Selenium Abstraction from Diethyl Diselenide by Tertiary Phosphines†

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Summary The photochemical deselenation of Et_2Se_2 by Ph_2MeP proceeds by an EtSe· 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

$$Et_2Se_2 + Ph_2MeP \xrightarrow{h\nu} Et_2Se + Ph_2MePSe \quad (1)$$

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).

$$Et_2Se_2 \xrightarrow{h\nu} EtSe\cdot \quad (2)$$

$$EtSe\cdot + Ph_2MeP \rightarrow [Ph_2MePSeEt]\cdot \quad (3)$$

$$[Ph_2MePSeEt]\cdot \rightarrow Ph_2MePSe + Et\cdot \quad (4)$$

$$Et\cdot + Et_2Se_2 \rightarrow Et_2Se + EtSe\cdot \quad (5)$$

Further evidence that irradiation of diselenides can produce RSe· 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 $(PhCH_2)_2Se_2$.[2] The lowest energy absorption of Et_2S_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 RSe· radicals, the high yield and mild conditions of the present

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deselenation reaction make the process a potentially valuable synthetic route. Conventional conversions of diselenides into monoselenides[5] can be unpredictable and prone to low yields; the photolysis of $(PhCH_2)_2Se_2$ alone afforded only 60% of $(PhCH_2)_2Se$.[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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