

The Photolytic Reaction of Thiols with Diphenylvinylphosphine †

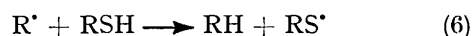
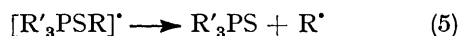
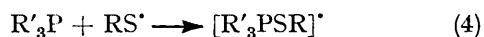
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The thiols RSH react with diphenylvinylphosphine under u.v. irradiation to give $\text{Ph}_2\text{PC}_2\text{H}_4\text{SR}$ when R is Et, Pr^n , Bu^n , Ph, or C_6F_5 . If R is Bu^t or PhCH_2 , however, $\text{Ph}_2(\text{vinyl})\text{PS}$ and RH are formed instead. The behaviour of Pr^nSH is intermediate, and it produces $\text{Ph}_2\text{PC}_2\text{H}_4\text{SPr}^n$, $\text{Ph}_2(\text{vinyl})\text{PS}$, and $\text{Ph}_2\text{P}(\text{S})\text{C}_2\text{H}_4\text{SPr}^n$. Excess of thiol leads to $\text{Ph}_2\text{P}(\text{S})\text{C}_2\text{H}_4\text{SR}$ in every case. The formation of the different products can be accounted for by RS^\cdot radical attack on either olefin or phosphorus. The favoured route appears not to depend on the nature of RS^\cdot , however, but on the ease of elimination of R^\cdot , a step involved in the route to the phosphorus(v) sulphide. This mechanism demands either that RS^\cdot attack on P^{III} is readily reversible, or that the intermediate $[\text{Ph}_2(\text{vinyl})\text{PSR}]^\cdot$ readily undergoes intramolecular rearrangement. An equilibrium between the intermediates $\text{Ph}_2(\text{vinyl})\text{P}\cdot\text{SR}$ and $\text{Ph}_2\text{PC}\cdot\text{HCH}_2\text{SR}$ is probably established.

THIYL radicals, RS^\cdot , are conveniently generated¹ from thiols, RSH, or disulphides, RSSR, either by u.v. photolysis or by the action of free-radical initiators, and their chemistry has been extensively investigated. Thus the addition of thiols to olefins proceeds by a radical-chain mechanism² [equations (2) and (3)]. The products are anti-Markownikow.



A radical-chain mechanism also operates for the reaction of thiyls with tertiary phosphines or phosphites³ [equations (4)–(6)]. The final products are phosphorus(v) sulphides, produced by β -scission of the S–R bonds of the radical intermediate $[\text{R}'_3\text{PSR}]^\cdot$. The eliminated organic radicals R^\cdot have been detected by e.s.r. spectroscopy in some cases.⁴ Alkoxy-radicals, RO^\cdot , can also



† No reprints available.

¹ See e.g., L. Almasi in 'Sulphur in Organic and Inorganic Chemistry,' ed. A. Senning, Marcel Dekker, New York, 1971, ch. 4, p. 39.

² C. Walling and W. Helmreich, *J. Amer. Chem. Soc.*, 1959, **81**, 1144.

³ (a) C. Walling, O. H. Basedow, and E. S. Savas, *J. Amer. Chem. Soc.*, 1960, **82**, 2181; (b) C. Walling and M. S. Pearson, *J. Amer. Chem. Soc.*, 1964, **86**, 2262.

react in this manner, producing phosphine oxides,^{3a,4} and we have recently shown that the selenium analogues, RSe^\cdot , behave similarly, giving $\text{R}'_3\text{PSe}$.⁵ Additional reaction pathways involving α -scission of P–C^{3a,4} or P–O⁶ have also been identified, however, for the interaction of RO^\cdot with tertiary phosphines or phosphites. Such pathways have not been reported for any thiyl radical reactions. We have examined the photochemical reactions of several thiols with diphenylvinylphosphine (dvp) with the intention of producing unsymmetrical sulphur–phosphorus chelate ligands $\text{Ph}_2\text{PC}_2\text{H}_4\text{SR}$. Such a process operates smoothly for the photolytic addition of hydridophosphines to olefins such as dvp, forming, for example, $\text{Ph}_2\text{PC}_2\text{H}_4\text{P}(\text{CF}_3)_2$.⁷ Also, $\text{C}_6\text{F}_5\text{SH}$ reacts readily with dvp to yield $\text{Ph}_2\text{PC}_2\text{H}_4\text{SC}_6\text{F}_5$.⁸

RESULTS

An equimolar mixture of Pr^nSH and dvp under a nitrogen atmosphere was irradiated at room temperature for 19 h in a Pyrex vessel. The anti-Markownikow addition product, $\text{Ph}_2\text{PC}_2\text{H}_4\text{SPr}^n$, was formed in high yield as a pale yellow, rather viscous liquid. A trace amount of the phosphorus(v) derivative, $\text{Ph}_2\text{P}(\text{S})\text{C}_2\text{H}_4\text{SPr}^n$, was also identified from the ³¹P n.m.r. and mass spectra of the crude reaction product. A similar reaction using

⁴ J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 1969, **91**, 3944.

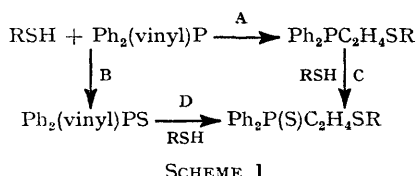
⁵ R. J. Cross and D. Millington, *J.C.S. Chem. Comm.*, 1975, 455.

⁶ W. G. Bentrude, *Tetrahedron Letters*, 1965, 3543.

⁷ L. Manojlović-Muir, D. Millington, K. W. Muir, D. W. A. Sharp, W. E. Hill, J. V. Quagliano, and L. M. Vallarino, *J.C.S. Chem. Comm.*, 1974, 999.

⁸ D. Millington and D. W. A. Sharp, unpublished results.

EtSH produced $\text{Ph}_2\text{PC}_2\text{H}_4\text{SEt}$ as the major product, along with a barely detectable amount of $\text{Ph}_2\text{P}(\text{S})\text{C}_2\text{H}_4\text{SEt}$. PhSH and $\text{C}_6\text{F}_5\text{SH}$ ⁸ react similarly with dvp to give $\text{Ph}_2\text{PC}_2\text{H}_4\text{SPh}$ and $\text{Ph}_2\text{PC}_2\text{H}_4\text{SC}_6\text{F}_5$, respectively and, in addition, irradiation of a 1 : 1 mixture of Bu^nSH -dvp was shown by n.m.r. to conform to this reaction pattern. Thus pathway A of Scheme 1 is followed [involv-



ing steps analogous to reactions (1), (2), and (3)] when R is Et, Pr^n , Bu^n , Ph, or C_6F_5 .

When these reactions were performed using a RSH : dvp ratio of 2 : 1 or greater, the products were exclusively the phosphorus(v) sulphides $\text{Ph}_2\text{P}(\text{S})\text{C}_2\text{H}_4\text{SR}$, presumably formed by the operations of pathways A and C. Steps analogous to (1), (4), (5), and (6) are implicated for pathway C.

In contrast to the above reactions, however, 1 : 1 mixtures of Bu^tSH and dvp or PhCH_2SH and dvp produced no detectable amount of $\text{Ph}_2\text{PC}_2\text{H}_4\text{SR}$ after irradiation. Instead, $\text{Ph}_2(\text{vinyl})\text{PS}$ and RH were formed (pathway B) along with traces of $\text{Ph}_2\text{P}(\text{S})\text{C}_2\text{H}_4\text{SR}$. Higher ratios of thiol to dvp led to $\text{Ph}_2\text{P}(\text{S})\text{C}_2\text{H}_4\text{SR}$, presumably *via* pathways B followed by D.

Pr^iSH appears to be of intermediate character in its reactions with dvp. 2 : 1 Mixtures lead, as expected, to good yields of $\text{Ph}_2\text{P}(\text{S})\text{C}_2\text{H}_4\text{SPr}^i$, but 1 : 1 reactions produced mixtures of $\text{Ph}_2\text{PC}_2\text{H}_4\text{SPr}^i$ and unchanged $\text{Ph}_2(\text{vinyl})\text{P}$, along with smaller amounts of $\text{Ph}_2(\text{vinyl})\text{PS}$ and $\text{Ph}_2\text{P}(\text{S})\text{C}_2\text{H}_4\text{SPr}^i$, suggesting that in this case pathways A, B, C, and D (Scheme 1) can all compete.

Several n.m.r. parameters are quite characteristic of the P^{III} and P^{V} products of these reactions making n.m.r. spectrometry particularly useful in identifying the presence of minor components. Most useful are the ^{31}P chemical shifts (Table 1). In addition the ^1H n.m.r.

TABLE 1

 ^{31}P Chemical shifts

$\text{Ph}_2\text{PC}_2\text{H}_4\text{SR}$		$\text{Ph}_2\text{P}(\text{S})\text{C}_2\text{H}_4\text{SR}$	
R	$\delta(^{31}\text{P})/\text{p.p.m.}$	R	$\delta(^{31}\text{P})/\text{p.p.m.}$
Et	-16.6	Et	+40.3
Pr^n	-17.1	Pr^n	+38.5
Pr^i	-17.0	Pr^i	+39.3
Bu^n	-17.1	Bu^n	+39.5
Bu^t		Bu^t	+39.5
PhCH_2		PhCH_2	+39.0
Ph	-21.1	Ph	

spectra show low-field multiplets (δ 7.8) assigned to the *ortho*-protons of the Ph(P) rings in the P^{V} derivatives only. Also, the protons of the C_2H_4 bridges form a relatively sharp unresolved multiplet (δ 2.75) for the

pentavalent phosphines, whereas two multiplets δ (ca. 2.3 and 2.6) are observed instead for $\text{Ph}_2\text{PC}_2\text{H}_4\text{SR}$.

DISCUSSION

The different products obtained from these reactions are consistent with RS^{\cdot} attack at the olefinic group when R is n-alkyl, aryl, or perfluoroaryl, but attack at the phosphorus atom when R is Bu^t or PhCH_2 . The behaviour of Pr^iSH would then indicate that $\text{Pr}^i\text{S}^{\cdot}$ can attack with similar facility at either site.

There appears, however, to be no compelling reason why some thiyls should attack one site in preference to another. The n-alkyl groups are electron donating, whereas Ph and C_6F_5 are respectively mildly and strongly electron attracting, yet all appear to attack the olefinic site preferentially. Moreover, while some π bonding in RS^{\cdot} might occur between sulphur and aryl, none would be expected between sulphur and alkyl. Thus, the electronic nature of the thiyl radicals seems unlikely to account for the marked difference in their reaction characteristics. The steric bulk of the thiyls can be similarly discounted as a directing influence in these reactions. The steric demand of EtS^{\cdot} can be contrasted with $\text{C}_6\text{F}_5\text{S}^{\cdot}$, as can $\text{Bu}^t\text{S}^{\cdot}$ with $\text{PhCH}_2\text{S}^{\cdot}$. (Moreover, $\text{Bu}^t\text{S}^{\cdot}$ radicals have been successfully attached to styrene, when no competing pathways are available.)⁹

Since the nature of RS^{\cdot} does not appear to direct the course of the 1 : 1 reactions between RSH and dvp, we propose that the directing influence is the character of the relevant R $^{\cdot}$ radical. The ease of formation of R $^{\cdot}$ can be (roughly) compared by considering the bond dissociation energies of R-H (Table 2). It is apparent

TABLE 2

Bond dissociation energies of R-H		
R	D/kcal mol ⁻¹	Ref.
PhCH_2	77	a
Bu^t	89.5	a
Pr^i	94	a
Et	97	a
Pr^n	99	a
Bu^n	101	a
Ph	103, 110	a, b
C_6F_5	152	b

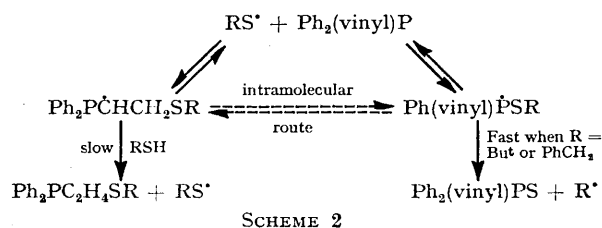
^a C. T. Mortimer, 'Reaction Heats and Bond Strengths,' Pergamon, London, 1962. ^b M. J. Krech, S. J. W. Price, and W. F. Yared, *Canad. J. Chem.*, 1974, **52**, 2673.

that the two most easily formed radicals, PhCH_2^{\cdot} and Bu^t , are the R groups of those thiols which react to produce $\text{Ph}_2(\text{vinyl})\text{PS}$. Free R $^{\cdot}$ radicals are liberated during this reaction sequence [reaction (5)]. The n-alkyl and aryl radicals are more difficult to produce, however, (any π bonding between sulphur and aryl would make Ar $^{\cdot}$ liberation from sulphur even less favourable than Table 2 suggests) and thiyls incorporating these radicals appear preferentially to attack the vinyl group of dvp, a reaction sequence that does not involve free R $^{\cdot}$. Energetically the Pr^i radicals fall between these two groups.

⁹ R. A. Gregg, D. M. Alderman, and F. R. Mayo, *J. Amer. Chem. Soc.*, 1948, **70**, 3740.

Thus the reaction products can be related directly to the ease of formation of R^\cdot . This alone, however, cannot account for the different reaction courses. The mechanisms of both sequences are well understood,²⁻⁴ and both involve initial attack of RS^\cdot , the characters of which do not explain which path is adopted (*vide ultra*). We therefore further propose that the attack of RS^\cdot at P^{III} to give $Ph_2(vinyl)\dot{P}SR$ must be readily reversible. The addition of RS^\cdot to olefins is already known to be so.² Our observed product distribution can now be accounted for by the prevalence of one of two situations.

First, and most likely, an equilibrium between the radical intermediates $Ph_2(vinyl)\dot{P}SR$ and $Ph_2P\dot{C}HCH_2SR$ would be rapidly established (Scheme 2). Although an



intramolecular rearrangement here cannot be ruled out, a dissociative equilibrium involving free RS^\cdot is more likely, as there is a precedent for the loss of RS^\cdot from $RSCH_2\dot{C}HR'$, and RS^\cdot loss from R'_3PSR is an example of α -scission, which is already known for oxygen analogues.⁶ (Also RS^\cdot attack on $R'_2P-PR'_2$ leads to α -scission of the P-P bond in $[(RS)R'_2P-PR'_2]^{10}$.) When R^\cdot is an easily formed radical, this will be rapidly lost from the phosphoranyl radical as the rate-determining step in the formation of $Ph_2(vinyl)PS$. When R^\cdot is difficult to produce, however, the (slower) proton abstraction from RSH by $Ph_2P\dot{C}HCH_2SR$ will displace the equilibrium in the other direction, forming $Ph_2PC_2H_4SR$ as product (Scheme 2). The second option could prevail if the addition of RS^\cdot to olefins is *not* readily reversible. This seems unlikely, but it cannot be dismissed since the loss of RS^\cdot from $RSCH_2\dot{C}HR'$ is less important when the odd electron can be delocalised, and a terminal olefin is involved^{2,3b} (both apply in our case). If this is the case, the rate-limiting step in the formation of $Ph_2PC_2H_4SR$ may not be the proton abstraction from RSH , but the conversion of $Ph_2(vinyl)\dot{P}SR$ into $Ph_2P\dot{C}HCH_2SR$, and the two radical intermediates would not equilibrate. This route demands a preferential attack of RS^\cdot at phosphorus(III) in every example.

The radical addition of $EtSH$ to $Bu^a_2PC\equiv CH$ ¹¹ is reported to give, in the first instance, $Bu^a_2PCH=CHSEt$ by a chain mechanism analogous to reactions (1)–(3). The similarity of this study to our system is obvious and it would be interesting to see if, for example, $PhCH_2SH$ produced the sulphide $Bu^a_2(HC_2)_2PS$ instead. A comparison between the rate of thiyl radical attack on phosphorus(III) and olefins has been made, using the results of product distribution in a competitive reaction.^{3b} It was concluded that attack at phosphorus was generally

quite easy. Although the reversible nature of the addition of thiyls to olefins was considered, no allowance was made for a reverse step operating on the addition to P^{III} (although such a possibility was briefly mentioned later in the same paper). Furthermore, only one thiol, Bu^aSH , was used in that study. This is one of the cases to which we would assign a slow R^\cdot elimination, so a reversible step here [countering reaction (4)] could markedly affect the product distribution. This could mean a much greater rate of RS^\cdot attack on P^{III} than was reported. These studies might therefore bear reinvestigation, allowing for the possibility that reaction (5) is the rate-limiting step in the formation of (at least some) phosphorus(v) sulphides.

The same paper also reported generally disappointing results in attempts to use the RSH/R'_3P system as an R^\cdot radical generator for addition to olefins.^{3b} From our results it would seem that if $PhCH_2SH$ or Bu^tSH were used instead of Bu^aSH , the value as an R^\cdot generator should be improved. It is interesting to note in this context that from the ³¹P n.m.r. spectrum of the products, our Bu^tSH/dvp reaction produced three P^V derivatives. Two are readily assignable to $Ph_2(vinyl)PS$ (δ , +35 p.p.m.) and $Ph_2P(S)C_2H_4SBu^t$ (δ , +39.5 p.p.m.): the third signal might speculatively be assigned to $Ph_2P(S)C_2H_4Bu^t$.

EXPERIMENTAL

Photolytic reactions were performed under an atmosphere of pure oxygen-free nitrogen using a Hanovia medium-pressure mercury lamp (PCR 11). N.m.r. spectra were recorded on JEOL C-60HL or Varian HA-100 instruments. ³¹P Chemical shifts are relative to external H_3PO_4 . Mass spectra were recorded on an AEI MS12 spectrometer. Representative experiments are described below.

Preparation of 1-Diphenylphosphino-3-thiahexane, $Ph_2PC_2H_4SPR^a$.—A mixture of *dvp* (1 ml, 6.12 mmol) and *n*-propanethiol (0.47 g, 6.24 mmol) was irradiated with u.v. light for 19 h in a Pyrex vessel. Any volatile materials were removed by pumping, to leave as final product a pale yellow, slightly viscous, liquid, $Ph_2PC_2H_4SPR^a$ (Found: C, 70.65; H, 7.2; P, 10.9; S, 10.8%; *M* (mass spec.), 288. Calc. for $C_{17}H_{21}PS$: C, 70.8; H, 7.3; P, 10.8; S, 11.1; *M*, 288). A peak at 320 in the mass spectrum was assigned to a trace of $Ph_2P(S)C_2H_4SPR^a$.

Similarly were prepared: $Ph_2PC_2H_4SEt$ (Found: C, 69.44; H, 6.8; P, 12.6. $C_{16}H_{19}PS$ requires C, 70.1; H, 6.9; P, 11.3%); $Ph_2PC_2H_4SPh$, m.p. 85–86 °C, *ex. MeOH* (Found: C, 74.3; H, 6.1. $C_{20}H_{19}PS$ requires C, 74.5; H, 5.9%).

Preparation of 1-Diphenylphosphinothiyl-4-methyl-3-thiapentane, $Ph_2P(S)C_2H_4SPR^1$.—A mixture of *dvp* (0.5 ml, 3.06 mmol) and Pr^1SH (0.49 g, 6.47 mmol) was irradiated for 65 h. Any remaining volatile material was removed by pumping to leave the product as a pale yellow viscous liquid (Found: C, 64.0; H, 6.8; P, 9.5; S, 19.8%; *M* (mass spec.), 320. $C_{17}H_{21}PS_2$ requires C, 63.8; H, 6.6; P, 9.7; S, 20.0%; *M*, 320.)

¹⁰ I. N. Shlik, G. M. Bogoliubov, and A. A. Petrov, *Doklady Akad. Nauk, S.S.S.R.*, 1967, **176**, 1327.

¹¹ W. Voscuil and J. F. Arens, *Rec. Trav. chim.*, 1962, **81**, 933.

Similarly were prepared: $\text{Ph}_2\text{P}(\text{S})\text{C}_2\text{H}_4\text{SEt}$ [Found: C, 62.8; H, 6.6; P, 10.4; S, 21.7%; M (mass spec.), 306. $\text{C}_{16}\text{H}_{19}\text{PS}_2$ requires C, 62.7; H, 6.2; P, 10.1; S, 20.9%; M , 306.]; $\text{Ph}_2\text{P}(\text{S})\text{C}_2\text{H}_4\text{SPr}^n$ (Found: C, 63.6; H, 6.7; P, 9.5; S, 20.5%; M (mass spec.), 320. $\text{C}_{17}\text{H}_{21}\text{PS}_2$ requires C, 63.8; H, 6.6; P, 9.7; S, 20.0%; M , 320.); $\text{Ph}_2\text{P}(\text{S})\text{C}_2\text{H}_4\text{SBu}^n$ (Found: C, 65.3; H, 6.95; P, 9.95%; M (mass spec.), 332; $\text{C}_{18}\text{H}_{23}\text{PS}_2$ requires C, 64.8; H, 6.9; P, 10.25%; M , 332].

Reaction between Bu^tSH and dvp .—A mixture of dvp (0.78 g, 3.7 mmol) and Bu^tSH (0.33 g, 3.7 mmol) was irradiated in an n.m.r. tube for 58 h. The ^{31}P n.m.r. showed the presence of $\text{Ph}_2(\text{vinyl})\text{PS}$ (δ , 35 p.p.m., compared to an authentic sample prepared from dvp and sulphur), and two

other P^{V} compounds (δ , +39.5 and +42.3 p.p.m.) tentatively assigned to $\text{Ph}_2\text{P}(\text{S})\text{C}_2\text{H}_4\text{SBu}^t$ and $\text{Ph}_2\text{P}(\text{S})\text{C}_2\text{H}_4\text{Bu}^t$ respectively. The ^1H n.m.r. revealed methyl signals which could be assigned to these latter two compounds, and isobutane.¹² Volatile materials were trapped at 77 K after vacuum transfer, and the presence of isobutane was shown by its gas i.r. spectrum¹³ and mass spectrum.¹⁴ Larger scale 1:1 and 2:1 reactions indicated the same result, and no trace of $\text{Ph}_2\text{PC}_2\text{H}_4\text{SBu}^t$ was detected.

Similar n.m.r. investigations of the reactions between dvp and PhCH_2SH , dvp and Bu^nSH , dvp and Pr^tSH , and dvp and PhSH were made.

[5/1318 Received, 4th July, 1975]

¹² E. Pretsch and W. Simon, *Helv. Chim. Acta*, 1969, **52**, 2133.

¹³ J. C. Evans and H. J. Bernstein, *Canad. J. Chem.*, 1956, **34**, 1037.

¹⁴ C. D. Flesch and H. J. Svec, *J.C.S. Faraday II*, 1973, **69**, 1187.