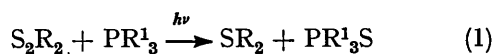


Photochemical Reactions between Tertiary Phosphines and Organic Diselenides †

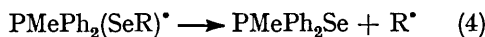
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Tertiary phosphines, PR^1_3 , react with organic diselenides, $Se_2R^2_2$, under u.v. radiation to produce PR^1_3Se and SeR^2_2 . The reaction rates decrease in the orders $R^1_3 = Me_2Ph > MePh_2 > Ph_3$ and $R^2 = CH_2Ph > Et > Me > Ph$. A radical-chain mechanism appears to operate *via* $SeR^2\cdot$ and $PR^1_3(SeR^2)\cdot$. Although cleavage of Se-C bonds may be involved in the u.v. irradiation of $Se_2R^2_2$, cleavage of Se-Se bonds seems more important in these reactions, even for $R^2 = CH_2Ph$.

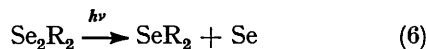
THE photochemically initiated chain reactions between organic disulphides and tertiary phosphines or phosphites to give phosphorus(v) sulphides [equation (1)] are well understood.¹ Recently we observed a close similarity



between the reactions of methyldiphenylphosphine with diethyl disulphide and diethyl diselenide and proposed an analogous mechanism for the reaction of diselenides [equations (2)–(5); $R = Et$].² Since then, Chu



*et al.*³ have reported a quantitative study of the photolysis of dibenzyl diselenide in acetonitrile or benzene [equation (6); $R = CH_2Ph$]. They proposed equations



(2), (5), and (7)–(10) ($R = CH_2Ph$) to account for their

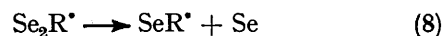
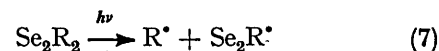
† No reprints available.

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¹ (a) C. Walling and R. Rabinowitz, *J. Amer. Chem. Soc.*, 1959, **81**, 1243; (b) C. Walling, O. H. Basedow, and E. S. Savas, *ibid.*, 1960, **82**, 2181.

² R. J. Cross and D. Millington, *J.C.S. Chem. Comm.*, 1975, 455.

observations. Thus, although photochemical cleavage of Se-Se may be occurring, only cleavage of Se-C leads to their observed products. The photochemical cleavage



of sulphur-carbon bonds in organic disulphides is well known, although it tends to be important only if the carbon radicals produced are stabilised (*e.g.* $R = CH_2Ph$ or Bu^t).⁴ Nevertheless, cleavage of Se-R bonds by u.v. radiation has been observed even for Se_2Ph_2 .⁵

This poses the question whether the phosphine selenide produced from Se_2Et_2 and $PMePh_2$ was formed by the cyclic chain mechanism [equations (2)–(5)] or by the operation of reaction (6) followed by reaction (11) of



the phosphine with elemental selenium. This latter step is well documented.⁶

³ J. Y. C. Chu, D. G. Marsh, and W. H. H. Gunther, *J. Amer. Chem. Soc.*, 1975, **97**, 4905.

⁴ G. W. Byers, H. Gruen, H. G. Giles, H. N. Schott, and J. A. Kampmeier, *J. Amer. Chem. Soc.*, 1972, **94**, 1016.

⁵ U. Schmidt, A. Muller, and K. Markau, *Chem. Ber.*, 1964, **97**, 405.

⁶ R. A. Zingaro and R. E. McGlothlin, *J. Chem. and Eng. Data*, 1963, **8**, 226.

EXPERIMENTAL

Ultraviolet irradiations were performed using a Hanovia (PCR11) medium-pressure mercury lamp. Ultraviolet-visible spectra were recorded on a Unicam SP 800B spectrophotometer, n.m.r. spectra on JEOL C-60HL or Varian T-60 instruments. Organic diselenides were prepared by standard methods.⁷

Equivalent concentrations (*ca.* 0.17 mol dm⁻³) of the tertiary phosphine and organic diselenide in deuteriobenzene were irradiated in Pyrex n.m.r. tubes in a rigorous nitrogen atmosphere. Control experiments on solutions of Se₂R₂ alone were carried out simultaneously. The progress of the reactions was regularly monitored by n.m.r. spectrometry. The relevant n.m.r. characteristics of both the reactants and products are listed in Table 1. During irradiation the n.m.r. tubes were maintained at 285 K in a water-bath to avoid complicating thermal side reactions.⁸

RESULTS AND DISCUSSION

The lowest-energy absorption in the u.v.-visible spectra of each of the organic diselenides is in the range 300–335 nm (Table 2). This band is analogous to the

was essentially complete after irradiation for 30 min. Under identical conditions, a slower reaction of Se₂-(CH₂Ph)₂ alone proceeded to only 5% completion. The slower reaction could not be accounted for by scattering of light by the selenium produced, as experiments in u.v. cells showed that there was not a significant decrease in transmittance at 304 nm in the reaction periods employed between monitoring the reaction (5 min). Furthermore, careful removal of the selenium from the n.m.r. tube produced no measurable increase in reaction rate. Thus in the reaction time available no more than *ca.* 5% of the PMePh₂Se produced would have been formed from a reaction of PMePh₂ and elemental selenium.

The observation of bibenzyl among the reaction products of PMePh₂ and Se₂(CH₂Ph)₂ is significant. None was found by us, or reported by Chu *et al.*,³ in the photolysis of Se₂(CH₂Ph)₂ alone. The bibenzyl is presumably formed by coupling of benzyl radicals [equation (12); R = CH₂Ph]. Benzyl radicals will be involved in the chain-propagation cycle [equations

TABLE 1
N.m.r. characteristics

Compound	N.m.r. characteristics ^a	Literature values	Solvent	Ref.
Se ₂ (CH ₂ Ph) ₂	Ph, 7.10 (s); CH ₂ , 3.60 (s)	Ph, 6.91; CH ₂ , 3.67	CD ₃ CN	3
Se ₂ Et ₂	CH ₃ , 1.22 (t); CH ₂ , 2.60 (q)	CH ₃ , 1.43; CH ₂ , 2.86	None	b
Se ₂ Me ₂	CH ₃ , 2.17 (s)	CH ₃ , 2.55	None	b
Se ₂ Ph ₂	<i>o</i> -Ph, 7.52 (m); <i>m,p</i> -Ph, 6.92 (m)	<i>o</i> -Ph, 7.62; <i>m,p</i> -Ph, 7.22	CH ₂ Cl ₂	c
Se(CH ₂ Ph) ₂	Ph, 7.10 (s); CH ₂ , 3.47 (s)	Ph, 6.91; CH ₂ , 3.55	CD ₃ CN	3
SeEt ₂	CH ₃ , 1.20 (t); CH ₂ , 2.30 (q)	CH ₃ , 1.37; CH ₂ , 2.53	None	b
SeMe ₂	CH ₃ , 1.62 (s)	CH ₃ , 1.96	None	b
SePh ₂	<i>o</i> -Ph, 7.38 (m)	<i>o</i> -Ph, 7.45	None	b
PMePh ₂	CH ₃ , 1.37 (d); ² J _{PH} 3.9 Hz	CH ₃ , 1.42; ² J _{PH} 4.4 Hz	None	d
PMe ₂ Ph	CH ₃ , 1.07 (d); ² J _{PH} 3.3 Hz	CH ₃ , 1.11; ² J _{PH} 3.7 Hz	C ₆ H ₆	e
PMePh ₂ Se	CH ₃ , 1.95 (d); ² J _{PH} 13.4 Hz ³¹ P, +22.8	CH ₃ , 2.33; ² J _{PH} 13.2 Hz ³¹ P, +22.3	CH ₂ Cl ₂	f
PMe ₂ PhSe	CH ₃ , 1.58 (d); ² J _{PH} 13.4 Hz ³¹ P, +14.8	CH ₃ , 2.12; ² J _{PH} 13.2 Hz ³¹ P, +15.1	CH ₂ Cl ₂	f
PPh ₂ Se	³¹ P, +30.8	³¹ P, +34.1	CDCl ₃	f

^a In C₆D₆. Proton chemical shifts (δ/p.p.m.) relative to internal SiMe₄. Phosphorus chemical shifts are relative to external H₃PO₄. ^b M. Lardon, *J. Amer. Chem. Soc.*, 1970, **92**, 5063. ^c K. J. Wynne and P. S. Pearson, *Inorg. Chem.*, 1972, **11**, 1196. ^d H. H. Sisler and S. R. Jain, *Inorg. Chem.*, 1968, **7**, 104. ^e J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. (A)*, 1966, 770. ^f W. McFarlane and D. S. Rycroft, *J.C.S. Dalton*, 1973, 2162.

bond-rupturing $n \rightarrow \sigma^*$ (or $\pi^* \rightarrow \sigma^*$, depending on the dihedral angle) transition of organic disulphides.⁸ Both Pyrex and deuteriobenzene are transparent in this region.

The reaction between PMePh₂ and dibenzyl diselenide

TABLE 2

Lowest-energy u.v. absorption of the diselenides in cyclohexane

Compound	λ_{\max}/nm	$10^{-3}\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$
Se ₂ (CH ₂ Ph) ₂	304	0.75
Se ₂ Et ₂	310	1.12
Se ₂ Me ₂	317	0.47
Se ₂ Ph ₂	332	1.03

produced PMePh₂Se (100), Se(CH₂Ph)₂ (53), and bibenzyl (16%), with some unchanged Se₂(CH₂Ph)₂ (10%), and

⁷ G. M. Bogolyubov, Y. N. Shlyk, and A. A. Petrov, *J. Gen. Chem. U.S.S.R.*, 1969, **39**, 1768.

⁸ G. Bergson, *Arkiv. Kemi*, 1958, **12**, 233.

(3)–(5); R = CH₂Ph] for the formation of PMePh₂Se, whereas their role in the photolysis of Se₂(CH₂Ph)₂ alone is less important (this is not a chain reaction).

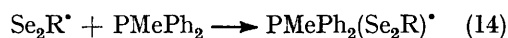
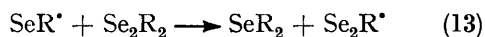


The low reactivity of benzyl radicals probably favours reaction (12) at the expense of (5). Similar observations have been reported for the reaction between Se₂(CH₂Ph)₂ and P(OEt)₃.^{1a}

We therefore conclude that the bulk of the phosphine selenide at least is produced *via* reactions (3)–(5), involving the phosphoranyl radical intermediate PMePh₂-(SeCH₂Ph)[•], and reactions (9), (10), and (12) act as chain terminators. The benzylselenyl radicals responsible for the chain process can be formed directly by Se–Se cleavage [equation (2); R = CH₂Ph] or indirectly by C–Se cleavage [equation (7) followed by (5) and (8)]. The production of 16% of bibenzyl means that chain-

termination steps account for at least 16% of the benzyl-containing products [steps (9) and (10) cannot be independently monitored]. This requires that the photochemical-initiation steps must act on at least 16% of $\text{Se}_2(\text{CH}_2\text{Ph})_2$. Carbon-selenium cleavage, leading to $\text{Se}(\text{CH}_2\text{Ph})_2$ and Se , proceeds only 5% in 30 min, however, so the more important initiation step is selenium-selenium cleavage.

Before moving on to discuss the reactions of other diselenides, three other radical processes, (13)–(15), might be considered. Any participation of (13) must be



limited, since it would convert the photochemical decomposition of $\text{Se}_2(\text{CH}_2\text{Ph})_2$ into a chain reaction. The quantum yield for this process (0.16) suggests that this is not so.³ This in turn means that steps (14) and (15) can only contribute 5% or less [the maximum contribution of step (7)] to the reaction between $\text{Se}_2(\text{CH}_2\text{Ph})_2$ and PMePh_2 . Radical-termination steps forming RSe_nR ($n > 2$) can also be envisaged, but no such polyselenides were detected in any of our experiments.

The reactions of several other diselenides and tertiary phosphines were examined. All proceeded smoothly under u.v. irradiation to give phosphorus(v) selenides and organic monoselenides, SeR_2 , although requiring a longer reaction time than $\text{Se}_2(\text{CH}_2\text{Ph})_2$ and PMePh_2 (see Table 3). Under identical conditions, none of the other diselenides alone produced measurable amounts of selenium and SeR_2 . This would be expected, since carbon-selenium cleavage would be less facile for these organic radicals.⁴ Thus the operation of the radical-chain route involving the phosphoranyl intermediates $\text{PR}_3(\text{SeR})^*$ appears to apply generally to all the reactions of tertiary phosphines and diselenides studied.

There are at least two explanations for the variations in reaction times. First, the rate of Se-Se cleavage to generate SeR^* may vary. This will require the slower-reacting diselenides to have available more efficient non-

dissociative paths to regain their ground states after absorbing u.v. radiation. Secondly, the rate-determining step may be the elimination of a carbon radical from the phosphoranyl intermediates [reaction (4)]. If this is slow, α scission of P-Se [the reverse of (3)] will compete more favourably and lead *via* (10) to the reformation of the starting compounds. We have recently shown that carbon-radical elimination is critical in the reaction of thiyl radicals with tertiary phosphines.⁹

We marginally favour the second interpretation. The different reaction rates observed for different phosphines ($\text{PMe}_2\text{Ph} > \text{PMePh}_2 > \text{PPh}_3$) are difficult to rationalise in terms of control by step (2). Also, the effect of the alkyl groups ($\text{CH}_2\text{Ph} > \text{Et} > \text{Me} > \text{Ph}$) is consistent

TABLE 3

Relative times of irradiation producing 50% reaction between tertiary phosphines and diselenides

Phosphine	Diselenide	t/h
PMePh_2	$\text{Se}_2(\text{CH}_2\text{Ph})_2$	0.25
PMePh_2	Se_2Et_2	1.5
PMePh_2	Se_2Me_2	6.0
PMePh_3	Se_2Ph_2	60
PMe_2Ph	Se_2Me_2	2.5
PMe_2Ph	Se_2Ph_2	40
PPh_3	Se_2Me_2	13

with increasing energy of radical formation.⁹ Attempts to confirm this by examining other photochemical reactions of diselenides failed, however. No reaction was observed between Se_2Ph_2 and either $\text{PhMeC}=\text{CH}_2$ or $\text{PhC}\equiv\text{CH}$ after irradiation for 40 h, and n.m.r. spectroscopy failed to detect any mixed diselenides after irradiation of $\text{Se}_2\text{Me}_2 + \text{Se}_2\text{Ph}_2$ or $\text{Se}_2\text{Me}_2 + \text{Se}_2\text{Et}_2$ for 20 h.* The former failure is understandable in view of the likely reversible nature of the reaction and the difficulties encountered in analogous reactions of disulphides.¹⁰ Also, variable results have been reported for irradiation experiments on mixtures of disulphides.¹¹ Nevertheless, the latter failure is difficult to interpret.

We thank Mr. D. R. Wilson for a gift of $\text{Se}_2(\text{CH}_2\text{Ph})_2$ and Se_2Ph_2 , and the S.R.C. for a maintenance award (to D. H. B.).

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* A reaction did occur between Se_2Et_2 and Se_2Ph_2 , but it also proceeded (rather more slowly) in the absence of u.v. irradiation.

⁹ D. H. Brown, R. J. Cross, and D. Millington, *J.C.S. Dalton*, 1976, 334.

¹⁰ J. L. Kice, 'Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, New York, 1973, vol. 2, ch. 24, pp. 723–724.

¹¹ D. D. Carlson and A. R. Knight, *Canad. J. Chem.*, 1973, 51, 1410.