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THIOKETONES AS SPIN TRAPS FOR GROUP VI RADICALS

Angelo ALBERTI
I.Co.C.E.A. - C.N.R., 40064 OZZANO EMILIA, Italy

Bianca Flavia BONINI and Gian Franco PEDULLI
Dipartimento di Chimica Organica, Università di Bologna
15 Via S. Donato, 40127 BOLOGNA, Italy

SUMMARY: *Dyaryl-, dialkyl-, and aryltriphenylsilyl- thioketones have been shown to efficiently scavenge thiyl, sulphonyl and selenyl radicals affording adducts identified by ESR spectroscopy. Unprecedented evidence of the trapping of* ^{t}*BuO·* *radicals by thiones has also been obtained.*

Thiones are known to be efficient spin traps for a variety of free radicals centred at carbon and other Group IV elements, at phosphorus, and at transition metals such as manganese and rhenium.[1] Compelling evidence for the addition of these radicals to the C=S double bond has been obtained by ESR spectroscopy. On the basis of product studies it was concluded that thiyl radicals can also add to thiones; examples include the reaction, promoted either by visible light or by radical initiators, between adamantanethione and adamantanethiol,[2] and the reaction between thyohydroxamic acid esters and tri(phenylthio)antimony.[3] Despite this chemical evidence, there are no positive reports of the direct ESR observation of the resulting spin adducts. In fact, the alleged detection of the methylthio adduct to thiocamphor was not substantiated by any spectroscopic data,[4] while photolysis of the disulphide CF_3SSCF_3 in the presence of di-*tert*-butylthioketone led to the detection of $^t\mathrm{Bu}_2\dot{\mathrm{C}}\text{-}\mathrm{SCF}_3$ whose formation implies trapping of $\cdot CF_3$ instead of $\cdot SCF_3$ radicals.[1b]

The addition of alkoxyl radicals, from photolysis of $^t\mathrm{BuOO}^t\mathrm{Bu}$ or CF_3OOCF_3, to di-*tert*-butylthioketone has been attempted, but apparently failed to afford the $^t\mathrm{Bu}_2\dot{\mathrm{C}}\text{-}\mathrm{SOR}$ adducts.[1b] We are not aware of any ESR or chemical study of the reaction of sulphinyl or sulphonyl radicals with thiocarbonyl compounds.

In principle addition of thiyl or alkoxyl radicals to thiones should occur as easily as addition of carbon centred radicals, all these processes being strongly exothermic.

$$\mathrm{CH_2{=}S} + \cdot\mathrm{Me} \longrightarrow \cdot\mathrm{CH_2\text{-}SMe} \qquad (1)$$
$$\mathrm{CH_2{=}S} + \cdot\mathrm{SR} \longrightarrow \cdot\mathrm{CH_2\text{-}SSR} \qquad (2)$$
$$\mathrm{CH_2{=}S} + \cdot\mathrm{OR} \longrightarrow \cdot\mathrm{CH_2\text{-}SOR} \qquad (3)$$

Indeed a ΔH of reaction of *ca.* -23 kcal mol^{-1} can be calculated for reaction (1) by using heats of formation[5] and bond dissociation energies[6] available in the literature. Since S-S (74 kcal mol^{-1}) and S-O (70-80 kcal mol^{-1}) bonds have strengths comparable to that of C-S bonds (77 kcal mol^{-1}),[5] the exothermicities of reactions (2) and (3) should be similar to that of reaction (1). In the case of the addition of thiyl radicals, the kinetic requirements for the ESR detection of their spin adducts with thiones should also be satisfied since the rate constant for this process has been estimated to be greater than 4×10^5 $M^{-1}s^{-1}$.[2b]

The failure of previous investigators to detect adducts between thiones and sulphur or oxygen centred radicals is thus unexpected. We have, therefore, carried ou the reaction of three thiocarbonyl compounds, *i.e.* thiobenzophenone, $Ph_2C=S$, thiobenzoyltriphenylsilane, $Ph(Ph_3Si)C=S$,[7] and di-*tert*-butylthioketone, $^tBu_2C=S$, with a number of thiyl radicals and with $^tBuO\cdot$ inside the cavity of an ESR spectrometer, and succeeded in observing the corresponding spin adducts. We subsequently extended our study to sulphonyl, $R\dot{S}O_2$, phenylselenyl, $PhSe\cdot$, and

TABLE 1 - ESR spectral parameters

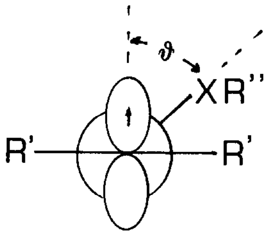
R	a_o	a_m	a_p	a(R)	g	T/K	Solv.
$Ph_2\dot{C}-SR$							
SMe	2.89	1.21	3.20	0.74(3H)	2.00323	298	B
SEt	2.86	1.20	3.17	0.89(2H), 0.16(3H)	2.00321	298	BB
$SCHMe_2$	2.87	1.20	3.18	0.68(1H), 0.20(6H)	2.00329	298	B
SCH_2Ph	2.86	1.20	3.17	0.66(2H)	2.00311	273	T
$SCMe_3$	2.89	1.20	3.22	0.24(9H)	2.00343	298	B
SPh	2.81	1.17	3.16	0.09(2H), 0.15(3H)	2.00304	298	B
SO_2Me	2.92	1.21	3.28		2.00249	296	BB
SO_2Tol	2.90	1.23	3.31		2.00250	295	BB
SePh	2.84	1.16	2.84		2.00534	298	B
OBu^t	2.77	1.19	3.12	0.24(9H)	2.00289	273	BB
$Ph(Ph_3Si)\dot{C}-SR$							
SMe	3.26	1.30	3.56	0.88(3H)	2.00403	299	BB
$SCHMe_2$	3.28	1.32	3.48	0.52(1H), 0.26(6H)	2.00403	296	BB
$SCMe_3$	3.26	1.30	3.50	0.30(9H)	2.00414	298	BB
SPh	3.22	1.27	3.40		2.00391	297	BB
SO_2Me	4.02	1.41	4.74	0.21(3H)	2.00272	295	BB
SO_2Tol	3.81	1.39	4.48		2.00279	295	BB
SePh	3.23	1.29	3.35		2.00710	297	BB
OBu^t	2.99	1.20	3.19	0.20(9H)	2.00362	295	BB
$^tBu_2\dot{C}-SR$							
SMe		0.46(18H)		1.69(3H)	2.00246	223	BB
$SCMe_3$		0.43(18H)		0.21(9H)	2.00262	263	T

Couplings in Gauss = 10^{-4} Tesla; B, Benzene; BB, ^{t}Butylbenzene; T, Toluene without success, to sulphinyl radicals, $R\dot{S}O$. The radicals were generated *in situ* by photolysis of alkyl disulphides ($RS\cdot$), di-*tert*-butylperoxide ($^{t}BuO\cdot$), phenyl diselenide ($PhSe\cdot$), methanesulphonyl chloride ($Me\dot{S}O_2$), *p*-toluenesulphonyl chloride ($MeC_6H_4\dot{S}O_2$) and methane sulphinyl chloride ($Me\dot{S}O$).

Table 1 reports the ESR spectral parameters for all the observed radicals, which generally showed fairly intense ESR spectra; in some cases the incident radiation, coming from a high pressure 1kW mercury lamp, was filtered through a $NiSO_4/CoSO_4$ aqueous solution in order to get better signal to noise ratios and to avoid rapid sample depletion. In addition to the expected couplings with the nuclei of the thionic substrates, an unambiguous means of identification of the spin adducts was provided by the hyperfine splittings due to the protons of the entering alkylthio or butoxy groups. The alkyl splittings always differed from those of the species formed by attack of the corresponding alkyl radicals on the same thiones,[1b,8,9] thus indicating that the transient radicals trapped are $RS\cdot$ or $^{t}BuO\cdot$ instead of $R\cdot$. This applies also to the $MeSO_2$ adduct to $Ph(Ph_3Si)C=S$ whose spectrum exhibits a small methyl splitting of 0.21 G. The other sulphonyl adducts, for which no couplings due to the entering group were detected, were identified on the basis of the typically low *g*-factors. Conversely, the high *g*-value of the spin adducts obtained in the reaction of the thiones with phenyl diselenide is clearly indicative of the trapping of the $PhSe\cdot$ radical. The sulphonyl radicals do not seem to add to di-*tert*-butylthioketone, since when the latter was photolyzed in the presence of methanesulphonyl chloride, $Me\dot{S}O_2$ ($g=2.0048$, $a_H(Me)=0.54$ G) was the only detectable species.

Product studies were performed for the photolytic reaction between thiobenzophenone and methyldisulphide. On irradiating at room temperature a benzene solution of 0.167 g (0.84 mmols) of $Ph_2C=S$ and 0.395 g (4.2 mmols) of MeSSMe, the blue colour turned to yellow within a few minutes. Concentration of the solution gave an oil that, by chromatography on silica gel plates with pentane, afforded methylthio(methyldithio)diphenylmethane, $MeS(MeSS)CPh_2$ (0.12 g, 50% yield,[10] m.p. 44-47°from EtOH), as the main product,[11] along with three minor compounds whose amount was too small to allow characterization. The fast consumption of thiobenzophenone and the nature of the main product suggest that the latter is formed in a radical chain reaction involving an S_H2 displacement of a $MeS\cdot$ radical from the disulphide brought about by the primary radical adduct.[12]

Some considerations about the preferred geometry of the radical adducts can be made on the basis of the *g*-factors collected in Table 1. Referring to structure (A), larger values are expected for $\vartheta = 90^{\circ}$ owing to easy delocaliza-



(A)

tion of the unpaired electron onto the sulphur atom, while for ϑ = 0° the *g*-factor should not be significantly different from that of hydrocarbon radicals, *i.e.* 2.0025.[13] The latter is clearly the case for the adducts to di-*tert*-butylthioketone, the eclipsed conformation (ϑ = 0°) being preferred because of steric hindrance.[1b] The larger *g*-values measured in the thiyl adducts of thiobenzophenone, and even more so those of thiobenzoyltriphenylsilane are instead indicative that the preferred conformation of these radicals is closer to the coplanar one. By comparison with the *g*-factors of other adducts to the same substrates, the ϑ angle can be roughly estimated to be in the range 50 to 60°.[9] On the same basis it can be inferred that the sulphonyl adducts adopt the eclipsed geometry (ϑ = 0°).

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10) Yield is lowered by losses during chromatographic isolation.

11) Analysis: found (%) C, 62.0; H, 5.6; S, 32.5; $C_{15}H_{16}S_3$ requires C, 61.6; H, 5.5; S, 32.9. NMR: $\delta_H(CDCl_3)$ 1.55 (3H, s, SCH_3), 1.78 (3H, s, $SSCH_3$), 7÷7.7 (10H, m, ArH). IR: ν_{max} 3060, 2920, 755, 720, 695. m/z: 245 ($M^+ - SCH_3$), 213 ($M^+ - SSCH_3$), 198, 165, 121.

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