Radical Additions to Di-t-butyl Selenoketone

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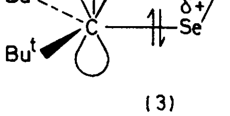
Summary The e.s.r. parameters and half-lives at 25 °C for several persistent selenoalkyl radicals, $R_nMSe\dot{C}Bu^t_2$, which have the R_nM group eclipsed by the $C_\alpha 2p_z$ orbital, are reported: the $^{13}C_\alpha$ and ^{77}Se hyperfine splittings are dependent on the electronegativity, rather than on the size, of R_nM.

OUR earlier studies on radical additions to 1,1-di-t-butylethylene,[1] di-t-butylketimine,[2] and di-t-butyl thioketone[3] suggested that the recently reported di-t-butyl selenoketone[4] (**1**) would also trap transient radicals, $R_nM\cdot$.

$$\underset{}{R_nM\cdot} + \underset{(\mathbf{1})}{Se{=}CBu^t_2} \longrightarrow \underset{(\mathbf{2})}{R_nMSe\dot{C}Bu^t_2}$$

A variety of $R_nM\cdot$ radicals, having M from Groups IV, V, and VI, add rapidly† to (**1**) and yield fairly persistent[5] adducts (**2**) that decay with first-order kinetics (see Table for half-lives at 25 °C) and form diamagnetic dimers at low temperatures. To the best of our knowledge, selenoalkyl radicals have not been reported previously.



(3)

The adducts (**2**) show an exceptional variation in their *g*-factors and in their $^{13}C_\alpha$ and ^{77}Se hyperfine splittings (h.f.s.). This was surprising because all other $R_nMX\dot{C}Bu^t_2$ radicals ($X = CH_2$,[1] $C{=}\overline{CCMe_2C}Me_2$,[6] and S[3]) show little variation in *g* or in $^{13}C_\alpha$ h.f.s. All these other radicals

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† The addition of $Me_3CO\cdot$, for example, competes with its attack on good H-donors such as Me_3SiH and $(EtO)_2POH$, even when the latter are present in 10—100 fold excess over (**1**).

TABLE. E.s.r. parameters in cyclopropane[a] and half-lives at 25 °C in isopentane for $R_nMSe\dot{C}Bu^t_2$ radicals (hyperfine splitting are in Gauss)

R_nM	g	$a(C_\alpha)$	a(Se)	a(M)	a(other)	$\tau_{\frac{1}{2}}$/s (25 °C)
Me	2·0021	49·5	24·6	19·06[b]	9·9,[c], 0·28[d]	2·2
Bu^t	2·0020	48·5	21·3	e		0·7
CF_3	2·0005	46·5	36·6	e	9·5[c], 0·6,[f],4·6[g]	>3700
Me_3CO	2·0024	39·0	65·0		0·33[f]	0·09[h]
Me_3Sn	2·0043	52	10·9	190·5,[i,j]	199·5[j,k]	49
$(EtO)_2P{=}O$	2·0016	e	e	89·3		—

[a] Temperature invariant unless noted otherwise. [b] Using ^{13}C enriched (90 atom %) MeI. [c] $6C\gamma$. [d] Multiplet with ⩾ 23 lines. [e] Not resolved. [f] Multiplet due to Bu^t protons. [g] 3F. [h] In Bu^tOOBu^t. [i] ^{117}Sn. [j] Temperature coefficient of 56 mG/°C (*cf.* ref. 3). [k] ^{119}Sn.

adopt a conformation in which, for steric reasons, R_nM eclipses the C_α $2p_z$ orbital and in which the radicals are either planar at C_α,[1b] or if non-planar,[1c] do not differ much in their geometry at this atom (to judge by $^{13}C_\alpha$ h.f.s.). Despite the large atomic radius of selenium, the M h.f.s. for (**2**) imply a similar 'eclipsed' conformation. For example,[3] with X = S the M h.f.s. for R_nM = Me, $(EtO)_2P{=}O$, and Me_3Sn, are 23·5 (^{13}C), 101 (^{31}P), and 243 and 254 G (^{117}Sn and ^{119}Sn at −30 °C), *cf.* Table.

Since all the radicals (**2**) adopt the 'eclipsed' conformation, spin will reach the selenium principally by spin polarization and so all ^{77}Se h.f.s. are probably of negative sign. The $^{13}C_\alpha$ h.f.s. increase along the series R_nM = Me_3CO, F_3C, Bu^t, Me, and Me_3Sn, and the ^{77}Se h.f.s. decrease along almost the same series.‡ Obviously these orders are *not* determined by the size of R_nM. However, they do appear to be related to R_nM electronegativities. We suggest, therefore, that the large variations in $^{13}C_\alpha$ and ^{77}Se h.f.s. are a consequence, not of steric factors, but of the high polarizability of selenium. That is, an electron-withdrawing R_nM group will deshield (increase the positive charge on) selenium and the C_α–Se σ-bonding electrons will thereby be polarized away from C_α and towards the Se, *i.e.* (**3**). This will increase the ^{77}Se h.f.s. and decrease the $^{13}C_\alpha$ h.f.s. since both h.f.s. arise by *spin* polarization of these σ-electrons. An electron-donating R_nM group will have the opposite effect.§ Our results show that the h.f.s. of nuclei that receive their spin *via* polarization may be just as sensitive to inductive effects as are the h.f.s. of nuclei that receive their spin *via* hyperconjugation.[7]

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‡ The $^{13}C_\alpha(+)$ and $^{77}Se(-)$ h.f.s. can be correlated by the equation $a(^{13}C_\alpha) = 54{\cdot}2 + 0{\cdot}2\, a(^{77}Se)$.

§ The electronegativity of R_nM may also have a small influence on the C_α geometry and on the C_α–Se bond length.

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