Photoreduction and Photoarylation of *O*-Ethyl *S*-n-Propyl Phenylphosphonothioate

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U.v. irradiation (254 nm) of *O*-ethyl *S*-n-propyl phenylphosphonothioate (1) in EtOH leads to a rapid photoreductive cleavage of the phosphorus–sulphur (ϕ = 0.14) or the sulphur–carbon (ϕ = 0.05) bond, as evidenced by the formation of *O*-ethyl phenylphosphinate, n-propanethiol, *O*-ethyl phenylphosphonothioic acid, and propane as the major reaction products. The concomitant photo-oxidation of EtOH to acetaldehyde is also observed. The rate of photoreduction of (1) is independent of the hydrogen-donor capacity of the solvent (MeOH, EtOH, or Pr^iOH). Hence, the reaction proceeds without prior hydrogen abstraction, probably by direct homolysis of the excited state of (1). In accordance with this, *in situ* spin-trapping experiments show the intermediacy of the phosphonyl radical EtO(Ph)$\dot{P}$(O).

Sensitizers with a triplet energy >80 kcal mol^{-1} sensitize the photoreduction of (1). Sensitization by aromatic hydrocarbons, *e.g.* benzene, is found to be complicated by simultaneous photoarylation of (1), which leads to the formation of *O*-ethyl diphenylphosphinate.

THE photodegradation of various organophosphate pesticides,[1] *e.g.* Parathion,[2] Dioxathion,[3] Methidathion,[4] and Inezin,[5] has been investigated in order to assess their persistance and properties as toxicological hazards in the environment. These studies were mainly qualitative and the underlying reaction mechanisms have received little attention.

We here report a quantitative study of the photoreduction (254 nm) of the title compound (1) in EtOH, serving as a model reaction for the photodegradation of organophosphate pesticides, in continuation of an earlier study on the photolysis of trimethyl phosphate.[6]

EXPERIMENTAL

U.v. spectra were recorded by means of a Zeiss PMQ 20A spectrometer. Mass spectrometric analyses were performed with a JEOL JMS-01SG-2 mass spectrometer, coupled with a JEOL JGC-1100 gas chromatograph.

Materials.—The title compound *O*-ethyl *S*-n-propyl phenylphosphonothioate (1) was prepared by alkylation of the dicyclohexylammonium salt of *O*-ethyl phenylphosphonothioic acid with a four-fold excess of n-propyl iodide in refluxing 1,2-dimethoxyethane. The product was purified successively by means of distillation under reduced pressure (b.p. 115 °C at 5 × 10^{-3} mmHg), molecular distillation and by preparative h.p.l.c. on a silica column, using ethyl acetate as an eluant. The gas chromatographic (g.c.) purity of the product was ⩾99.5% (SE-30). The i.r., n.m.r., and mass spectra of the product were in accordance with the proposed structure (Found: C, 54.2; H, 7.0; P, 12.7; S, 13.1. $C_{11}H_{17}O_2PS$ requires C, 54.1; H, 7.0; P, 12.7; S, 13.1%).

O-Ethyl phenylphosphinate and *OO*-diethyl phenylphosphonate were prepared according to standard procedures and were distilled under reduced pressure (purities ⩾99%, g.c., SE-30). *O*-Ethyl phenylphosphonothioic acid and *O*-ethyl phenylphosphonic acid were isolated from their respective dicyclohexylammonium salts (purities ⩾98%, acidimetric titration). For identification purposes, a small amount of *O*-ethyl *O*-n-propyl phenylphosphonothionate was isolated by means of preparative g.c. (SE-30) from the reaction mixture of *O*-ethyl phenylphosphonochloridothionate with sodium n-propoxide. The product was characterized by means of its mass spectrum.

Di-n-propyl disulphide was prepared by oxidation of the sodium salt of n-propanethiol with iodine (b.p. 132 °C at 40 mmHg; purity 99%, g.c., SE-30). *N*-Benzylidene-t-butylamine *N*-oxide was prepared according to Emmons.[7] All prepared compounds had satisfactory elemental analyses.

Methanol (Merck, Uvasol), isopropyl alcohol (Merck, Uvasol), and ethanol (Merck, p.a.), used in the irradiation experiments were dried on molecular sieves prior to use.

The following products were obtained commercially and were used without further purification: n-propanethiol (Fluka, 97%), propane (Matheson, 99.5%), acetaldehyde (B.D.H, 99%), n-heptadecane (Merck, 99.4%), t-butyl alcohol (Merck, p.a.), chloroacetic acid (Merck, 99.5%), benzophenone (Merck, 98%), *m*-methoxyacetophenone (Aldrich, 99%), triphenylene (Aldrich, 98%), *p*-xylene (Merck, 98%), anisole (Merck, p.a.), benzonitrile (B.D.H., 97%), diphenylamine (Riedel-de Haen, p.a.), fluorene (Aldrich, 98%), and perfluorohexane (Fluka, ⩾99%).

Irradiation Procedures.—Irradiations were carried out in a Rayonet RPR 208 reactor (Southern New England Ultraviolet Company, U.S.A.), equipped with either RPR-2537 Å or with RPR-3000 Å lamps. Before irradiation, helium was passed for 2 h through the solution (*ca.* 15 ml) in a quartz vessel (*ca.* 25 ml) in order to remove oxygen. A slight positive pressure of helium was maintained during irradiation. Samples were removed during irradiation with a syringe *via* a rubber septum. Pyrex vessels were used for irradiations with the RPR-3000 Å lamps.

Analysis of the Reaction Products.—*Gas chromatographic procedures*. G.c.-analyses were performed with a Pye-Unicam 104 apparatus, equipped with a flame-ionization detector. Peak areas were measured with an Infotronics CRS 304 integrator (Techmation).

After addition of known amounts of internal standard to the irradiated samples, quantitative analysis of the reaction products was done by measurement of peak areas of product and of internal standard. For each product analysed, the relationship between relative peak areas of product and of internal standard *versus* known amounts of product and of standard were determined separately.

O-Ethyl *S*-n-propyl phenylphosphonothioate (1), *O*-ethyl

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phenylphosphinate, *OO*-diethyl phenylphosphonate, and n-propyl disulphide were determined on a column packed with 15% SE-30 on Chromosorb W.A.W.-D.M.C.S., 80—mesh (length 2 m, ϕ 3—4 mm) at a column temperature of 220 °C, with n-heptadecane as the internal standard.

The volatile products n-propanethiol and acetaldehyde were analysed on a column (length 2 m, ϕ 3—4 mm) packed with Poropak Q (80—100 mesh) at a column temperature of 150 °C, using t-butyl alcohol as the internal standard.

Results on both columns were reproducible within 3%.

H.p.l.c. Procedures.—High-performance liquid chromatography was carried out at room temperature with a system consisting of a Waters Associates 6000A pump, a Valco universal injector, a steel column (length 0.25 m, internal diameter 4.6 mm) packed with Lichrosorb Si-60-5 (Merck) according to the procedure of Linder *et al.*,[8] and a variable-wavelength u.v.-detector (Techmation, model 970). *O*-Ethyl *S*-n-propyl phenylphosphonothioate and *O*-ethyl phenylphosphinate were chromatographed with n-hexane–EtOH (160/12.5) as a solvent (retention volumes 3.2 and 7.2 ml, respectively, at a flow rate of 1 ml min^{-1}), with the detector set at 260 nm. A calibration curve at this wavelength showed for both compounds a linear relationship between peak area and amount of product. Results were reproducible within 2.5%.

Paper Chromatography.—Quantitative paper chromatography of *O*-ethyl phenylphosphonothioic acid and of *O*-ethyl phenylphosphonic acid was performed on Whatman no. 1 paper, which had been washed thoroughly with 0.1M-aqueous hydrochloric acid and subsequently with distilled water.

Samples from the irradiated solution were applied directly to the paper by means of a microsyringe and were chromatographed in the ascending mode with n-butanol–pyridine–water (15 : 10 : 12, v/v) as the solvent system. The products were detected according to Hais.[9] Next, the spots were cut out, and the amount of phosphorus was analysed according to the procedure of Gerlach and Deuticke.[10] Blanks were substracted from the found values. Finally, the amounts of *O*-ethyl phenylphosphonothioic acid (R_F 0.65) and of *O*-ethyl phenylphosphonic acid (R_F 0.52) were determined from calibration curves. Results were found to be reproducible within *ca.* 7%.

Propane.—For the analysis of propane and, concomitantly, of *O*-ethyl phenylphosphonothioic acid, experiments were performed in quartz ampoules (25 ml), equipped with two straight-bore glass valves. *Ca.* 0.04M-solutions (12 ml) of *O*-ethyl *S*-n-propyl phenylphosphonothioate (1) in the ampoule were thoroughly degassed at the vacuum line through one of the valves by means of at least three freeze–thaw cycles. After irradiation for 20 min, air was admitted through the degassing valve. Samples were taken from the gas and liquid phases in the ampoule through a septum covering the other valve, and were analysed for propane by means of g.c. on a Poropak Q column at 150 °C. The amount of propane was calculated by comparison of its peak surface with that of a known amount of propane in a calibrated sample.

Determination of Quantum Yields.—Solutions of *O*-ethyl *S*-n-propyl phenylphosphonothioate (1) in EtOH (0.0045M, $E_{1\ \mathrm{cm}} > 10$ at 254 nm) and of chloroacetic acid in water (2M, $E_{1\ \mathrm{cm}} = 2.54$ at 254 nm) in quartz tubes, all filled to the same height, were deoxygenated by means of a stream of helium. The solutions were then pre-heated in a thermostatted bath at 34.8 °C and were placed alternatively into a 'merry-go-round' set up in the Rayonet reactor, in which the lamps had been pre-heated. Immediately thereafter, the samples were irradiated for 35 min (*ca.* 20% conversion), during which period the temperature remained constant within 0.5 °C.

Samples of the irradiated solutions were analysed for organophosphate products as described above. The chloride content of the actinometer solutions was determined by titration with mercuric nitrate.[11] In separate experiments it was shown that the amount of chloride released from the actinometer did not increase when the concentration of chloroacetic acid in water was increased from 1 to 2M. Hence, the calculation of quantum yields was straightforward, since (i) the quantum yield for the actinometer at 34.8 °C could be calculated from the data of Smith *et al.*,[12] (ii) necessary conditions of total absorption in both sample and actinometer solutions prevailed, and (iii) absorption due to reaction products was proved to be insignificant relative to absorption by starting material.

Spin-trapping Experiments.—E.s.r. spectra were recorded on a JEOL ME-IX spectrometer, equipped with matching u.v. irradiation unit JES-UV-1. Thick-walled quartz tubes (Wilmad Glass Company) were employed when EtOH was used as a solvent; thin-walled quartz tubes were used for experiments in benzene.

The *in situ* spin trappings were carried out at approximately equimolar concentrations of *O*-ethyl *S*-n-propyl phenylphosphonothioate (1) and of the spin trap *N*-benzylidene-t-butylamine *N*-oxide: *ca.* 0.1M in benzene, whereas in EtOH 0.04 and 0.4M solutions were used.

All solutions were deoxygenated prior to e.s.r. measurements in the tubes by purging with nitrogen for several minutes.

RESULTS

Ultraviolet Spectroscopy.—The absorption spectrum of EtO(Ph)P(O)SnPr (1) in EtOH (Figure 1) has the characteristic long wavelength absorption maxima ($\varepsilon_{273} = 640 \pm 20$; $\varepsilon_{267} = 810 \pm 10$; $\varepsilon_{259} = 780 \pm 10$) and short wavelength absorption region ($\lambda_{\max.} < 230$ nm) of mono-substituted benzene derivatives. Additionally, we observe for (1) a broad absorption with a maximum at 236 nm ($\varepsilon = 3\,200 \pm 100$), which is absent in an oxygen analogue of (1), *i.e.* (EtO)$_2$P(Ph)O (see Figure 1) and in (EtO)$_2$P(O)SEt. In n-hexane this latter maximum in the absorption of (1) is shifted only slightly to longer wavelength (238 nm).

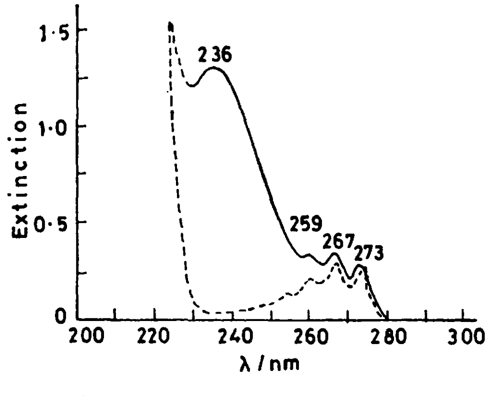

FIGURE 1 Absorption spectra of EtO(Ph)P(O)SnPr (——; 0.41 mM) and of (EtO)$_2$Ph(P)O (– – –; 0.36 mM) in EtOH

Qualitative Analysis of Irradiation Products.—Irradiation in the Rayonet reactor of a *ca.* 0.04M-solution of compound (1) in deoxygenated EtOH at 254 nm leads to a rapid disappearance of (1). The nature of the reaction products, as identified by comparison with authentic samples, indicates that concurrently at least the following three types of reaction take place: (i) photoreductive cleavage of the phosphorus–sulphur bond, as evidenced by the formation of *O*-ethyl phenylphosphinate, EtO(Ph)P(O)H (g.c.–m.s., h.p.l.c.), n-propanethiol (g.c.) and di-n-propyl disulphide (g.c.–m.s.); (ii) photoreductive cleavage of the sulphur–carbon bond, as shown by the formation of *O*-ethyl phenylphosphonothioic acid, EtO(Ph)P(S)OH (p.c.), its oxygen-analogue * EtO(Ph)P(O)OH (p.c.), and propane (g.c.); (iii) photosolvolysis of compound (1), as follows from the formation of *OO*-diethyl phenylphosphonate, $(EtO)_2Ph(P)O$ (g.c.–m.s., h.p.l.c.).

TABLE 1

Concentrations [a] (mmol l^{-1}) and balance of products after two separate irradiations of *O*-ethyl *S*-n-propyl phenylphosphonothioate (1) in EtOH (254 nm) at various times of irradiation

	Irradiation time (min)							
	0		10		20		30	
Product (mmol l^{-1})	Irr. 1	Irr. 2	Irr. 1	Irr. 2	Irr. 1	Irr. 2	Irr. 1	Irr. 2
EtO(Ph)P(O)SnPr	42.0	39.7	36.4	38.7	32.9	34.2	29.6	31.7
	(42.3) [b]	(41.1) [b]	(39.0) [b]	(41.8) [b]	(33.1) [b]	(35.6) [b]	(31.3) [b]	(31.7) [b]
EtO(Ph)P(O)H			2.4	1.7	4.1	5.0	7.8	6.4
			(2.1) [b]	(1.9) [b]	(3.9) [b]	(4.2) [b]	(5.4) [b]	(6.2) [b]
EtO(Ph)P(S)OH			0.5	0.4	1.2	0.9	1.4	1.2
EtO(Ph)P(O)OH			0.4	0.2	0.4	0.5	0.4	0.7
$(EtO)_2Ph(P)O$			0.1	0.2	0.5	0.7	0.7	1.0
P_{total}	42.0	39.7	39.8	41.2	39.1	41.3	39.9	41.0
Pr^nSH			2.6	2.5	4.8	5.0	7.0	6.7
$(Pr^nS-)_2$			0.1	0.1	0.1	0.3	0.2	0.4
Propane [c]								
Acetaldehyde			1.7	1.5	2.6	2.7	5.2	3.9

[a] Each concentration averaged from two measurements. Estimated error *ca.* 5%. [b] Values in parentheses refer to h.p.l.c.-analyses. [c] See Table 2.

The formation of benzene (g.c.) and of *OO*-diethyl phosphonate, $(EtO)_2P(O)H$ (g.c.–m.s.) upon prolonged irradiation (>1 h) indicates that the phosphorus–aryl bond of (1) is not completely stable with regard to photoreduction either. Tentatively, we assume that the primarily formed reaction product $EtO(Pr^nS)P(O)H$ is rapidly solvolysed to $(EtO)_2P(O)H$.[13]

Finally, the observed formation of acetaldehyde (g.c.) as a reaction product is in accordance with hydrogen donation by the solvent EtOH for the above-mentioned photoreduction reactions.[14]

Quantitative Analysis of Irradiation Products.—For a quantitative analysis of the reaction products, samples were taken from the quartz reaction vessel, through which a slow stream of helium was bubbled, at various time intervals without interruption of the irradiation. Volatile reaction products were determined by g.c.-analysis, after addition of an internal standard. The title compound (1), EtO(Ph)P(O)H, $(EtO)_2Ph(P)O$, and di-n-propyl disulphide were separated satisfactorily and were hence analysed on a silicone SE-30 column, whereas the low-boiling products n-propanethiol, propane, and acetaldehyde were analysed on a Porapak Q column. Additionally, (1) and EtO(Ph)P(O)H were analysed by means of h.p.l.c. on a silica column, with n-hexane–ethanol as an eluant. The acids EtO(Ph)P(S)OH and EtO(Ph)P(O)OH were determined by means of quantitative paper chromatography.[10]

In Table 1, the results are summarized for the quantitative analysis of the reaction products of two separate irradiations of (1), at various times of irradiation. Evidently, photoreduction of the phosphorus–sulphur bond of (1) is the main reaction taking place, with formation of equivalent amounts of EtO(Ph)P(O)H on the one hand and of n-propanethiol and disulphide (as far as not due to photosolvolysis, see below) on the other hand.

On comparison of the amounts of EtO(Ph)P(S)OH and of its oxidized derivative EtO(Ph)P(O)OH with the amount of EtO(Ph)P(O)H, it appears that photoreduction of the sulphur–carbon bond of (1) proceeds 2.5—3.5 times slower than the reduction of the phosphorus–sulphur bond of (1).

TABLE 2

Concentrations of products resulting from the photoreduction of the sulphur–carbon bond after irradiation (254 nm) of a 40mM solution of *O*-ethyl *S*-n-propyl phenylphosphonothioate (1) in EtOH for 20 min in a quartz ampoule *in vacuo*

	Concentration (mmol l^{-1})	
Product	Irrad. 3	Irrad. 4
EtO(Ph)P(S)OH [a]	0.5^5	0.4^5
Propane	0.5^5	0.3^5

[a] The formation of EtO(Ph)P(O)OH was not observed (p.c.), due to thorough degassing of the solution prior to irradiation. See Experimental section.

Separate irradiations were carried out in a quartz ampoule in order to determine the amount of propane which is formed on photoreduction of the sulphur–carbon bond of (1). As shown in Table 2, the amounts of EtO(Ph)P(S)OH and of propane formed are reasonably equivalent, within experimental error.

Photosolvolysis of (1) leading to $(EtO)_2Ph(P)O$ appears to be a minor process, which proceeds at least twice as slowly as photoreduction of the sulphur–carbon bond and nearly seven times slower than the photoreduction of the phosphorus–sulphur bond.

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* Probably formed by oxidation of EtO(Ph)P(S)OH with traces of oxygen in the solution. In separate experiments it was shown that the latter product is oxidized in the presence of oxygen under our irradiation conditions, whereas EtO(Ph)P(O)H is not significantly oxidized under these conditions.

As shown in Table 1, the sum total of the various organophosphate reaction products which have been determined quantitatively accounts almost completely for the total of compound (1) which disappears during the photolysis.

Finally, it should be mentioned that the amount of acetaldehyde in the reaction mixture is substantial, although less than expected on the basis of the overall amount of photoreduction which has taken place. This is probably due to secondary photolysis of acetaldehyde to methane and carbon monoxide.[15] No evidence was found for a photochemical condensation reaction of acetaldehyde with EtO(Ph)P(O)H.[16]

Quantum Yields.—Quantum yields for the photoreduction of the phosphorus–sulphur bond and of the sulphur–carbon bond of compound (1) in EtOH, as well as for the overall disappearance of (1), were determined in the Rayonet reactor in a ' merry-go-round ' set-up [17] at 34.8 °C ± 0.5 °C. A 2M-aqueous solution of chloroacetic acid was used as an actinometer ($\phi = 0.403$ at 34.8 °C).[12]

TABLE 3

Quantum yields for the photoreduction (254 nm) of the phosphorus–sulphur and sulphur–carbon bonds of *O*-ethyl *S*-n-propyl phenylphosphonothioate (1), as well as for the overall disappearance of (1) in EtOH (34.8 °C ± 0.5 °C)

Product	Quantum yield [a]
EtO(Ph)P(O)H	0.14 ± 0.01
EtO(Ph)P(S)OH	0.05 ± 0.01
Disappearance of (1)	0.20 ± 0.01

[a] Averaged value from two experiments.

The results summarized in Table 3, indicate that the overall photoreduction of (1) is a rather efficient process. To our knowledge, quantum yields for similar photoreactions are not available in the literature for comparison. The photoreduction of the sulphur–carbon bond of (1) might be compared with the benzophenone-sensitized scission of the carbon–sulphur bond in di-n-hexyl disulphide,[18] which is however a much less efficient process (ϕ *ca.* 10^{-3}).

Rates of Photoreduction in Solvents with Varying Hydrogen-donor Capacities.—In order to evaluate the dependence of the photoreduction rate of the title compound (1) on the homolytic hydrogen-donor capacity of the solvent, we have measured the rate of disappearance of (1) in deoxygenated MeOH, EtOH, and Pr^iOH, in which primary, secondary, and tertiary hydrogen, respectively, can be abstracted from the carbon–hydrogen bond.

TABLE 4

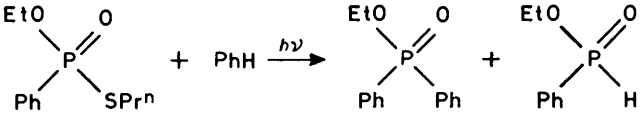
First-order reaction rates (k_1/min^{-1}) and half-lives (min) for the disappearance of *O*-ethyl *S*-n-propyl phenylphosphonothioate (1) during irradiation (254 nm) in MeOH, EtOH, and Pr^iOH, respectively (35 °C)

Solvent	k_1/min^{-1}	Half-life/min
MeOH	$(1.31 \pm 0.05)\ 10^{-2}$	53 ± 2
EtOH	$(1.33 \pm 0.04)\ 10^{-2}$	52 ± 2
Pr^iOH	$(1.34 \pm 0.07)\ 10^{-2}$	52 ± 2

Upon irradiation (1) disappears in all three solvents according to first-order kinetics for at least two half-lives of the reaction. Calculated first-order reaction rates and half-lives are summarized in Table 4.

Sensitization and Quenching Experiments.—In an attempt to obtain some information with regard to the excited state of (1), which is responsible for its photoreduction, we have studied the influence of several sensitizers, and of a quencher, on the reaction. Sensitization experiments at $\geqslant$300 nm were performed with Rayonet ' Sunlight Phosphor lamps ', by irradiation for 20 h of *ca.* 0.05M-solutions of (1) in EtOH in Pyrex vessels. The following sensitizers were added, respectively, in such concentrations that light absorption due to (1) was insignificant relative to absorption due to the sensitizer: acetone (1.72M, E_T 80 kcal mol^{-1}), *m*-methoxyacetophenone (0.0086M, E_T 72.4 kcal mol^{-1}), benzophenone (0.39M, E_T 68.5 kcal mol^{-1}), and triphenylene (0.0035M, E_T 66.6 kcal mol^{-1}).[19] Only in the presence of acetone could a substantial reactivity of (1) be observed, although the expected products, *e.g.* EtO(Ph)P(O)H, were not identified. In separate experiments, it was shown that the latter product undergoes a rapid photoreaction with acetone in EtOH at 300 nm.[16]

By adaptation of the concentration of the sensitizer and of (1), sensitization experiments at 254 nm were arranged in such a way, that $\geqslant$99% of light absorption was due to the sensitizer. Solutions of (1) in EtOH were irradiated for 1 h in quartz vessels with, respectively, benzene (8.5M, E_T 84.4 kcal mol^{-1}), anisole (3.7M, E_T 80.7 kcal mol^{-1}), *p*-xylene (6.4M, E_T 80.1 kcal mol^{-1}), benzonitrile (5.9M, E_T 77.0 kcal mol^{-1}), diphenylamine (0.4M, E_T 71.0 kcal mol^{-1}), and with fluorene (0.07M, E_T 67.6 kcal mol^{-1}).[19] In the presence of benzene and *p*-xylene, a rapid photoreduction of (1) took place with formation of EtO(Ph)P(O)H and EtO(Ph)P(S)OH as the expected products. With anisole only a trace of photoreduction took place, whereas no reaction at all was found in the presence of the other sensitizers.



In addition to the usual products, the reaction sensitized by benzene led to a new major reaction product, *i.e.* *O*-ethyl diphenylphosphinate $(EtO)P(Ph)_2O$ (g.c.–m.s.), whereas in the presence of *p*-xylene the corresponding product *O*-ethyl phenyl-2,5-dimethylphenylphosphinate is formed (g.c.–m.s.). The photoreduction in benzene also proceeds readily in complete absence of EtOH, leading to *O*-ethyl diphenylphosphinate and *O*-ethyl phenylphosphinate as the major reaction products of this novel photoarylation reaction.*[21]

Attempts to quench the photoreduction reaction of (1) in EtOH (0.01M) at 254 nm by addition of *trans*-piperylene (0.02M, E_T 58.8 kcal mol^{-1}) were unsuccessful, since the rate of disappearance of (1) was not depressed under these conditions, where $\geqslant$90% of the light absorption was due to (1).

In situ *Spin Trapping.*—The photoreactions of (1) both in EtOH and in benzene (sensitized) were also studied by *in situ* irradiation with a high-pressure mercury arc in the presence of *N*-benzylidene-t-butylamine *N*-oxide (2) as the spin trap.

The e.s.r. spectra showed hyperfine structure (h.f.s.). Variations in the relative intensities of the separate h.f.s. lines of the spectra of one single run at different times already revealed that several spin adducts were formed next to and after each other. This complicated the analysis of the various products that were being trapped. However,

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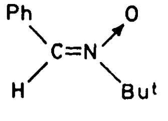
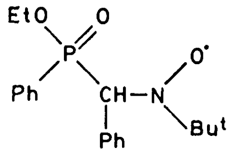
* For an analogous photoarylation reaction *via* thermally generated radicals, see ref. 20.

one feature in nearly all of the observed spectra is obvious, namely that the distance between the outermost h.f.s. lines exceeds 5 mT (see Figure 2a and 2b, spectra obtained in benzene and in EtOH, total width = 5.20 and 5.15 mT respectively).


(2)


(3)

A total width of *ca.* 5.2 mT is much larger than is encountered in the isotropic spectrum of those nitroxides in which the h.f.s. is due to splittings by nitrogen and hydrogen only. In the latter case a total width equal to $2A_N + A_H$, would come to *ca.* 3.5 mT at most. Hence, in the observed 5.2-mT wide spectra some additional splitting will be involved. On the assumption of this being due to a doublet splitting by ^{31}P, a value of A_P of *ca.* 2 mT is obtained. From a study by Brunton *et al.*[22] P-couplings in this order of magnitude are known to occur in P-centred adducts to (2). In view of their findings, we assign structure (3) to our spin adduct with the total width of 5.2 mT.

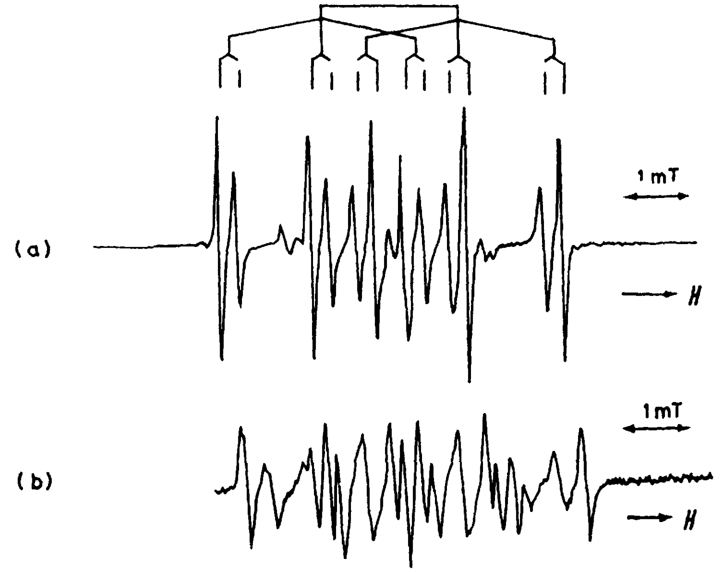
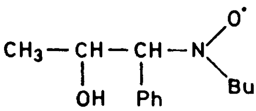
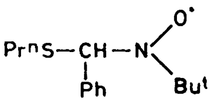


FIGURE 2

In benzene the complete spectrum of (3) could be identified by visual inspection of the series of spectra taken at different times during the irradiation experiments. A partial spectrum of the expected twelve lines could be traced. The outmost two lines on the high-field and the low-field side outside the range of 3.5 mT always showed the same rate of appearance and decay as did 10 other lines. The 12 lines thus singled out, however, do not all have equal intensities, but can be divided into two groups of almost equal intensity. Each of the stronger lines is accompanied by a weaker one at a separation of *ca.* 0.28 mT (see Figure 2).


(4)


(5)

We suggest that this abnormal appearance of the measured spectrum is due the presence of two diastereoisomers in the spin adduct (3), as a result of the addition of the chiral P-centred radical [23] to the prochiral carbon atom of the spin trap (2).

In EtOH as the solvent the full partial spectrum of the phosphonyl adduct (3) was less easy to identify. The spin trapping gave rise to additional spin adducts, always present in preponderance. At low concentrations of both (1) and spin trap (*ca.* 0.04M), the partial spectrum of (3) with the characteristic large total width (5.15 mT) was observed as a transient only, quickly decaying during the first hour of irradiation. On continued irradiation one single six-line spectrum persisted, consisting of a triplet (A = 1.50 mT), split into doublets (A = 0.35 mT). It was assigned to the α-hydroxyethyl spin adduct (4) (literature:[24,25] A_N = 1.535 mT, A_H = 0.360 mT, in EtOH).

At a high concentration level of both (1) and spin trap (0.4M), the partial spectrum with total width of 5.15 mT persisted and could still be observed in the dark after termination of the photolysis (see Figure 2b).

TABLE 5

E.s.r. coupling constants (in mT) of the diastereoisomeric forms (3a) and (3b) of the spin adduct EtO(Ph)P(O)–CH(Ph)N(Ȯ)Bu^t in EtOH [a]

	A_N	A_H	A_P
(3a)	1.44	0.36	1.96
(3b)	1.45	0.37	1.83

[a] In benzene unique sets of the coupling constants of the forms a and b could not be determined. The average values are: A_N = 1.41, A_H = 0.28, and A_P = 2.10 mT. However, from the regularities in the intensity ratios of the h.f.s. lines it was deduced that, as in EtOH, the sum $A_N + A_H + A_P$ in the two forms a and b in benzene is approximately equal.

The assigned coupling constants for the diastereoisomers a and b of (3) in EtOH, based on computer-generated spectral simulations are given in Table 5.

In addition to the aforementioned spin adducts, at least one extra free radical appeared to be present ($\leqslant 20\%$ of the percentage total). Its spectrum partially coincided with that of the α-hydroxyethyl adduct (4), due to a triplet splitting (A_N *ca.* 1.38 mT) and showed a further doublet splitting ($A_H = 0.18$ mT). In all likelihood, the latter spectrum should be assigned to the n-propylthiyl radical adduct (5) to the spin trap (2). An e.s.r. spectrum with the latter coupling constants was also obtained upon photolysis of a solution of propanethiol with (2) in EtOH.

DISCUSSION

The main reactions upon irradiation of (1) in EtOH can be described as photoreduction of the phosphorus–sulphur (α-scission) and of the sulphur–carbon bond (β-scission), as indicated by the obtained products. Both the nature of these products and the results of the spin-trapping experiments give strong indications that the reactions proceed by way of a free-radical mechanism.

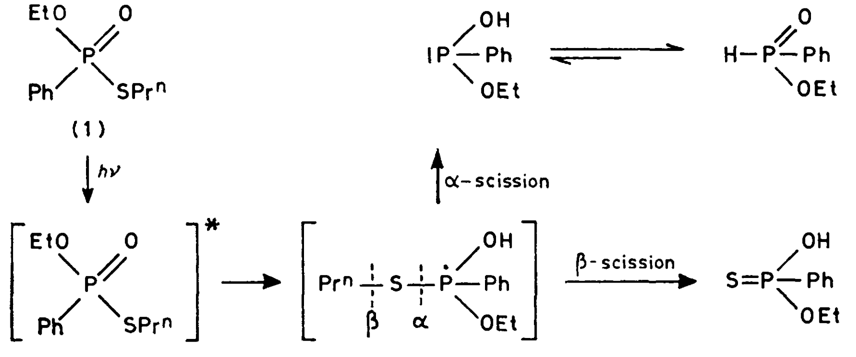
The simultaneous α- and β-scission reactions of (1) bear a strong resemblance to the chemistry of phosphoranyl radicals [26] formed *e.g.* by addition of thiyl radicals to P^{III}-compounds.* In principle, the intermediate formation of the phosphoranyl radical [29] $EtO(Ph)\dot{P}(OH)SnPr^n$, by means of hydrogen abstraction from the solvent by the excited state of (1), could explain the photoreduction reactions according to Scheme 1.

However, there are a number of arguments against the intermediacy of the phosphoranyl radical $(EtO(Ph)\dot{P}(OH)SnPr^n$. First, the rate of photoreduction of (1) is independent of the hydrogen-donor capacity (MeOH, EtOH, Pr^iOH). Evidently, hydrogen abstraction from the solvent is not a rate-determing step of the reaction sequence leading to the observed products, in contrast with the photoreduction of various ketones [30-32] and heteroaromatic compounds.[33] This result is at variance with the intermediacy of the phosphoranyl radical, since the subsequent α- and β-scission reactions would be expected to be rapid reaction steps, following rate-determining hydrogen abstraction. Secondly, we observed no photoreduction of (1) while benzophenone was being photoreduced by irradiation at 300 nm in EtOH, in its presence. If a phosphoranyl radical were a viable intermediate, it might be formed under these conditions by means of chemical sensitization:

$$\underset{(1)}{EtO(Ph)P(O)SPr^n} + Ph_2\dot{C}{-}OH \longrightarrow EtO(Ph)\dot{P}(OH)SPr^n + Ph_2CO$$

Thirdly, the photoarylation of (1) in benzene and *p*-xylene is difficult to envisage *via* a phosphoranyl radical as an intermediate.

Finally, (1) is also rapidly photolysed by irradiation at 254 nm in perfluorohexane, demonstrating that hydrogen abstraction is not at all a prerequisite for the photodecomposition of (1). We thus consider the abovementioned arguments as unequivocal evidence against the intermediacy of a phosphoranyl radical in our reaction sequence (Scheme 1).



Scheme 1

Alternatively, we suggest that homolysis of the phosphorus–sulphur and of the sulphur–carbon bond proceeds directly in the excited state of (1). These reactions lead primarily to the radical pairs (6) and (7), which give the main reaction products by subsequent abstraction of hydrogen from the solvent † as shown in Scheme 2.

The formation of the phosphonyl radical in the radical pair (6) is also supported by the results of our spin-trapping experiments. The appearance, upon irradiation of (1) with *N*-benzylidene-t-butylamine *N*-oxide (2) in EtOH, of the spin adducts with the assigned structures (3) and (5) is most readily explained by reaction of the two radicals in the radical pair (6) with the spin trap (Scheme 3).‡

The intermediacy of the radical pair (6) can also be accommodated with the observed (minor) photosolvolysis product $(EtO)_2Ph(P)O$. We assume that an electron transfer can take place in the (singlet) free-radical pair (6), eventually preceded by interconver-

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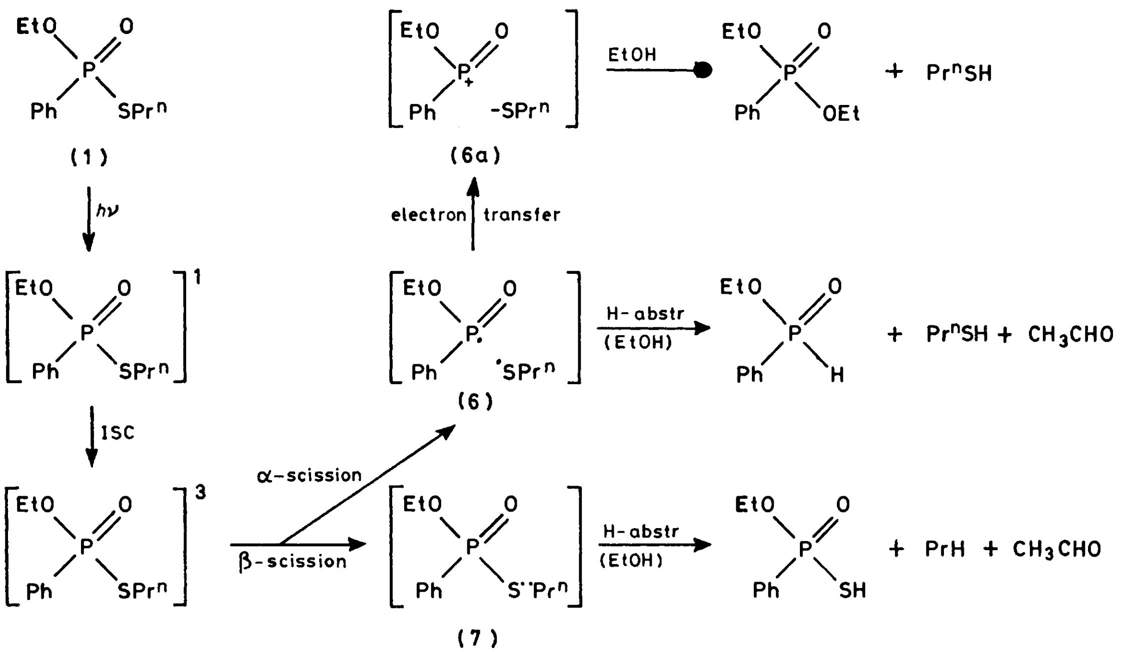
* The ready homolysis of the phosphorus–sulphur bond of (1) indicates that the addition of thiyl radicals to P^{III}-compounds might be a reversible process, as suggested earlier by Bentrude [27] and by Brown.[28]

† The aforementioned e.s.r.-evidence for the formation of the α-hydroxyethyl radical, as well as the formation of acetaldehyde as a major reaction product, indicates clearly a primary homolysis of a secondary C–H bond of EtOH, followed by homolysis of the O–H bond.

‡ Recently, Brunton *et al.*[22] obtained spin-adducts similar to (3), which were probably formed by thermal addition to the spin-trap and subsequent photochemical formation of the stable radical, rather than by addition of a phosphorus-centred radical to (2). However, such an addition reaction of (1), followed by photochemical generation of (3) cannot be envisaged in our case, in view of the low thermal reactivity of (1).



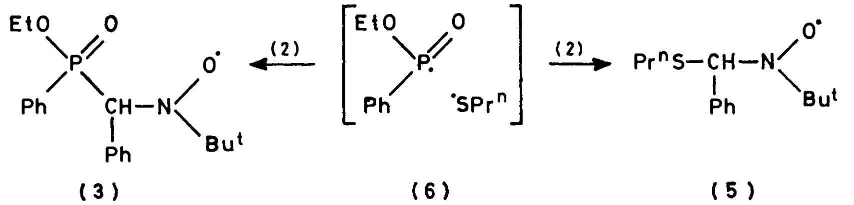
Scheme 2

sion of a triplet free-radical pair. This leads to the ion pair (6a), which would rapidly react with the solvent EtOH. Similar reaction mechanisms have also been assumed for the photosolvolysis of *e.g.* benzyl [34] and alkyl [35] halides.

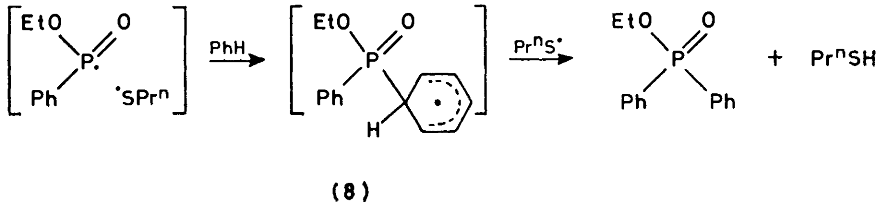
Finally, the photoarylation of (1) as the major reaction pathway in benzene and in *p*-xylene may also be explained by way of the phosphonyl radical EtO(Ph)$\dot{\mathrm{P}}$(O) in (6). Fields and Rolih [20] generated this type of free-radical by means of hydrogen abstraction from the phosphorus–hydrogen bond of *OO*-diethyl phosphonate, $(EtO)_2P(O)H$, with t-butoxyl radicals. In this way they obtained a ready phosphonation of methyl benzoate. Probably, the photoarylation of (1) proceeds by addition of the phosphonyl radical from (6) to benzene, followed by hydrogen abstraction from the intermediate cyclohexadienyl radical (8), *e.g.* by the n-propylthiyl radical (Scheme 4).

To our knowledge relevant information in the literature on the nature of the excited state(s) of (1) is virtually absent. The characteristic u.v.-absorption of (1) at 236 nm, absent when either the phenyl or the thiopropyl group of (1) is replaced by alkoxy (see Figure 1), suggests that the initially formed singlet state of (1) results from an n–π^* promotion of an electron from the lone pair on sulphur, possibly to the antibonding π-system of the phenyl group.[36,37] Alternatively, a trigonal bipyramid-like structure might be formed, in which an electron is promoted to an unoccupied *d*-orbital of the phosphorus atom.[38] If racemization of such a structure were possible, this could be relevant for the hitherto unexplained rapid photoepimerization [39] in n-heptane solution (254 nm) of *O*-menthyl *S*-methyl phenylphosphonothioate, which is structurally closely related to (1).

With regard to the multiplicity of excited states of (I), we suggest that the heavy-atom effect, due to the presence of both phosphorus and sulphur, will cause the



Scheme 3



Scheme 4

primarily formed singlet state to convert very rapidly into a triplet state. Such an intersystem crossing to a triplet as a reacting species would be in accordance with the results of our sensitization experiments, which might be explained as possibly involving a high-energy triplet (E_T *ca.* 80 kcal mol^{-1}) in the photoreduction reactions of (1).

Finally, it should be noted that the rather high quantum yield for the α- and β-scission reactions of (1) ($\phi = 0.14$ and 0.05 respectively, Table 3) represent minimal values, since the data cannot be corrected for cage return. Within the primarily formed intimate free-radical pairs, cage return probably takes place, albeit to an unknown degree, thus enhancing the formal analogy between the chemistry of the reacting excited species of (1) and of phosphoranyl radicals.[26]

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