

Selenium Abstraction from Diethyl Diselenide by Tertiary Phosphines †

By RONALD J. CROSS and DOUGLAS MILLINGTON*

(Chemistry Department, University of Glasgow, Glasgow G12 8QQ)

Summary The photochemical deselenation of Et_2Se_2 by Ph_2MeP proceeds by an $\text{EtSe}\cdot$ radical chain mechanism to form Et_2Se and Ph_2MePSe in high yield.

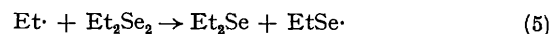
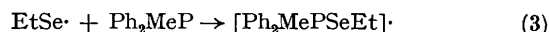
MANY photochemical and photochemically initiated reactions of organosulphides are known and mechanistically understood.¹ In contrast, there has been only one report on the photochemical behaviour of organoselenides, and no mechanistic interpretations were offered.² We report here the photochemically-initiated reaction of diethyl diselenide with diphenylmethylphosphine. Comparisons with known reactions between disulphides and tertiary phosphines suggest a free-radical chain mechanism which may also be related to some of the previously reported processes.

The reaction proceeds smoothly under u.v. irradiation (Hanovia medium-pressure mercury lamp) in a Pyrex vessel at room temperature, and in the absence of air [reaction (1)]. Almost quantitative yields were obtained



after 10 h (4 mmol scale), but the reaction stopped if irradiation was discontinued.

Di-organo-disulphides react with tertiary phosphines by a free-radical chain mechanism,³ which can be photochemically initiated, and a similar mechanism is likely to operate with the diselenides. This would involve the sequence of reactions (2)–(5).



Further evidence that irradiation of diselenides can produce $\text{RSe}\cdot$ is obtained from their u.v.–visible spectra. Et_2Se_2 shows a broad absorption at λ_{max} 310 nm (ϵ 890 l mol⁻¹ cm⁻¹), close to the reported 320 nm band of $(\text{PhCH}_2)_2\text{Se}_2$.² The lowest energy absorption of Et_2Se_2 , on the other hand, is at λ_{max} 250 nm (ϵ 435 l mol⁻¹ cm⁻¹). This band has been assigned to a bond-rupturing $n \rightarrow \sigma^*$ or $\pi^* \rightarrow \sigma^*$ transition, depending on the dihedral angle of the substituents.⁴ In accord with the positions of these absorptions we find that the analogous photochemical reaction between Et_2S_2 and Ph_2MeP (forming Et_2S and Ph_2MePS) is best performed in a silica vessel, which is transparent at 250 nm. Surprisingly, the reaction between diethyl ditelluride and Ph_2MeP was not successful under our conditions. Et_2Te_2 has a broad absorption at λ_{max} 400 nm (ϵ 1820 l mol⁻¹ cm⁻¹) tailing into the visible, and a band at λ_{max} 300 nm (ϵ 1073 l mol⁻¹ cm⁻¹). Possibly these bands are non-dissociative, or the reaction with tertiary phosphines is thermodynamically unfavourable.

As well as indicating a convenient way of generating $\text{RSe}\cdot$ radicals, the high yield and mild conditions of the present

† No reprints available

deselenation reaction make the process a potentially valuable synthetic route. Conventional conversions of diselenides into monoselenides⁵ can be unpredictable and prone to low yields; the photolysis of $(\text{PhCH}_2)_2\text{Se}_2$ alone afforded only 60% of $(\text{PhCH}_2)_2\text{Se}$.² Also as a route to

tertiary phosphine selenides, this reaction is ideally suited to small-scale preparations, where the usual method (R_3P and Se metal) is inconvenient.

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¹ A. Senning, ed., 'Sulfur in Organic and Inorganic Chemistry,' Vol. 1, Marcel Dekker, New York, 1971.

² W. Stanley, M. R. Van De Mark, and P. L. Kumler, *J.C.S. Chem. Comm.*, 1974, 700.

³ (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.

⁴ G. Bergson, *Arkiv Kemi*, 1958, **12**, 233.

⁵ E. E. Aynsley, N. N. Greenwood, and J. B. Leach, *Chem. and Ind.*, 1966, 379.