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

$$S_2R_2 + PR^1_3 \xrightarrow{h\nu} SR_2 + PR^1_3S \qquad (1)$$

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

$$Se_2R_2 \xrightarrow{h\nu} 2SeR^\cdot \qquad (2)$$

$$SeR^\cdot + PMePh_2 \longrightarrow PMePh_2(SeR)^\cdot \qquad (3)$$

$$PMePh_2(SeR)^\cdot \longrightarrow PMePh_2Se + R^\cdot \qquad (4)$$

$$R^\cdot + Se_2R_2 \longrightarrow SeR_2 + SeR^\cdot \qquad (5)$$

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

$$Se_2R_2 \xrightarrow{h\nu} SeR_2 + Se \qquad (6)$$

(2), (5), and (7)—(10) ($R = CH_2Ph$) to account for their observations. Thus, although photochemical cleavage of Se–Se may be occurring, only cleavage of Se–C leads to their observed products. The photochemical cleavage

$$Se_2R_2 \xrightarrow{h\nu} R^\cdot + Se_2R^\cdot \qquad (7)$$

$$Se_2R^\cdot \longrightarrow SeR^\cdot + Se \qquad (8)$$

$$R^\cdot + SeR^\cdot \longrightarrow SeR_2 \qquad (9)$$

$$2SeR^\cdot \longrightarrow Se_2R_2 \qquad (10)$$

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

$$PMePh_2 + Se \longrightarrow PMePh_2Se \qquad (11)$$

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

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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.

[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 Se_2R_2 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.[3]

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

TABLE 1

N.m.r. characteristics

Compound	N.m.r. characteristics [a]	Literature values	Solvent	Ref.
$Se_2(CH_2Ph)_2$	Ph, 7.10 (s); CH_2, 3.60 (s)	Ph, 6.91; CH_2, 3.67	CD_3CN	3
Se_2Et_2	CH_3, 1.22 (t); CH_2, 2.60 (q)	CH_3, 1.43; CH_2, 2.86	None	*b*
Se_2Me_2	CH_3, 2.17 (s)	CH_3, 2.55	None	*b*
Se_2Ph_2	*o*-Ph, 7.52 (m); *m,p*-Ph, 6.92 (m)	*o*-Ph, 7.62; *m,p*-Ph, 7.22	CH_2Cl_2	*c*
$Se(CH_2Ph)_2$	Ph, 7.10 (s); CH_2, 3.47 (s)	Ph, 6.91; CH_2, 3.55	CD_3CN	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*
$SePh_2$	*o*-Ph, 7.38 (m)	*o*-Ph, 7.45	None	*b*
$PMePh_2$	CH_3, 1.37 (d); $^2J_{PH}$ 3.9 Hz	CH_3, 1.42; $^2J_{PH}$ 4.4 Hz	None	*d*
PMe_2Ph	CH_3, 1.07 (d); $^2J_{PH}$ 3.3 Hz	CH_3, 1.11; $^2J_{PH}$ 3.7 Hz	C_6H_6	*e*
$PMePh_2Se$	CH_3, 1.95 (d); $^2J_{PH}$ 13.4 Hz	CH_3, 2.33; $^2J_{PH}$ 13.2 Hz	CH_2Cl_2	*f*
	^{31}P, +22.8	^{31}P, +22.3	CH_2Cl_2	*f*
PMe_2PhSe	CH_3, 1.58 (d), $^2J_{PH}$ 13.4 Hz	CH_3, 2.12; $^2J_{PH}$ 13.2 Hz	CH_2Cl_2	*f*
	^{31}P, +14.8	^{31}P, +15.1	CH_2Cl_2	*f*
PPh_3Se	^{31}P, +30.8	^{31}P, +34.1	$CDCl_3$	*f*

[a] In C_6D_6. Proton chemical shifts (δ/p.p.m.) relative to internal $SiMe_4$. Phosphorus chemical shifts are relative to external H_3PO_4. [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.

The reaction between $PMePh_2$ and dibenzyl diselenide produced $PMePh_2Se$ (100), $Se(CH_2Ph)_2$ (53), and bibenzyl (16%), with some unchanged $Se_2(CH_2Ph)_2$ (10%), and was essentially complete after irradiation for 30 min. Under identical conditions, a slower reaction of $Se_2(CH_2Ph)_2$ 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 $PMePh_2Se$ produced would have been formed from a reaction of $PMePh_2$ and elemental selenium.

TABLE 2

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

Compound	$\lambda_{max.}$/nm	$10^{-3}\varepsilon$/dm^3 mol^{-1} cm^{-1}
$Se_2(CH_2Ph)_2$	304	0.75
Se_2Et_2	310	1.12
Se_2Me_2	317	0.47
Se_2Ph_2	332	1.03

The observation of bibenzyl among the reaction products of $PMePh_2$ and $Se_2(CH_2Ph)_2$ is significant. None was found by us, or reported by Chu *et al.*,[3] in the photolysis of $Se_2(CH_2Ph)_2$ alone. The bibenzyl is presumably formed by coupling of benzyl radicals [equation (12); $R = CH_2Ph$]. Benzyl radicals will be involved in the chain-propagation cycle [equations (3)—(5); $R = CH_2Ph$] for the formation of $PMePh_2Se$, whereas their role in the photolysis of $Se_2(CH_2Ph)_2$ alone is less important (this is not a chain reaction).

$$2R^\bullet \longrightarrow R_2 \qquad (12)$$

The low reactivity of benzyl radicals probably favours reaction (12) at the expense of (5). Similar observations have been reported for the reaction between $S_2(CH_2Ph)_2$ 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 $PMePh_2(SeCH_2Ph)^\bullet$, 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); $R = CH_2Ph$] or indirectly by C–Se cleavage [equation (7) followed by (5) and (8)]. The production of 16% of bibenzyl means that chain-

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[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.

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 $Se_2(CH_2Ph)_2$. Carbon–selenium cleavage, leading to $Se(CH_2Ph)_2$ 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

$$SeR^{\bullet} + Se_2R_2 \longrightarrow SeR_2 + Se_2R^{\bullet} \qquad (13)$$

$$Se_2R^{\bullet} + PMePh_2 \longrightarrow PMePh_2(Se_2R)^{\bullet} \qquad (14)$$

$$PMePh_2(Se_2R)^{\bullet} \longrightarrow PMePh_2Se + SeR^{\bullet} \qquad (15)$$

limited, since it would convert the photochemical decomposition of $Se_2(CH_2Ph)_2$ 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 $Se_2(CH_2Ph)_2$ 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 $Se_2(CH_2Ph)_2$ 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 $PR^1_3(SeR)^{\bullet}$ 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 $SeR^{\bullet}$ may vary. This will require the slower-reacting diselenides to have available more efficient non-dissociative paths to reattain 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 ($PMe_2Ph > PMePh_2 > PPh_3$) are difficult to rationalise in terms of control by step (2). Also, the effect of the alkyl groups ($CH_2Ph > Et > Me > Ph$) is consistent 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 $PhMeC{=}CH_2$ or $PhC{\equiv}CH$ after irradiation for 40 h, and n.m.r. spectroscopy failed to detect any mixed diselenides after irradiation of $Se_2Me_2 + Se_2Ph_2$ or $Se_2Me_2 + Se_2Et_2$ 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.

TABLE 3

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

Phosphine	Diselenide	t/h
$PMePh_2$	$Se_2(CH_2Ph)_2$	0.25
$PMePh_2$	Se_2Et_2	1.5
$PMePh_2$	Se_2Me_2	6.0
$PMePh_2$	Se_2Ph_2	60
PMe_2Ph	Se_2Me_2	2.5
PMe_2Ph	Se_2Ph_2	40
PPh_3	Se_2Me_2	13

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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.