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

By HENDRIK P. BENSCHOP,* CORNELIS A. G. KONINGS, and DOMINIQUE H. J. M. PLATENBURG
(*Prins Maurits Laboratory TNO*, 2280 AA *Rijswijk, The Netherlands*)

and RUDOLF DEEN
(*Central Laboratory TNO*, 2600 AE *Delft, The Netherlands*)

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 $(MeO)_2P(S)SMe$ [(**1**), λ_{max} 202 nm, ϵ_{254} 83 ± 2 l mol^{-1},Pr^iOH] in Pr^iOH the photosolvolysis product $(MeO)_2P(S)OPr^i$ (**2**) (Scheme 1) becomes the major reaction product (66%).†

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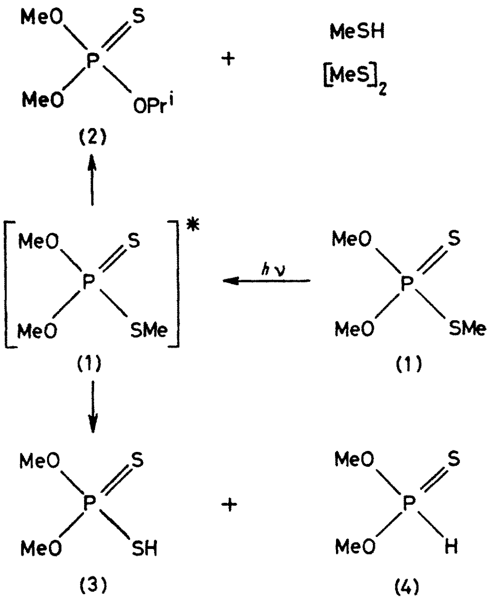
† Pesticides with the general structure $(MeO)_2P(S)SR$, *e.g.* malathion [R = $[CH(CO_2Et)CH_2(CO_2Et)]$] and dimethoate [R = $CH_2C(O)NHMe$], show qualitatively the same photochemistry as the title compound (R = Me).

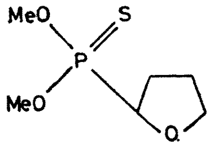
The photoreduction products (**3**) and (**4**) are formed to a minor extent (<6%).



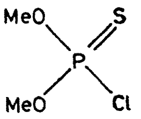
Scheme 1

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 $\mathrm{Pr^iOH}$, (ii) photosolvolysis *via* the radical cation $[(\mathrm{MeO})_2\mathrm{P(S)SMe}]^{\bullet+}$, (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 $\mathrm{Pr^iOH}$ (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 $\mathrm{Pr^iOH}$ concentration. At high concentrations of $\mathrm{Pr^iOH}$ ($\geqslant 0{\cdot}4$ 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 $\mathrm{Pr^iOH}$ ($\mathrm{MeOH/Pr^iOH} = 0{\cdot}8$—$4{\cdot}0$), we have calculated a capture ratio for MeOH *vs.* $\mathrm{Pr^iOH}$ of $1{\cdot}9 \pm 0{\cdot}4$. 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 $[(\mathrm{MeO})_2\mathrm{P(S)SMe}]^{\bullet+}$ 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 $\mathrm{H_2O}$–MeOH, in the presence of $\mathrm{N_2O}$, does not yield nitrogen, indicating that solvated electrons are not involved[7] in the photoreactions of (**1**).

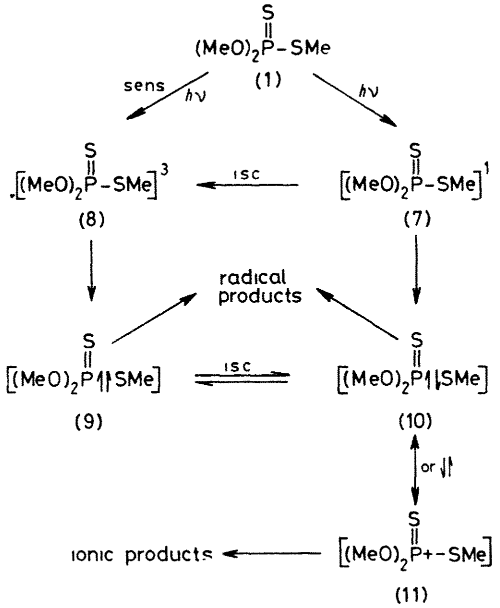


(5)



(6)

Thus, we propose that the photosolvolysis of (**1**) proceeds *via* an $S_{\mathrm{N}}1$(P)-mechanism with the thiophosphorylium ion $(\mathrm{MeO})_2\overset{+}{\mathrm{P}}(\mathrm{S})$ 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 $(\mathrm{MeO})_2\mathrm{P(S)}^{\bullet}$ 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 $\mathrm{CH_2Cl_2}$ yields *O,O*-dimethyl phosphorochloridothionate (**6**) as the major reaction product. (b) Irradiation of (**1**), either in $\mathrm{Pr^iOH}$ 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 $(\mathrm{MeO})_2\mathrm{P(S)}$–$\mathrm{CH(Ph)}$–$\mathrm{N(O^{\bullet})Bu^t}$ [in benzene: $a(\mathrm{P}) = 2{\cdot}54$, $a(\mathrm{N}) = 1{\cdot}43$, $a(\mathrm{H}) = 0{\cdot}28$ mT; *cf.* Brunton *et al.*[8]].



Scheme 2

The irradiations in THF and in $\mathrm{CH_2Cl_2}$ give end products which are evidently derived from radical-type reactions, whereas the e.s.r. evidence also shows that the radical $(\mathrm{MeO})_2\mathrm{P(S)}^{\bullet}$ 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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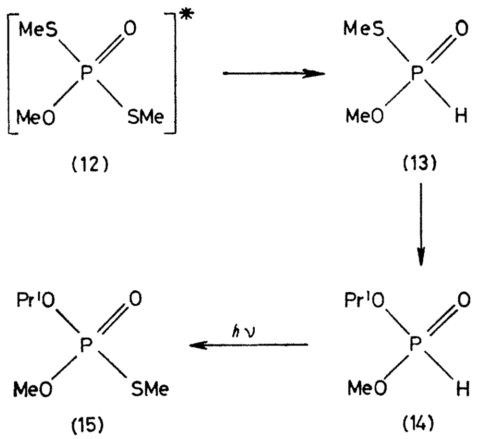
‡ Additional ionization energies were observed at 9·71 and 10·69 eV.

The alternative formation of (**2**) *via* direct addition of the radical $(MeO)_2\dot{P}(S)$ to Pr^{i}OH 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^{i}OH 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^{i}OH *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^{i}OH] in Pr^{i}OH This resulted in the rapid formation of MeO(Pr^{i}O) 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 $(MeS)_2$

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 *E*1*cb* hydrolysis of phosphoramidic halides[16]



Scheme 3

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