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Notes

Photochemistry of Organochalcogen Compounds. 2.[1] Photochemical Deselenation of Benzyl Diselenide by Triphenylphosphine

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Although the chemistry of organoselenides is well documented,[2] little is known about their photochemical reactions. By contrast, the photoreactions of many organosulfides have been studied and their mechanisms understood.[3] We have reported recently the first quantitative study on the photolysis of benzyl diselenide (1) in solution.[1] It was found that irradiation of 1 in degassed acetonitrile at wavelengths greater than 280 nm results in formation of elemental selenium and dibenzyl selenide. Photoinduced cleavages of Se–Se and C–Se bonds were proposed as possible primary processes.

Walling and Rabinowitz[4] discovered that trivalent phosphorus compounds convert thiyl radicals into alkyl radicals. This led us to investigate analogous reactions for organoselenides. A recent communication by Cross and Millington[5] on the deselenation of diethyl diselenide by tertiary phosphines prompts us now to report some quantitative details of our studies of photodeselenation of 1 by triphenylphosphine (2).

Irradiation of 1 (2×10^{-2} M) and an excess of 2 (4×10^{-2} M) in degassed acetonitrile at 350 nm for 45 min yields 66.1% of dibenzyl selenide (3), 32.3% of bibenzyl (4), and 65.1% of triphenylphosphine selenide (5).

$$\underset{\textbf{1}}{\mathrm{PhCH_2SeSeCH_2Ph}} + \underset{\textbf{2}}{\mathrm{Ph_3P}} \xrightarrow[\mathrm{CH_3CN}]{h\nu\,(350\ \mathrm{nm})} \underset{\textbf{3}}{\mathrm{PhCH_2SeCH_2Ph}} + \underset{\textbf{4}}{\mathrm{PhCH_2CH_2Ph}} + \underset{\textbf{5}}{\mathrm{Ph_3PSe}}$$

Under these conditions, the formation of elemental selenium is completely suppressed. If molecular oxygen is present, 5 reacts further to produce triphenylphosphine oxide and elemental selenium. The photoproducts were isolated by preparative layer chromatography and identified by comparison with authentic samples prepared by independent syntheses. The progress of the reaction was monitored by NMR as described previously.[1] The methylene protons of 1 (δ 3.81), 3 (δ 3.70), and 4 (δ 2.88) have sufficiently different chemical shifts to permit quantitative analysis. The results are shown in Figure 1. Formation of 5 cannot be monitored by NMR; however, it was demonstrated by GLC that 5 is formed rapidly and reaches constant concentration after about 40 min of irradiation (compare to Figure 1). NMR analyses indicate significant photoreaction in 10 min and complete disappearance of diselenide (1) in 45 min. No detectable reaction occurs in a nonirradiated aliquot of the degassed reaction mixture stored in the dark at room temperature for 7 days.

In contrast to the direct irradiation (quantum yield $\Phi = 0.16$ for disappearance of 1 in benzene at 313 nm),[1] the photodeselenation of 1 by 2 in benzene is remarkably efficient. Table I shows the increase of quantum yield with increasing concentration of 2. The large quantum yields provide strong evidence for a free-radical chain reaction.

For irradiations of 1, in the absence of 2, at 366 nm less than 7% decomposition of 1 was detected after 3 h exposure.[1] This result has been interpreted as evidence for a Se–Se bond cleavage (eq 1) as the major primary process in 1, followed by

$$\mathrm{RSeSeR} \xrightarrow{h\nu} 2\mathrm{RSe}\cdot \quad (\mathrm{R} = \mathrm{PhCH_2}) \tag{1}$$

$$\mathrm{RSeSeR} \xrightarrow{h\nu} \mathrm{R}\cdot + \mathrm{RSeSe}\cdot \longrightarrow \mathrm{RSe}\cdot + \mathrm{Se}^0 + \mathrm{R}\cdot \tag{2}$$

efficient benzylselenyl radical combination to give 1, or benzylselenyl radical displacement reaction at the Se–Se bond resulting in generation of 1 and an additional benzylselenyl radical.[1] We have no data on the relative importance of combination vs. displacement reactions for benzylselenyl radicals. Sayamol and Knight,[3] however, have reported that displacement reactions play a major role for thiyl radical reactions. Regardless of the relative importance of these reactions for benzylselenyl radicals these processes lead to no photoproduct formation.

The observed photoproducts can be explained on the basis of eq 2.[1] The very low quantum efficiency suggests that benzylselenyl radicals do not dissociate to yield Se^0 and benzyl radicals.

In contrast to these results, irradiation of 1 in the presence of 2 under identical reaction conditions results in total reaction

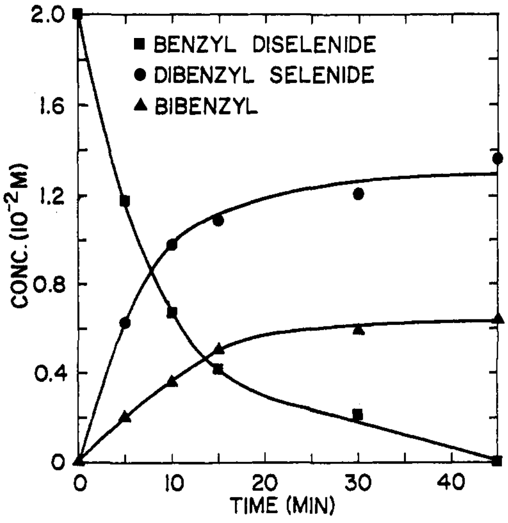

Figure 1. The concentration of reactant and photoproducts plotted vs. photolysis time.

Table I. Quantum Yields for Disappearance of Benzyl Diselenide[a] in the Presence of Triphenylphosphine

No.	Ph_3P, M	$-\Phi_{RSeSeR}$
1	0.000	0.16
2	0.050	1.44
3	0.075	2.66
4	0.100	4.70
5	0.200	6.80

[a] 0.1 M RSeSeR in purified, degassed benzene at 298 K exposed with 313-nm light.

of **1** within 1 h. The major primary photoprocess remains facile Se–Se bond cleavage. It appears that benzylselenyl radicals are trapped by **2** to form triphenylphosphine selenide (**5**) and benzyl radicals which subsequently react to form all photoproducts observed. The following radical chain mechanism is proposed for the reaction:

$$RSe\cdot + Ph_3P \longrightarrow Ph_3\dot{P}SeR \qquad (3)$$

$$RSe\dot{P}Ph_3 \longrightarrow R\cdot + Ph_3PSe \qquad (4)$$

$$R\cdot + RSeSeR \longrightarrow RSeR + RSe\cdot \qquad (5)$$

$$2R\cdot \longrightarrow R{-}R \qquad (6)$$

Our results suggest that benzylselenyl radicals formed in reactions 1 and 2 can attack phosphorus atoms to yield a tetracovalent phosphoranyl radical[4,6] with an expanded valence shell (eq 3). Reactions 3, 4, and 5 are the propagation steps with 5 representing the chain transfer reaction. The relatively stable benzyl radicals produced in 4 combine to yield **4** and terminate the radical chain reaction. This reaction mechanism is analogous to that proposed for thiyl radicals in the presence of trialkyl phosphites.[4]

A reviewer has suggested the possible intermediacy of a structure containing a Se═Se moiety:

$$Ph{-}CH_2{-}\overset{\overset{\displaystyle Se}{\|}}{Se}{-}CH_2{-}Ph$$

We have no spectroscopic evidence for such an intermediate. Furthermore, this intermediate is not consistent with the experimental results. Assuming that this intermediate reacts with Ph_3P to yield $Ph_3P{=}Se$ and dibenzyl selenide, no further free-radical chain mechanisms are possible.[7] Thus, the quantum yield for disappearance of **1** could not exceed unity, and no formation of bibenzyl could occur. We may, therefore, rule out this structure as a possible intermediate in the photochemistry of **1**.

Experimental Section

General. Melting points were determined using a Thomas-Hoover apparatus and are not corrected. NMR spectra were obtained with a JEOL C6OH instrument using tetramethylsilane as internal standard. Uv spectra were measured on a Cary 15 spectrophotometer. GLC analyses were carried out on a Hewlett-Packard 5750 research chromatograph using a 6 ft × 0.125 in. stainless steel column packed with 10% UCON-98 on 80–100 Chromosorb W and temperature programming. EM precoated silica gel F-254 plates (20 × 20 cm) were used for preparative layer chromatography, with benzene–hexane as eluent.

Materials. Benzyl diselenide and dibenzyl selenide were prepared according to previously reported procedures.[1]

Triphenylphosphine selenide was prepared by adapting the procedure of Nicpon and Meek.[8] The crude product was recrystallized from absolute ethanol, mp 187–188° (lit.[8] 187–188 °C).

Solvents. Thiophene-free reagent grade benzene was further purified by storing the solvent over 4A molecular sieves, filtering, and fractionally distilling. Acetonitrile (Burdick & Jackson spectrographic quality) was purified by passing it through a column of alumina (Woelm, activity 1). Deuterated solvents were commercial spectral grade.

General Irradiation Procedures. Preparative photolyses were carried out in water-cooled Pyrex reactors equipped with dry nitrogen purging and magnetic stirring. Solutions containing benzyl diselenide (2×10^{-2} M) and triphenylphosphine (4×10^{-2} M) were deoxygenated by bubbling nitrogen for 50 min and irradiated under nitrogen atmosphere with eight RUL-3500 Å lamps in a Rayonet RPR-208 photochemical reactor. The progress of the reaction was monitored by NMR as described previously.[1] The photoproducts were isolated by preparative layer chromatography on a precoated silica gel plate and identified by comparison with authentic samples. Yields were calculated by using the NMR and GLC integration data. Quantum yield determinations were carried out in degassed benzene and obtained as previously described.[1]

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Steric Effects in the Base-Catalyzed Hydrolysis of *p*-Nitrophenyl Esters. Relative Behavior of Bridged and Nonbridged Trialkyl Acetates

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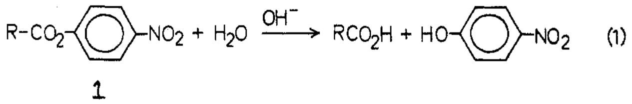
The 1-adamantyl group (1-tricyclo[3.3.1.$3^{3,7}$]decyl) is a substituent which confers a marked increase in lipophilicity on a wide variety of pharmaceuticals without altering their function. The lack of significant information on the substituent effect of this interesting group led us to investigate the base-catalyzed hydrolysis (eq 1) of a series of *p*-nitrophenyl esters (**1**). In light of Charton's recent findings that alkyl groups do not differ significantly in their electrical effects in base-catalyzed ester hydrolysis,[1] such a study should provide



(1)

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