS)_2P(O)OMe$ [(**12**) λ_{max} 230 nm Pr^iOH] in Pr^iOH This resulted in the rapid formation of $MeO(Pr^iO)P(O)H$ (**14**) presumably by way of (dark) solvolysis[14] of the photoreduction product $MeO(MeS)P(O)H$ (**13**) Since the photoreduction of the P S bond is essentially a reversible process[2, 15] the end product (**15**) can be formed by reaction of (**14**) with thiyl radicals resulting *e g* from secondary photolysis of MeSH or $(MeS)_2$



SCHEME 3

Hence the P(O)SR unit [*e g* (**12**) *cf* also ref 2] appears to undergo photoreduction reactions of the P–S and S C bonds preferentially whereas the P(S)SR unit [*e g* (**1**)] preferentially gives ionic reaction products This observed regularity might be due to a better stabilization of positive charge on phosphorus in the ion pair [*e g* (**11**)] by sulphur than by the highly electronegative oxygen atom A similar effect has been invoked in the *E1cb* hydrolysis of phosphoramidic halides[16]

We thank Dr J Cornelisse (Leiden University) for helpful discussions and Dr C A de Lange (Free University Amsterdam) for measuring the photoelectron spectrum of the title compound

(*Received* 26*th March* 1979 *Com* 309)

[1] Presented in part at The International Conference on Phosphorus Chemistry Halle (GDR) September 1979 (abstract 92 in abstracts)

[2] H P Benschop C A G Konings D H J M Platenburg and R Deen *J Chem Soc Perkin Trans* 2 1980 198 H P Benschop and M Halmann *ibid* 1974 1175

[3] S J Cristol and B E Greenwald *Tetrahedron Lett* 1976 2105

[4] R F Hudson and L Keay *J Chem Soc* 1960 1865

[5] J H Baxendale *Radiat Res Suppl* 1964 **4** 139

[6] V D Parker *J Am Chem Soc* 1976 **98** 98

[7] N Getoff and S Solar *Monatsh Chem* 1974 **105** 241

[8] G Brunton B C Gilbert and R J Mawby *J Chem Soc Perkin Trans* 2 1976 650

[9] D C Appleton B Brocklehurst J McKenna M J Smith P S Taylor S Thackerey and A R Walley *J Chem Soc Chem Commun* 1977 108

[10] P J Kropp G S Poindexter N J Pienta and D C Hamilton *J Am Chem Soc* 1976 **98** 8135

[11] R S Givens and L Strebowski *J Am Chem Soc* 1975 **97** 5867

[12] S J Cristol D P Stull and R R Daussin *J Am Chem Soc* 1978 **100** 6674

[13] T Emoto R Okazaki and N Inamoto *Bull Chem Soc Jpn* 1973 **46** 898 R S Davidson R A Sheldon and S Trippett *J Chem Soc (C)* 1966 722 S K Wong W Sytnyk and J K S Wan *Can J Chem* 1971 **49** 994

[14] E E Nifant ev A I Zavalishina S F Sorokina and A A Borisenko *J Gen Chem USSR (Engl Transl)* 1976 **46** 469

[15] W A Mosher and R R Irino *J Am Chem Soc* 1969 **91** 756

[16] A F Gerrard and N K Hamer *J Chem Soc (B)* 1969 369 N K Hamer and R D Tack *J Chem Soc Perkin Trans* 2 1974 1184