

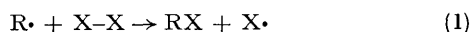
S_H2 Reactions of Diphenyl Diselenide; Preparation and Reactions of Bridgehead Selenides

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Summary For the S_H2 process $R\cdot + PhSeSePh \rightarrow PhSeR + PhSe\cdot$, $k = ca. 5 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ at 80 °C in benzene when R is primary alkyl; with 1-adamantyl radicals this S_H2 displacement affords a route to 1-adamantyl phenyl selenide which, on oxidation and pyrolysis of the resultant selenoxide, gives adamantan-1-ol; in contrast the selenoxide from bicyclo[3.3.1]nonan-1-yl phenyl selenide decomposes *via* bicyclo[3.3.1]non-1-ene.

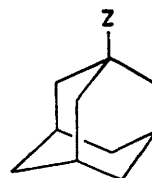
S_H2 REACTIONS of carbon-centred radicals with disulphides are known to be rapid (equation 1; $X = SR$);¹ similar reactions with halogens are generally considered to be diffusion-controlled (equation 1; $X = Hal$).² By analogy therefore, it seemed reasonable to expect very fast reactions with a diselenide (*e.g.*, equation 1; $X = SePh$); such a process would constitute a route to compounds of the type $RSePh$ in which R is a group not readily introduced into selenides by conventional ionic reactions. In view of the mild fragmentation of selenoxides, we have made a preliminary study of the S_H2 reactions of $PhSeSePh$ with alkyl radicals, in particular as a route to possible precursors of unusual alkenes such as 'adamantene'.³



Of our attempts to generate 1-adamantyl radicals in the presence of $PhSeSePh$, only lead tetra-acetate oxidation of adamantane-1-carboxylic acid, and the thermal decomposition of its *t*-butyl peroxyester, each in the presence of a large excess of $PhSeSePh$, yielded the required 1-adamantyl phenyl selenide (1) (m.p. 35 °C).[†] In each case the yield was poor (< 20%), probably because of consumption of the reagents in competing processes which by-pass adamantyl radicals. Although this result established the feasibility of

the radical synthesis, it was found that the mixed selenide (1) could be obtained in far better yield (80%) by apparent nucleophilic attack of $PhSeH$ on 1-adamantyl trifluoroacetate. This was based on a literature procedure⁴ for the preparation of the sulphide (2).

Di-1-adamantyl selenide⁵ (55%; m.p. 216–218 °C) was prepared in a similar manner by reaction of the trifluoroacetate with hydrogen selenide.



- (1) Z = SePh
- (2) Z = SⁿBuⁿ
- (3) Z = Se⁺(O⁻)Ph
- (4) Z = Se⁺(OAd)Ph

Ad = 1-adamantyl

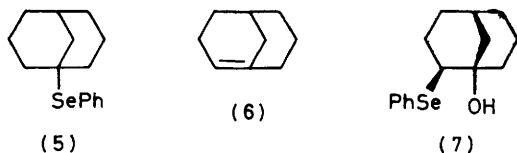
Oxidation of the selenide (1) (aqueous H_2O_2 -acetone) gave the selenoxide (3) [95%; m.p. 78 °C (decomp.)]. Thermolysis of this compound (neat or in *o*-dichlorobenzene) gave no evidence of products derived from adamantene³ but instead yielded adamantan-1-ol essentially quantitatively; the only selenium-containing product was diphenyl diselenide. Although a mechanism for this transformation, involving the sequence $AdSe^+(O^-)Ph \rightarrow [Ad\cdot PhSeO\cdot] \rightarrow [AdOSePh] \rightarrow [AdO\cdot] \rightarrow AdOH$, is supported by successful spin trapping [$PhCH=N^+(O^-)Bu^t$] of 1-AdO \cdot radicals, the origin of the hydrogen is not clear. An alternative chain

[†] New compounds gave satisfactory analytical and spectroscopic data.

mechanism, involving the intermediacy of the radical⁴ (4), seems to be precluded by our observation that the rate of thermal decomposition of benzyl phenyl selenoxide, which, it has been suggested, proceeds in a somewhat similar fashion,⁶ is not noticeably increased on addition of lauroyl peroxide.

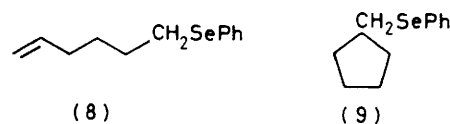
In an analogous manner, 1-adamantyl iodide was oxidised quantitatively by *m*-chloroperbenzoic acid to adamantan-1-ol, presumably by the following sequence 1-AdI → [1-AdIO] → [1-Ad· IO·] → [1-AdOI] → [1-AdO·] → 1-AdOH (*cf.* ref. 7).

Preparation of bicyclo[3.3.1]nonan-1-yl phenyl selenide (5) (70% as an oil) *via* the corresponding trifluoroacetate, and subsequent oxidation (aq. H₂O₂-acetone, room temp.), gave the hydroxy-selenide (7)[‡] (m.p. 63–65 °C). In this case, the strain in the transition state, and/or in the incipient alkene, is insufficient to preclude the normal elimination pathway, since the 'anti-Bredt' alkene (6) appears to be formed, and then trapped by benzeneselenenic acid liberated in the reaction.⁸ Similar chemistry has been reported previously for the 3-oxo-derivative of (5), prepared by a different route.⁹



In order to evaluate further the initial free-radical synthesis of alkyl phenyl selenides, an attempt was made to 'time' the reaction of primary alkyl radicals with diphenyl diselenide. It was first demonstrated that lauroyl

peroxide does indeed give phenyl undecyl selenide on thermal decomposition in a solution of diphenyl diselenide in benzene or *o*-dichlorobenzene. That this was formed predominantly in a rapid S_H2 process as envisaged was supported by a strong multiplet effect (AE), with no net polarization, in a CIDNP spectrum of the α -methylene protons of the product. Repetition of the reaction using hept-6-enoyl peroxide and a variety of concentrations of diphenyl diselenide (0.25×10^{-2} to 4×10^{-2} M; always present in large excess) in refluxing benzene yielded the key products (8) and (9). From the ratios of [(8)] to [(9)], the concentrations of diphenyl diselenide, and the known¹⁰ rate constant for isomerisation of the hex-5-enyl radical, it was possible to estimate a rate constant of *ca.* 5×10^7 l mol⁻¹ s⁻¹ at 80 °C for the S_H2 step.



Clearly, the reaction of primary alkyl radicals with diphenyl diselenide is very fast. The yields of mixed alkyl aryl selenides from diacyl peroxide decompositions are good when allowance is made for the removal of alkyl radicals in cage reactions; the inefficiency of the synthesis with adamantyl radicals is due to our inability to find a suitable precursor which is compatible with the diselenide. (Bis-1-adamantylcarbonyl peroxide is unstable).¹¹

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‡ The stereochemical assignment is based on spectroscopic and mechanistic considerations.

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