Photochemistry of Organoselenium Compounds

By Walter Stanley, Michael R. VanDeMark, and Philip L. Kumler*
(*Department of Chemistry, Saginaw Valley College, University Centre, Michigan,* 48710)

Summary Irradiation of dibenzyl diselenide (I) with 350 nm light in the presence of oxygen afforded benzaldehyde and elemental selenium, whereas irradiation in the absence of oxygen produced dibenzyl monoselenide (II); irradiation of dibenzyl triselenocarbonate (III) produced dibenzyl diselenide.

We report the first study on the solution-phase photochemical behaviour of organoselenium compounds. Irradiation† of yellow dibenzyl diselenide (broad absorption maximum at *ca.* 320 nm, tailing into the visible) in dilute benzene solution open to the atmosphere resulted in the formation of benzaldehyde and elemental selenium [Equation (1)]. Based upon this stoicheiometry the yield of elemental selenium (isolated by filtration and determined gravimetrically) is 93%; the yield of benzaldehyde is variable but is consistently greater than 50%. The highest isolated yield of benzaldehyde thus far is 63% (isolated by direct distillation or preparative layer chromatography of the photolysate).

$$\underset{\text{(I)}}{\mathrm{PhCH_2{-}Se{-}Se{-}CH_2Ph}} \xrightarrow[\mathrm{O_2}]{h\nu,\ 350\ \mathrm{nm}} 2\ \mathrm{PhCHO} + 2\ \mathrm{Se} \qquad (1)$$

It has been established that the oxygen atom in benzaldehyde arises from atmospheric oxygen (and not from traces of water in the system) by carrying out irradiations in the presence and absence of both water and oxygen. The presence of water does not affect the course of the photolysis but in the absence of oxygen no benzaldehyde is produced and the reaction takes a different course. Thus, irradiation of degassed systems which are saturated with water lead to no detectable benzaldehyde and very little (less than 5%) selenium production. Preparative scale irradiation of (I) in the absence of oxygen leads to produc-

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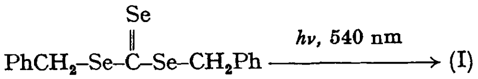
† Unless noted otherwise irradiations were performed in 10^{-2} M solutions using a Rayonet reactor and continued until complete disappearance of starting material as evidenced by t.l.c.

tion of dibenzyl monoselenide (II)‡ as the major product in good yield (60%), isolated by preparative layer chromatography of the photolysate [Equation (2)]. Although other products (as yet unidentified) are produced during irradiation only trace amounts of elemental selenium are formed.

$$(\mathrm{I}) \xrightarrow[\mathrm{O_2\ excluded}]{h\nu,\ 350\ \mathrm{nm}} \mathrm{PhCH_2{-}Se{-}CH_2Ph} \qquad (2)$$

(II)

We have also investigated the solution-phase photochemical behaviour of dibenzyl triselenocarbonate (III). The primary photochemical reaction is the expulsion of CSe with subsequent recombination of the remaining fragments to produce dibenzyl diselenide (I) in good yield. If the photolysis is carried out at 350 nm in benzene the reaction is complicated by secondary photolysis products of the diselenide; thus at 350 nm only small amounts of (I) can be isolated and the major products are benzaldehyde and selenium. However, if the irradiation is carried out using light whose wavelength is centred at the visible absorption maximum of the purple triselenocarbonate (540 nm),§ a good yield (58%) of the diselenide (I) results and there are no complications from secondary photolyses [Equation (3)].



$$\mathrm{PhCH_2{-}Se{-}\overset{\overset{\displaystyle Se}{\|}}{C}{-}Se{-}CH_2Ph} \xrightarrow{h\nu,\ 540\ \mathrm{nm}} (\mathrm{I}) \qquad (3)$$

(III)

We do not have any evidence as yet concerning the fate of the CSe but experiments designed to trap and/or identify this species are in progress.

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‡ All new compounds gave satisfactory spectral data and combustion analyses.

§ The light from a Hanovia 450 watt lamp was filtered through Pyrex, an aqueous solution of $CuCl_2$ and $CaCl_2$, and an aqueous solution of neodymium nitrate.