Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. 29. Free Radical Chemistry of Aliphatic Selenium Compounds[1]

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Abstract: The reactions of a variety of aliphatic selenium compounds with free radicals have been studied by EPR spectroscopy. The methylselenyl radical, $CH_3Se\cdot$, could not be directly observed by EPR, probably because of extreme line broadening by spin-orbit coupling. Sterically hindered β-selenoalkyls, $R_nMSeC(CMe)_2$, generated by addition of $R_nM\cdot$ radicals to di-*tert*-butyl selenoketone, are readily observed by EPR, but unhindered alkylselenoalkyls, such as CH_3SeCH_2, could not be detected directly. This difference is attributed to conformational factors. The hindered radicals adopt a conformation in which the unpaired electron interacts only weakly with the selenium nucleus because the selenium's lone pair lies in the C_α $2p_z$ nodal plane. The unhindered radicals adopt a conformation in which the lone pair is eclipsed by the C_α $2p_z$ orbital and the resultant strong interaction with the selenium nucleus leads to line broadening both by a spin-rotation mechanism and by the spin-orbit mechanism. The kinetics of decay of some $R_nMSeC(CMe_3)_2$ radicals are reported. At low temperatures these radicals exist in equilibrium with a diamagnetic dimer. The $(CH_3)_3COSeC(CMe_3)_2$ radical decays by a γ scission of the C-O bond. Dialkyl selenides readily undergo bimolecular homolytic substitution at selenium when attacked by reactive carbon-centered radicals such as $C_6H_5\cdot$. Relative and absolute rate constants for some of these reactions have been determined. Some γ- and δ-selenoalkyls have also been identified.

The free radical chemistry of aliphatic selenium compounds and the behavior of selenoalkyl radicals are virtually unknown. We become interested in this field when we discovered[3] that a variety of transient radicals, $R_nM\cdot$, could be added to Barton et al.'s[4] recently prepared di-*tert*-butyl selenoketone to give persistent[5] adduct radicals, **1**, that could be readily detected by EPR spectroscopy.

$$R_nM\cdot + Se{=}C(CMe_3)_2 \rightarrow R_nMSeC(CMe_3)_2$$
$$\mathbf{1}$$

These adduct radicals were the first selenoalkyl radicals to be observed by EPR spectroscopy in solution.[6-8]

There do not appear to have been any previous EPR studies on the reactions of free radicals with dialkyl selenides or with dialkyl diselenides. In this paper we report that although methylselenyl radicals, $CH_3Se\cdot$, unhindered β-selenoalkyl radicals, $RSeCR'R''$, and unhindered γ-selenoalkyl radicals, $RSeCH_2CH_2$, can be generated by various procedures, none of them could be directly observed by EPR spectroscopy. However, the hindered β-selenoalkyl radicals, **1**, could be readily detected and so could certain hindered γ- and δ- selenoalkyls. We also report some of the first examples of S_H2 reactions at selenium,[9,10] i.e.,

$$R_nM\cdot + R'_2Se \rightarrow R_nMSeR' + R\cdot'$$

Quantitative rate measurements have been made on radical forming reactions and on radical decay processes whenever possible.

Experimental Section

Materials. Dimethyl selenide, diethyl selenide, and dimethyl diselenide were obtained from the Ventron Corp. We gratefully acknowledge receipt of a generous sample of *n*-butyl *tert*-butyl selenide from Professor D. Seebach.

Methyl phenyl selenide[12] was prepared by reaction of phenylselenyl chloride (Aldrich) with methyllithium.[13]

Methyl 2-bromoethyl selenide was prepared by reaction of dimethyl diselenide with bromine and then with ethylene.[13]

Bis(trifluoromethyl) selenide was prepared from silver trifluoroacetate and metallic selenium[14] and was purified by trap-to-trap distillation.

Reduction of dimethyl diselenide with sodium ethoxide gave sodium methyl selenide.[13,15,16] Hydrolysis of this compound gave methyl selenol.[16] This reaction was carried out and the selenol was handled under high vacuum.

Di-*tert*-butyl selenoketone was prepared by a modification[3] of Barton's method.[4]

Ethylene episelenide was (presumably) prepared by reaction of ethylene oxide with tri-*n*-butyl phosphine selenide in the presence of trifluoroacetic acid according to the procedure of Chan and Finkenbine.[17,18] Analysis by VPC showed that the conversion of $(n\text{-Bu})_3P{=}Se$ to $(n\text{-Bu})_3P{=}O$ was $\geq$85%. However, our attempts to purify the episelenide by high vacuum distillation were not successful and for this reason EPR experiments had to be carried out using the reaction mixture from which only ethylene oxide and trifluoroacetic acid had been removed.

All other reagents were commercial materials. Benzene, propane, and *n*-pentane were most commonly employed as solvents.

Measurement of Relative Light Intensity. Radicals were generated photochemically in the cavity of a Varian E4-EPR spectrometer using previously described radical precursors.[3,19] The light source was a 500 W high-pressure mercury lamp and quartz optics were used. The light intensity could be varied by interspersing metallic screens between the lamp and spectrometer. The resultant changes in light intensity were calibrated from the changes in the intensity of the EPR signal due to the ketyl radicals produced by reaction of acetone triplets with 2-propanol in benzene, i.e.,

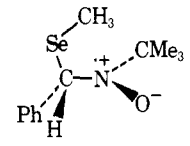
$$Me_2CO^{*3} + Me_2CHOH \rightarrow 2Me_2\dot{C}OH$$

$$2Me_2\dot{C}OH \rightarrow ME_2C(OH)C(OH)Me_2$$

This method of calibration was found to be both more convenient and more accurate than spectrophotometric measurements because that part of the screen that actually intersects the light falling on the cavity is calibrated.

Results

Generation of $CH_3Se\cdot$ Radicals. No radicals could be detected when dimethyl diselenide was photolyzed in hydrocarbon solvents[20] nor when mixtures of methyl selenol and di-*tert*-butyl peroxide were photolyzed. However, we had no trouble in trapping a radical that appeared to be $CH_3Se\cdot$ when the diselenide was photolyzed in the presence of *tert*-butyl phenyl nitrone, **2**.[22] The adduct had a well resolved EPR spectrum, the parameters for which are $g = 2.0097$, $a^N = 13.5$ G, $a^H(1\text{ H}) = 2.06$ G, and $a^H(3\text{ H}) = 0.85$ G at -50 °C. The presence of selenium is suggested by the high g value. The small splitting by three equivalent protons implies that the

$CH_3Se\cdot$ + $PhCH{=}N(O)CMe_3$ ⟶ 

2 3

$CH_3Se\cdot$ radical has been trapped. We therefore assign structure **3** to this adduct.

We were unable to identify an adduct when 2-methyl-2-nitrosopropane or 1,1-di-*tert*-butylethylene were used as spin traps. However, di-*tert*-butyl selenoketone gave a short lived ($\tau_{1/2}$ = 0.5 s at −80 °C) adduct having g = 2.0026 to which we have previously assigned the $CH_3SeSeC(CMe_3)_2$ structure.[3] With di-*tert*-butyl thioketone at −105 °C a weak signal due to $CH_3SC(CMe_3)_2$ could be obtained together with an even weaker signal at g = 2.0056 which we attribute to $CH_3SeSC(CMe_3)_2$.

Generation of Unhindered β-Selenoalkyl Radicals. All attempts at the direct observation by EPR spectroscopy of the radicals formed by hydrogen atom abstraction from dimethyl selenide, diethyl selenide, *n*-butyl-*tert*-butyl selenide, methyl phenyl selenide, and dimethyl diselenide were unsuccessful. These experiments were carried out at temperatures from 70 to −160 °C, in solvents such as benzene, tridecane, *n*-pentane, propane, cyclopropane, di-*tert*-butyl peroxide, and CF_2Cl_2, using species that are normally extremely efficient hydrogen atom abstracting agents such as the *tert*-butoxy and trifluoromethoxy free radicals, and the triplets from acetone, perfluoroacetone, and benzophenone.

The question soon became: are β-selenoalkyl radicals formed by hydrogen abstraction and, if so, why are they not observable in solution by EPR spectroscopy? That the *tert*-butoxy radical reacts readily with dimethyl selenide was shown by adding the selenide to irradiated mixtures of di-*tert*-butyl peroxide and cyclopentane. In the absence of the selenide there is a strong signal due to cyclopentyl, but as the selenide is added in increasing amounts this signal decreases in intensity and eventually disappears, no new signal taking its place (see, e.g., Table I). Since the selenide absorbs at wavelengths too short for it to interfere with the photolysis of the peroxide and since an S_H2 reaction of *tert*-butoxy at selenium can be ruled out by the absence of a methyl radical signal (see below), it is clear that hydrogen atom abstraction must indeed occur. This was confirmed by the observation that photolysis of a 2:1 mixture of di-*tert*-butyl peroxide and dimethyl selenide at room temperature gave an [acetone]/[*tert*-butyl alcohol] ratio that was at least 70 times smaller than the ratio obtained when the neat peroxide was photolyzed under the same conditions.

$$(CH_3)_3CO\cdot \xrightarrow{RH} \begin{cases} (CH_3)_3COH & (+R\cdot) \\ CH_3COCH_3 & (+CH_3\cdot) \end{cases}$$

The rate constant, k_1, for hydrogen abstraction from dimethyl selenide by *tert*-butoxy radicals can be estimated from the results of the cyclopentane/dimethyl selenide competition.

$$(CH_3)_3CO\cdot + CH_3SeCH_3 \xrightarrow{k_1} (CH_3)_3COH + CH_3SeCH_2\cdot \quad (1)$$

$$(CH_3)_3CO\cdot + C_5H_{10} \xrightarrow{k_2} (CH_3)_3COH + C_5H_9\cdot \quad (2)$$

If we make the reasonable assumptions that the rate constants for the bimolecular reactions by which $C_5H_9\cdot$ and $CH_3SeCH_2\cdot$ radicals are destroyed are equal[23] and that the sum of the concentrations of the two radicals is a constant, then,

$$\frac{k_2}{k_1} = \frac{[C_5H_9\cdot][CH_3SeCH_3]}{([C_5H_9\cdot]_0 - [C_5H_9\cdot])[C_5H_{10}]}$$

In this equation,[24] $[C_5H_9\cdot]_0$ refers to the radical's concentration in the absence of dimethyl selenide. From the data in Table I we obtain $k_2/k_1 = 0.81 \pm 0.14$ at −30 °C. Taking k_2 to be 2×10^4 M^{-1} s^{-1} at this temperature[24] yields $k_1 = 2.5 \times 10^4$ M^{-1} s^{-1}.

Table I. Competition between Cyclopentane (1.7 M) and Dimethyl Selenide at −30 °C for *tert*-Butoxy Radicals at Constant Light Intensity

$[Me_2Se]/[C_5H_{10}]$	Rel $[C_5H_9\cdot]$
0	1.00
1.06	0.55
2.08	0.36
3.50	0.29
6.50	0.20

Final confirmation that the reaction of *tert*-butoxy radicals with dimethyl selenide yields CH_3SeCH_2 was provided by trapping this radical with di-*tert*-butyl thioketone.[25] This spin trap was chosen because it is unreactive toward *tert*-butoxy but is extremely reactive toward carbon-centered radicals.[25] Photolysis at 0 °C of a 1:1 di-*tert*-butyl peroxide/benzene solution containing dimethyl selenide and the thione gave a radical with a half-life of 8 s at 0 °C and with the following EPR parameters: g = 2.0038, a^H(18 H) = 0.50 G, $a^{^{13}C_\alpha}$ = 43.9 G, and $a^{^{13}C}$(1 C) = 27.8 G. We assign this radical the structure $CH_3SeCH_2SC(CMe_3)_2$ on the basis of its high g value[26] and the 27.8 G splitting by one carbon which is not the α-carbon.[26] The rapid and efficient abstraction of hydrogen from dimethyl selenide by *tert*-butoxy radicals was confirmed by measuring the initial (i.e., first 1-2 s) rate of formation of the spin adduct upon irradiation of the sample. This rate was found to be 2.2×10^{-5} M s^{-1} at 0 °C which is equal (within a factor of 2) to the rate of cyclopentyl radical formation when mixtures of di-*tert*-butyl peroxide and cyclopentane were irradiated under similar conditions.

Irradiation of diethyl selenide, di-*tert*-butyl peroxide, and the thione in *n*-pentane at −35 °C gave a relatively short-lived ($\tau_{1/2} \sim 1$ s) spin adduct with a g value of 2.0039 which we presume was $CH_3CH_2SeCH(CH_3)SC(CMe_3)_2$.

Generation and Decay of Hindered β-Selenoalkyl Radicals. In contrast to the unhindered β-selenoalkyls, well resolved EPR spectra of **1** were obtained when transient radicals add to di-*tert*-butyl selenoketone.[3] The concentration of the *n*-Bu_3Si-$SeC(CMe_3)_2$ radical at −50 °C under steady illumination was found to be proportional to the first power of the light intensity. This adduct and others decay with first order kinetics. The Arrhenius parameters for decay and the half-lives at 25 °C of a number of **1** are listed in Table II.

$$R_nMSeC(CMe_3)_2 \xrightarrow{k^1_{EPR}} \text{products}$$

1

The Arrhenius plot for the $(CH_3)_3CSeC(CMe_3)_2$ radical shows distinct curvature (see Figure 1) which implies that decay occurs by different processes at high and at low temperatures. The Arrhenius parameters for both processes are given in Table II.

Irradiation of hydrocarbon solutions of di-*tert*-butyl peroxide and the selenoketone gives the *tert*-butoxy adduct, $(CH_3)_3COSeC(CMe_3)_2$. On prolonged reaction there is a precipitation of red selenium[27] which implies that this adduct decays by C-O bond fission, i.e., decay occurs by a γ scission.[29]

Table II. Arrhenius Parameters and Half-Lives for Decay of $R_nMSeC(CMe_3)_2$ in Pentane

R_nM	Temp range, °C	log A^1_{EPR}, s^{-1} [a]	E^1_{EPR}, kcal/mol [b]	$\tau_{1/2}^{25°C}$, s
CH_3 [c]	30 to −120	2.8	4.7	3.0
$(CH_3)_3C$ [d]	55 to −16	12.3	16.1	0.23
	−25 to −87	2.0	4.5	
CF_3	25			≥3700 [e]
C_6H_5	25			≥6100 [e]
n-Bu_3Si	0 to −75	4.3	4.7	0.09
$(CH_3)_3Sn$	35 to −27	4.5	8.7	49
$(CH_3)_3CO$	25 to −70	10.0	12.5	0.09
$(CH_3)_3CS$	25 to −70	5.2	6.3	4.7

[a] Typical least-squares error ±0.6. [b] Typical least-squares error ±0.8 kcal/mol. [c] CH_3· generated from azomethane (cf. ref 25). [d] $(CH_3)_3C$· generated from azoisobutane. [e] Lower limit. Slow decays frequently correspond to reactions with impurities in the system.

$$(CH_3)_3COSeC(CMe_3)_2 \xrightarrow{k_\gamma} (CH_3)_3C + [O{=}Se{=}C(CMe_3)_2$$

or

$$\overbrace{O{-}Se{-}C(CMe_3)_2}] \rightarrow \text{red Se} + O{=}C(CMe_3)_2$$

The Arrhenius parameters for decay (Table II) are not inconsistent with a γ scission. Furthermore, comparison with the decay of $(CD_3)_3COSeC(CMe_3)_2$ indicates that the reaction has a small kinetic secondary deuterium isotope effect, $k_\gamma^H/k_\gamma^D = 1.24 \pm 0.20$ at −60 °C.[30] Neither cumyloxy nor benzyloxy radicals gave detectable concentrations of adducts with the selenoketone[3] but red selenium was deposited during the reactions. The more rapid γ scissions of the (presumed) alkoxy adducts can be attributed to the formation of resonance stabilized alkyl radicals.[3]

Most $R_nMSeC(CMe_3)_2$ radicals (and perhaps all of them) exist in equilibrium with a diamagnetic dimer at ambient or lower temperatures.

$$2R_nMSeC(CMe_3)_2 \rightleftharpoons [R_nMSeC(CMe_3)_2]_2$$

This equilibrium can sometimes be demonstrated directly by raising and lowering the temperature in a range where the irreversible decay of the radical is relatively slow. By this means it was shown that $CF_3SeC(CMe_3)_2$ dimerizes at ca. −120 °C, $(CH_3)_3GeSeC(CMe_3)_2$ at ca. −70 °C, and $(CH_3)_3CSeC(CMe_3)_2$ at ca. −40 °C.

An alternative procedure for demonstrating the presence of reversible dimerization when irreversible decay is relatively rapid is to generate the adduct in a series of short light flashes which are sufficiently intense that the rate of formation of $R_nMSeC(CMe_3)_2$ is much faster than its rate of dimerization. The results of such an experiment with $(CH_3)_3SnSeC(CMe_3)_2$ radicals at 30 °C are illustrated in Figure 2. In this figure, the arrows represent light flashes of variable length. With each flash the concentration of $(CH_3)_3SnSeC(CMe_3)_2$ radicals increased rapidly while the light is on. When the light was cut-off there was an initial rapid decay which approximately obeyed second-order kinetics. This was followed by a very much slower first-order decay. Points A, B, and C show that for a given concentration of radicals the rate of decay depends on whether the observation is made immediately following a light flash or after an interval of a few seconds. The initial fast decay clearly corresponds to the rapid formation of the dimer, while the subsequent slow reaction must reflect the irreversible destruction of the radical and its dimer.

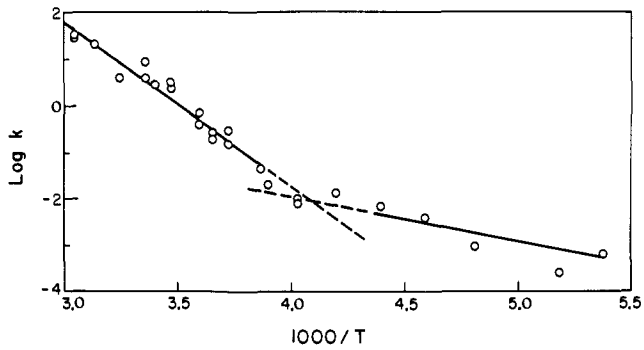


Figure 1. Arrhenius plot for the decay of $(CH_3)_3CSeC(CMe_3)_2$.

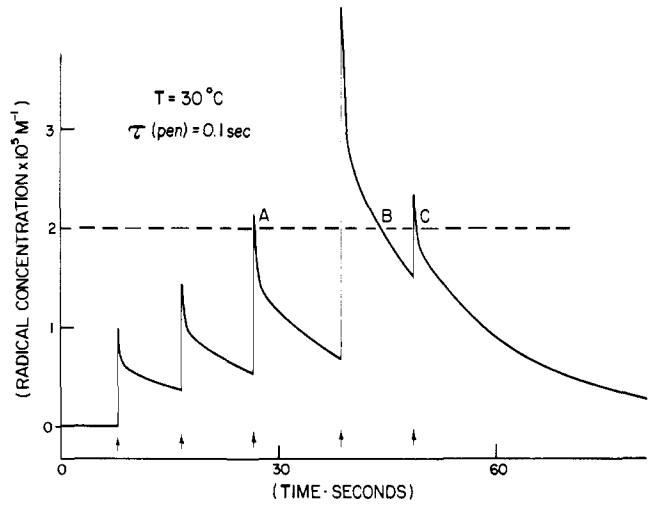


Figure 2. Generation and decay of $(CH_3)_3SnSeC(CMe_3)_2$ radicals at 30 °C in a series of light flashes (arrows) of different duration. The upward movement of the pen was limited by the time constant of the recorder, so that the actual radical concentrations formed in each light flash are larger than is indicated.

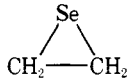
It was not possible to measure the equilibrium constant for the dimerization of most $R_nMSeC(CMe_3)_2$ radicals because decay and dimerization occurred over similar temperature ranges. However, this was not the case for $(CH_3)_3CSeC(CMe_3)_2$ at temperatures from −15 to −50 °C, and ΔH was readily obtained from the variation in the radical concentration with temperature. The measurement of ΔS was more difficult because there was no direct way to measure the concentration of dimer. However, this concentration could be estimated by generating a known quantity of radicals and measuring their actual concentration at equilibrium. The known quantity of radicals was determined at −25 °C from the *initial* rate of radical formation when the sample was irradiated at low light intensity for a known length of time. The variation with temperature of the equilibrium constant for dimerization of the $(CH_3)_3CSeC(CMe_3)_2$ radical can be represented by,

$$R \ln K = (37.5 \pm 7.0) \text{ (gibbs/mol)} - \frac{(18.2 \pm 2.0)}{T} \text{ (kcal/mol)}$$

Generation of γ- and δ-Selenoalkyl Radicals. The formation of γ-selenoalkyl radicals presents no major problems *provided* the intervening β atom is not carbon. Thus, the $CH_3SeSeC(CMe_3)_2$ and $CH_3SeSC(CMe_3)_2$ radicals can be formed by addition of CH_2Se· to the selenoketone and thioketone (see above) and the $(Me_3C)_2CHSeSeC(CMe_3)_2$ radical can be formed by irradiation of the selenoketone in systems containing good hydrogen donors.[3,32] However, no γ-selenoalkyl radicals having a β-carbon could be detected by EPR spectroscopy.

Three basic reactions were employed in our attempts to generate and observe such radicals. These reactions are indicated below. They were carried out at temperatures from 25 to −160 °C and in no case could *any* radicals be observed.

$$CH_3SeCH_2CH_2Br \xrightarrow{(CH_3)_3Si\cdot} CH_3SeCH_2\dot{C}H_2 \quad (I)$$



$$\xrightarrow{R_nM\cdot} R_nMSeCH_2\dot{C}H_2 \quad (II)$$

$$CH_3SeSeCH_3 \xrightarrow{h\nu} CH_3Se\cdot \xrightarrow{CH_2=CR_2} CH_3SeCH_2\dot{C}R_2 \quad (III)$$

In method I, the absence of the signal due to $(CH_3)_3Si\cdot$ radicals (from the silane and *tert*-butoxy radicals) indicates that the reaction is occurring. Separate competitive experiments with mixtures of CH_3SeCH_3 and CH_3CH_2Br showed that the trimethylsilyl has a strong preference (>40 at all temperatures) for attack at bromine (to form $CH_3CH_2\cdot$) relative to attack at selenium (to form $CH_3\cdot$). In method II, the absence of a signal due to methyl (from azomethane) indicates that reaction is occurring. Unfortunately, no radicals could be trapped when **2** was added to this reaction mixture because the episelenide and the nitrone were destroyed in a direct reaction with one another. Method II was also unsuccessful with $R_nM\cdot$ = *n*-$Bu_3Sn\cdot$, $C_6H_5\cdot$, and $C_6F_5\cdot$. In method III, no radicals were observed with ethylene from −70 to −160 °C nor with 1,1-di-*tert*-butylethylene from 25 to −110 °C.

The formation of δ-selenoalkyl radicals is exemplified by the addition of $CH_3Se\dot{C}H_2$ and $CH_3CH_2Se\dot{C}HCH_3$ radicals to di-*tert*-butyl thioketone (see above). No attempt was made to generate any other δ-selenoalkyls.

Bimolecular Homolytic Substitution (S_H2) Reaction with Dialkyl Selenides. Our failure to detect selenoalkyl radicals when alkoxy radicals or triplet ketones were generated in the presence of dialkyl selenides lead us to examine the reactions of these compounds with other active radicals.

Photolysis of azomethane in the presence of diethyl selenide at temperatures from −20 to −60 °C gave an EPR spectrum which showed both methyl and ethyl radicals. Since no radicals were detected when diethyl selenide was photolyzed alone, it is clear that the methyl radicals are effecting a bimolecular homolytic substitution (S_H2) at the selenium atom.[9]

$$CH_3\cdot + (C_2H_5)_2Se \xrightarrow{k_3} CH_3SeC_2H_5 + C_2H_5\cdot \quad (3)$$

For the two alkyl radicals to be observed simultaneously it is necessary that $k_3[(C_2H_5)_2Se] \approx 2k_t[CH_3\cdot]^2$, where $2k_t$ is the rate constant for methyl radical combination. From this relationship, we estimate that k_3 is ca. 10^3 M^{-1} s^{-1}.

Phenyl and perfluorophenyl radicals[23] also entered into S_H2 reactions with dialkyl selenides. These S_H2 reactions were each run competitively[24] with hydrogen abstraction from cyclopentane.

$$Ar\cdot + (CH_3)_2Se \xrightarrow{k_4} ArSeCH_3 + CH_3\cdot \quad (4)$$

$$Ar\cdot + (C_2H_5)_2Se \xrightarrow{k_5} ArSeC_2H_5 + C_2H_5\cdot \quad (5)$$

$$Ar\cdot + C_5H_{10} \xrightarrow{k_6} ArH + C_5H_9\cdot \quad (6)$$

The ratios of the three rate constants were determined from the ratio of the radical concentrations under steady state conditions. Thus, at −30 °C with $C_6H_5\cdot$ the ratios of the three rate constants, k_4:k_5:k_6, were 3.1:70:1.0 and with Ar· = $C_6F_5\cdot$ the ratios were 2.1:11:1.0. The $C_6F_5\cdot$ radical is, therefore, less selective than phenyl. For the $C_6F_5\cdot$ radical, the variation in the k_4/k_6 ratio was measured over a temperature range from −10 to −90 °C. It can be represented by,

$$\log (k_4/k_6) = (-0.24 \pm 0.20) + (0.61 \pm 0.25)/\theta$$

where $\theta = 2.3RT$ kcal/mol. Other S_H2 reactions of interest include the production of $CF_3\cdot$ from $C_6F_5\cdot$ and $(CF_3)_2Se$ and the production of $CH_3\cdot$ from $(CH_3)_3CO\cdot + C_6H_5SeCH_3$.

Generation of $CF_3\cdot$ from CF_3I and hexa-*n*-butylditin in the presence of dimethyl selenide or diethyl selenide did not give the expected alkyl radicals. Instead, a radical was obtained from both selenides which had the same EPR parameters, viz., g = 2.0027, a(2 nuclei with spin of ½) = 27.43 G, and a(3 nuclei with spin of ½) = 21.96 G at −15 °C. These parameters do not correspond to those reported for $CH_3CH_2\cdot$, $CF_3CH_2\cdot$, $CH_3CF_2\cdot$, or $CF_3CF_2\cdot$ radicals.[34] Since the same radical was produced during the photolysis of hexa-*n*-butylditin and $(CF_3)_2Se$ we *tentatively* suggest that it may be the $CF_3SeCF_2\cdot$ radical. If this assignment is correct (the signal was never strong enough to pick up splitting by ^{77}Se), it would seem that S_H2 reactions must be involved in its formation from the dimethyl selenide and diethyl selenide. The mechanism by which it is formed remains obscure.[35] This radical gave a much weaker EPR signal, or could not be detected, when hexamethylditin was used in place of hexa-*n*-butylditin.

Discussion

Detection of Selenoalkyl Radicals by EPR Spectroscopy. Our failure to detect the methylselenyl radical, $CH_3Se\cdot$, directly by EPR spectroscopy is hardly unexpected since alkoxy radicals[36] and alkylthiyl radicals[37,38] are also undetectable by EPR in solution.[39] This is due to the fact that these radicals have orbitally degenerate (or nearly degenerate) ground states which lead, by spin-orbit coupling, to a markedly anisotropic g factor. As a consequence, these radicals have very short relaxation times and hence extremely broad lines.[36-38]

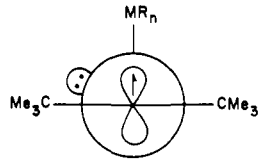
We attribute our failure to detect any γ-selenoalkyl radicals having a β-carbon to a facile,[40] and probably exothermic,[41] β-scission reaction, i.e.,

$$R_nMSeCH_2\dot{C}H_2 \rightarrow R_nMSe\cdot + CH_2{=}CH_2$$

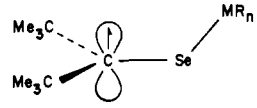
The β scission of γ-selenoalkyls having a β-selenium or β-sulfur atom must be significantly slower, since such radicals could be produced by addition of $CH_3Se\cdot$ to di-*tert*-butyl selenoketone and thioketone.

Since *hindered* β-selenoalkyl radicals, $R_nMSe\dot{C}(CMe_3)_2$, can readily be detected by EPR spectroscopy, it becomes necessary to account for our failure to detect *unhindered* β-selenoalkyls. In the first place, the spin trapping experiments show that such radicals are produced when dimethyl selenide or diethyl selenide reacts with *tert*-butoxy radicals. Second, these radicals are produced just as efficiently as are the radicals from alkanes. In fact, the estimated rate constant for hydrogen abstraction by *tert*-butoxy at −30 °C indicates that the primary hydrogen atoms in CH_3SeCH_3 are more reactive (k_1/H = 4×10^3 M^{-1} s^{-1}) than are the secondary hydrogens in cyclopentane (k_2/H = 2×10^3 M^{-1} s^{-1}). If we make the reasonable assumptions[23] that $CH_3Se\dot{C}H_2$ radicals decay with second-order kinetics and with a rate constant $2k_t \sim 2 \times 10^9$ M^{-1} s^{-1}, then their steady state concentration will be $\geq 1 \times 10^{-7}$ M during photolysis of di-*tert*-butyl peroxide solutions of dimethyl selenide. By comparison with the signal-to-noise ratio in other photolytic systems we calculate that $CH_3Se\dot{C}H_2$ radicals can only be "invisible" if their line widths (ΔH_{pp}) are ≥4.5 G.[44] For comparison, certain $R_nMSe\dot{C}(CMe_3)_2$ radicals have line widths as small as 0.1-0.2 G.[3]

We attribute the great difference in line widths between hindered and unhindered β-selenoalkyls to conformational effects. The hindered radicals adopt a conformation, **4**, in which R_nM is eclipsed by the C_α $2p_z$ orbital.[3] Since there appears to be very little hybridization of the selenium 4s and 4p orbitals in dialkyl selenides[45] the selenium has essentially



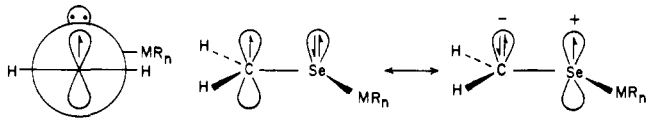
4a



4b

a single lone pair in a p orbital. In conformation **4** this lone pair will lie in the C_α $2p_z$ nodal plane. The unpaired electron cannot, therefore, be appreciably delocalized onto the selenium and most of the spin that reaches the selenium will arrive by spin polarization. One consequence of the comparatively small interaction between the selenium and the unpaired electron in $R_nMSeC(CMe_3)_2$ radicals is that their g values center around the free electron value (2.0023) despite the high spin-orbit coupling constant of selenium (1688 cm^{-1}).[3]

Unhindered β-selenoalkyl radicals, on the other hand, are expected to adopt a conformation in which overlap between the selenium lone pair and the the $C\alpha$ $2p_z$ orbital is maximized, i.e., **5**.[47] This will cause the isotropic g values to be appreciably



5a 5b 5c

greater in unhindered β-selenoalkyls than in simple alkyls or hindered β-selenoalkyls. In addition, it will cause the g tensor to be significantly anisotropic.

Numerous studies have established that spin-rotation interactions are important in radicals which have large *isotropic* g shifts and that such interactions lead to enhanced line widths.[49] The line width, ΔH_{pp}, has been shown to be proportional to $(g - 2.0023)^2T/a^3\eta$, where T is the absolute temperature, a is the diameter of the radical, and η is the viscosity of the solution.[49] A relatively small deviation in g from the free electron value can, therefore, produce line widths that would make an entire class of transient radicals invisible under normal EPR conditions. Since $\Delta H_{pp} \propto T/a^3\eta$, the possibility of detecting the radicals in such a class can be increased by working at low temperatures, or in viscous solvents, or with the more bulky radicals in the class.[50]

In the present work, we failed to detect CH_3SeCH_2 even at very low temperatures and had no better success with the more massive alkylselenoalkyl radicals which are presumably formed by hydrogen atom abstraction from $(C_2H_5)_2Se$ and from $(CH_3)_3CSe(CH_2)_3CH_3$.[51] This failure does not automatically imply that the (presumed) broadening of the EPR lines of unhindered alkylselenoalkyl radicals cannot be due to the spin-rotation mechanism, since the g values might be very different from the free electron value. Fortunately, we can estimate the g value and line width in a very approximate manner. Nishikida and Williams[7,52] have reported the spin density distribution in congeneric selenium and sulfur containing radicals is similar. If this is true for CH_3SeCH_2 and CH_3SCH_2 then the positive deviation in their g values should be determined by the ratio of the spin-orbit coupling constants for Se and S, i.e., 1688/382 = 4.4. The g value for CH_3SCH_2 is 2.0051 and hence, for CH_3SeCH_2, $g = 2.0023 + (2.0051 - 2.0023) \times 4.4 = 2.0146$. Similarly, we have determined that the line width for CH_3SCH_2 is 0.34 G at −100 °C in cyclopropane. If we can assume that the diameters of CH_3SCH_2 and CH_3SeCH_2 are similar then the line width for CH_3SeCH_2 under the same conditions should be ca. $0.34 \times (4.4)^2 = 6.6$ G.

The spin-rotation mechanism of line broadening would appear, therefore, to be just adequate *by itself* to account for our failure to detect CH_3SeCH_2,[53] although it would not appear to be adequate to account for our failure to detect more massive unhindered alkylselenoalkyls. However, we can get around this difficulty by invoking a second mechanism of line broadening which should be operative in all unhindered alkylselenoalkyls. This second mechanism arises because interaction of the unpaired electron with the selenium's lone pair (**5c**) introduces, by spin-orbit coupling, a high degree of anisotropy into the g tensor. This will lead to radicals having short relaxation times and hence to radicals having broad EPR lines.[36,49b] Moreover, in this mechanism of line broadening, $\Delta H_{pp} \propto \eta/T$, so that the radicals become *more* difficult to detect as the temperature is lowered. We suggest that our failure to detect any unhindered alkylselenoalkyl is due to the operation of *both* the spin-rotation and the spin-orbit line broadening mechanisms.[49f,g,54]

Decay of $R_nMSeC(CMe_3)_2$ Radicals. All adducts to di-*tert*-butyl selenoketone decay with first-order kinetics (see Table I). However, the Arrhenius preexponential factors, A^1_{EPR}, imply that only $(CH_3)_3CSeC(CMe_3)_2$, at temperatures above −16 °C, and $(CH_3)_3COSeC(CMe_3)_2$ can possibly be decaying by true unimolecular processes. In all other cases, the A^1_{EPR} values are far too small for the radicals to be decaying by simple unimolecular reactions. Their magnitudes are undoubtedly a consequence of the fact that the radicals exist in equilibrium with their diamagnetic dimers.

It has been established in numerous studies[55] that free radicals will decay with first-order kinetics when they are in equilibrium with their dimers *provided* the concentration of the dimer is greater than the concentration of the radical. The reaction scheme can be represented either by,

$$2R\cdot \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} R_2 \xrightarrow{k_8} \text{products}$$

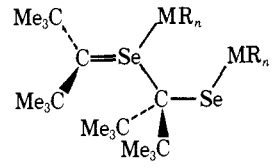
in which case, the measured rate constant for decay, k^1_{EPR}, is given by $k_8/2$, or by

$$\text{products} \xleftarrow{k_9} 2R\cdot \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} R_2$$

in which case, $k^1_{EPR} = k_9k_{-7}/2k_7$.

These two schemes are not always distinguishable. However, in the present instance, the second mechanism seems improbable because there is no obvious reason why, when A^1_{EPR} is given by $A_9A_{-7}/2A_7$, it should be so very small. That is, for the $(CH_3)_3CSeC(CMe_3)_2$ radical-dimer equilibrium the measured value of ΔS was 37.5 ± 7.0 gibbs/mol (which yields $A_{-7}/A_7 = 10^{8.2\pm1.5}$ M) and there is no reason to suppose that ΔS would be very different for the equilibria involving the other $R_nMSeC(CMe_3)_2$ radicals. To obtain A^1_{EPR} values in the range 10^2–10^5 s^{-1} would therefore require impossibly small values for A_9.

The first mechanism would appear to be much more probable. Indeed, low values for A^1_{EPR} would be expected since the reaction being monitored is the irreversible decomposition of a sterically hindered dimer, a reaction which might well suffer from severe conformational restraints. Unfortunately, all our attempts to identify the products formed by the decay of an $R_nMSeC(CMe_3)_2$ dimer were unsuccessful. We presume that these dimers, like those formed from $R_nMSC(CMe_3)_2$ radicals,[25] probably have a head-to-tail structure, **6**. However, they



6

are much more stable with respect to their reversible decomposition,[56] presumably because selenium is larger than sulfur and has a much greater tendency to behave as a tetravalent center.

S_H2 Reactions with Dialkyl Selenides. There are no previous reports identifying bimolecular homolytic substitution by carbon-centered radicals at the selenium atom in dialkyl selenides,[9] although the Se–Se bond in diethyl diselenide has been reported to be cleaved by ethyl radicals.[21b] These reactions follow the path that has become familiar through studies of S_H2 reactions at other heavy, and sterically unencumbered, atoms.[9] That is, exothermic S_H2 reactions are fast and, for a given attacking radical, the rate increases as more stabilized alkyls are displaced.

The rate constant for $C_6H_5\cdot$ attack on $(CH_3)_2Se$ and $(C_2H_5)_2Se$ can be estimated as follows. At 40 °C the rate constant for abstraction by $C_6H_5\cdot$ of a single secondary aliphatic hydrogen is ca. 10^6 M^{-1} s^{-1}.[23] Assuming a normal preexponential factor of $10^{8.5}$ M^{-1} s^{-1} for this reaction yields $k/s\text{-H} = 2 \times 10^5$ M^{-1} s^{-1} at −30 °C, i.e., the rate constant for hydrogen abstraction from cyclopentane, k_6, is ca. 2×10^6 M^{-1} s^{-1} at this temperature. The relative reactivity data therefore yield, $k_4 \sim 6 \times 10^6$ M^{-1} s^{-1} for $C_6H_5\cdot$ attack on $(CH_3)_2Se$ at −30 °C, and $k_5 \sim 1.4 \times 10^8$ M^{-1} s^{-1} for attack on $(C_2H_5)_2Se$. Substitution for more stabilized radicals would presumably occur at rates even closer to the diffusion-controlled limit. The S_H2 reaction of $CH_3\cdot$ with $(C_2H_5)_2Se$ is relatively slow (k_3 is ca. 10^3 M^{-1} s^{-1}). However, substitution by $C_6F_5\cdot$ is probably[57] even faster than by $C_6H_5\cdot$ since the former radical is less selective than the latter.

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