The β-sulfur substituent effect in radical reactions. Chlorine-atom abstraction from alkyl 2-chloroethyl sulfides, hydrogen-atom abstraction from dialkyl sulfides and the question of possible 1,4-hydrogen-atom transfer in β-alkylthioethyl radicals

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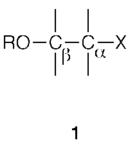
The reactions of $MeSCH_2CH_2Cl$ with the nucleophilic metalloidal radicals $Me_3N{\rightarrow}\dot{B}HBu$ and $Et_3Si^{\bullet}$ have been studied in solution between 180 and 240 K using EPR spectroscopy. With the amine-boryl radical the dominant reaction is abstraction of chlorine, while with the silyl radical S_H2 dealkylation at sulfur takes place more rapidly than the abstraction of halogen. The relative rates of abstraction of chlorine from YCH_2CH_2Cl by $Me_3N{\rightarrow}\dot{B}HBu$ or $Et_3Si^{\bullet}$ increase along the series $Y = MeCH_2 < MeO < MeS$ and the high reactivity of the 2-chloroethyl sulfide is attributed to a combination of favourable polar and enthalpic factors. In contrast, the relative reactivities of $MeSCH_2CH_3$ and $MeSCH_2CH_2SMe$ towards hydrogen-atom abstraction by the *tert*-butoxyl radical indicate that a β-MeS group slightly retards hydrogen transfer from the SCH_2 groups to this electrophilic radical. No evidence was found to support the proposed rearrangement of the β-alkylthioalkyl radicals $MeSCH_2\dot{C}H_2$ or $EtSCH_2\dot{C}H_2$ to the more stable isomeric α-alkylthioalkyl radicals $H_2\dot{C}SCH_2Me$ or $Me\dot{C}HSCH_2Me$, respectively, by an intramolecular 1,4-H-atom shift. UV photolysis of dimethyl disulfide in the presence of ethene at low temperatures affords the EPR spectra of $MeSCH_2\dot{C}H_2$ and of an α-alkylthioalkyl radical identified as $MeSCH_2CH_2S\dot{C}H_2$. The latter radical is thought to arise by addition of $MeSCH_2\dot{C}H_2$ to thioformaldehyde, itself formed as a product of disproportionation of methanethiyl radicals. A series of *ab initio* molecular orbital calculations has been carried out in support of the experimental work and the computed activation energy for the rearrangement of $MeSCH_2\dot{C}H_2$ to $H_2\dot{C}SCH_2Me$ by a 1,4-H-atom shift is very large (89.9 kJ mol^{-1}), such that this process would not be detectable in solution by EPR spectroscopy at moderate temperatures.

The influence of the β-oxygen substituent on the homolytic reactivity of the α-C–X group in molecules of the type **1** remained a subject of controversy for many years. By considering the overall rates of a number of chain reactions that involve β-oxyalkyl radicals as intermediates, Barton, Hartwig and Motherwell proposed that the β-oxygen substituent exerts a marked thermodynamic stabilising effect on such radicals and thus facilitates their formation.[1] However, there appears to be no direct evidence for a stabilising interaction of this type and the strengths of the $HOCH_2CH_2$–H and CH_3CH_2–H bonds are evidently very similar[2] (see also the calculations reported herein). More recently, Crich *et al.*[3] have concluded that, for conformationally unrestricted molecules, there is no significant β-oxygen substituent effect for the deoxygenation of alcohols (ROH) by way of their thionocarbonyl esters [ROC(=S)X], one of the types of reaction discussed in the original paper by Barton and co-workers.[1]



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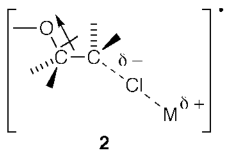

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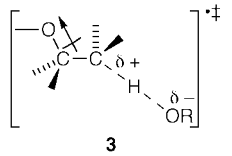

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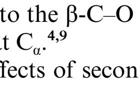
We have reported that β-alkoxy groups accelerate the abstraction of halogen from alkyl chlorides by nucleophilic metalloid-centred radicals ($M^{\bullet}$) and have attributed this to a polar effect that operates in the transition state and involves charge-transfer from $M^{\bullet}$ to the C–Cl group.[4] On the basis of *ab initio* molecular orbital calculations, it was concluded that the β-C–O bond dipole interacts electrostatically with the dipolar $C\cdots Cl\cdots M$ grouping, to stabilise the transition state for chlorine-atom abstraction. On the other hand, a β-oxygen substituent has been shown to retard abstraction of hydrogen from the α-carbon atom by electrophilic hydroxyl or alkoxyl radicals and this was similarly attributed to a polar effect that operates in the transition state.[5–8] Thus, it appears that the β-oxygen substituent effect is kinetic, rather than thermodynamic, in origin. It is primarily an electrostatic field effect and can act to either stabilise (as in **2**) or destabilise (as in **3**) the transition state, depending on the particular reaction involved.[4] For the abstraction of chlorine by nucleophilic metalloidal radicals, we have suggested that the transition state may also be stabilised by anomeric delocalisation of negative charge from the reaction centre into the β-C–O σ* orbital when a π donor substituent is present at C_{α}.[4,9]

The effects of second-row substituents are often appreciably different from those of their first-row congeners. For example, while β-alkoxyethyl radicals adopt the 'staggered' conformation **4**,[4,10] β-alkylthioethyl radicals prefer the 'eclipsed' conformation **5**,[10] because the stabilising hyperconjugative interaction between the unpaired electron and the β-C–Y σ bond in



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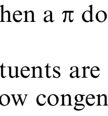

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$$RCH_2SCH_2\dot{C}H_2 \longrightarrow R\dot{C}HSCH_2CH_3 \qquad (1)$$

Table 1 EPR parameters for radicals in cyclopropane solvent

			Hyperfine splittings[a,b]/G		
Radical	T/K	g-Factor[a]	$a(H_\alpha)$	$a(H_\beta)$	Others
$MeSCH_2\dot{C}H_2$ **10**	200	2.0025	21.60 (2)	14.50[c] (2)	—
$MeOCH_2\dot{C}H_2$ **11**	200	2.0026	22.00 (2)	32.50[d] (2)	—
$ClCH_2\dot{C}H_2$ **12**	200	2.0021	21.70 (2)	10.95[c] (2)	18.05 (^{35}Cl), 15.05 (^{37}Cl)
$MeCH_2S\dot{C}H_2$ **15**	163	2.0048	16.50 (1), 17.38 (1)	—	2.06 (2 H_γ)
$MeCH_2S\dot{C}H_2$ **15**	240	2.0048	16.06 (1), 17.19 (1)	—	2.19 (2 H_γ)
$MeSCH_2CH_2S\dot{C}H_2$ **17**[e]	163	2.0048	16.52 (1), 17.59 (1)	—	1.53 (2 H_γ)
$MeSCH_2CH_2S\dot{C}H_2$ **17**[f,g]	163	2.0048	16.53 (1), 17.58 (1)	—	1.52 (2 H_γ)
$MeSCH_2CH_2S\dot{C}H_2$ **17**[f]	240	2.0048	16.00 (1), 17.38 (1)	—	1.75 (2 H_γ)
$EtSCH_2\dot{C}H_2$ **19**	200	2.0025	21.56 (2)	15.06[c] (2)	—
$Me\dot{C}HSCH_2Me$ **20**[h]	200	2.0045	17.06 (1)	20.38 (3)	1.41 (2 H_γ)
$MeS\dot{C}HCH_2SMe$ **23**[h]	240	2.0044	16.33 (1)	11.38[c] (2)	2.67 (3 H_γ), 0.45 (3 H_δ)
$MeS\dot{C}HCH_3$ **25**[h]	240	2.0044	16.88 (1)	20.35 (3)	2.47 (3 H_γ)

[a] g-Factors ±0.00005, hyperfine splittings ±0.05 G. [b] Numbers of nuclei indicated in parentheses. [c] Increases with increasing temperature. [d] Decreases with increasing temperature. [e] Likely assignment; detected alongside **10** during photolysis of MeSSMe in the presence of ethene (see text). [f] Authentic radical generated by hydrogen-atom abstraction from **18**. [g] Cyclopropane–dichloromethane solvent (5:2 v/v); the solubility of 2,5-dithiahexane in cyclopropane is poor at low temperature. [h] Presumed, on steric grounds, to be the E-rotamers with respect to the C_α–S bond.

$YCH_2\dot{C}H_2$ increases in the order $Y = RO < H < RS$.† It has also been proposed, on the basis of EPR evidence, that β-alkylthioalkyl radicals rearrange very rapidly at low temperature by a 1,4-hydrogen-atom transfer to give the thermodynamically more stable isomeric α-alkylthioalkyl radicals [*e.g.* eqn. (1)].[11,12] However, stereoelectronic considerations lead to the conclusion that stabilisation of the incipient α-alkylthioalkyl radical, by delocalisation of the unpaired electron onto sulfur, will be minimal in the transition state for this rearrangement. Both experimental[13] and theoretical[14] results indicate that high activation energies are associated with the corresponding rearrangements of simple alkyl radicals in which the sulfur atom is replaced by a methylene group.

Other aspects of neighbouring-group participation by divalent sulfur substituents in homolytic processes have been investigated from time to time,[15,16] but there is little quantitative information available concerning the effects of β-RS substituents on free-radical reactions. In the present paper we report an EPR spectroscopic study of the effects of a β-alkylthio group on the reactions of alkyl chlorides with metalloidal radicals and on the reactions of *tert*-butoxyl radicals with dialkyl sulfides, together with experimental and theoretical investigations of the proposed rearrangement of β-alkylthioalkyl radicals by an intramolecular 1,4-H-atom shift.

Results

Reactions of amine-boryl and silyl radicals with alkyl chlorides

EPR spectroscopy was used to monitor the radicals present during continuous UV irradiation of liquid samples positioned in the microwave cavity of the spectrometer.[17] Photolysis of di-*tert*-butyl peroxide (DTBP) provides a clean source of *tert*-butoxyl radicals [eqn. (2)] and these may be converted to metalloidal radicals $M^\bullet$ by their rapid hydrogen-atom abstraction reactions with trimethylamine-butylborane (TMBB; $Me_3N\rightarrow BH_2Bu$) or triethylsilane [eqn. (3)]. The highly nucleophilic trimethylamine-butylboryl radical $Me_3N\rightarrow\dot{B}HBu$ abstracts halogen atoms rapidly from alkyl chlorides or bromides and EPR spectra of $R^\bullet$ can be recorded at low temperatures during UV photolysis of DTBP in the presence of TMBB and RCl or RBr.[18] Even the unactivated primary alkyl chloride 1-chlorobutane **6** yields a high quality spectrum of the butyl radical **9**,

$$Bu^tOOBu^t \xrightarrow{h\nu} 2\,Bu^tO^\bullet \qquad (2)$$

$$Bu^tO^\bullet + MH \longrightarrow M^\bullet + Bu^tOH \qquad (3)$$

$$M^\bullet + R^1Cl \xrightarrow{k_1} MCl + R^{1\bullet} \qquad (4)$$

$$M^\bullet + R^2Cl \xrightarrow{k_2} MCl + R^{2\bullet} \qquad (5)$$

$MeCH_2CH_2CH_2Cl$ **6**

$MeSCH_2CH_2Cl$ **7**

$MeOCH_2CH_2Cl$ **8**

$MeCH_2CH_2\dot{C}H_2$ **9**

$MeSCH_2\dot{C}H_2$ **10**

$MeOCH_2\dot{C}H_2$ **11**

while triethylsilyl radicals abstract chlorine much more slowly from such halides.[18,19]

UV irradiation of a cyclopropane solution containing 2-chloroethyl methyl sulfide **7** (1–1.5 mol dm^{-3}), TMBB (*ca.* 1 mol dm^{-3}) and DTBP (*ca.* 15% v/v) afforded EPR spectra of the β-methylthioethyl radical **10** as shown in Fig. 1; the spectroscopic parameters for all the radicals investigated in this work are collected in Table 1. Although the complex multi-line spectrum of the β-chloroethyl radical[20] was not identifiable in these experiments, a very weak spectrum of the methyl radical was observed alongside that of **10** (see Fig. 1), indicating that the amine-boryl radical brings about an S_H2 dealkylation at sulfur to a very minor extent in competition with abstraction of chlorine from **7**. No EPR spectrum was observed during UV irradiation of **7** alone in cyclopropane.

Relative reactivities of pairs of chlorides R^1Cl and R^2Cl towards halogen abstraction by $Me_3N\rightarrow\dot{B}HBu$ were determined in competition experiments, as described previously.[4,21] UV irradiation of solutions containing DTBP (*ca.* 15% v/v), TMBB (*ca.* 1 mol dm^{-3}) and the two chlorides (total concentration *ca.* 1.5 mol dm^{-3}) afforded overlapping EPR spectra of $R^{1\bullet}$ and $R^{2\bullet}$ [eqns. (4) and (5)], from which the values of $[R^{1\bullet}]/[R^{2\bullet}]$ were obtained by double integration and confirmed by computer simulation.[21,‡] Provided that $R^{1\bullet}$ and $R^{2\bullet}$ are removed only by radical-radical reactions which have effectively equal diffusion-controlled rate constants, an assumption that should be valid for the unhindered primary alkyl radicals studied in this work, the value of k_1/k_2 will be given by eqn. (6).[22]

$$k_1/k_2 = [R^{1\bullet}][R^2Cl]/[R^{2\bullet}][R^1Cl] \qquad (6)$$

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† For simplicity,the radical centres in **4** and **5** are shown as planar, while in the equilibrium structures they are slightly pyramidal (see Fig. 5).

‡ To take account of the depletion of reagents during UV irradiation, it was sometimes necessary to extrapolate the value of $[R^{1\bullet}]/[R^{2\bullet}]$ to zero photolysis time. Corrections for chemically-induced dynamic electron polarisation effects[4] were not necessary in these experiments.

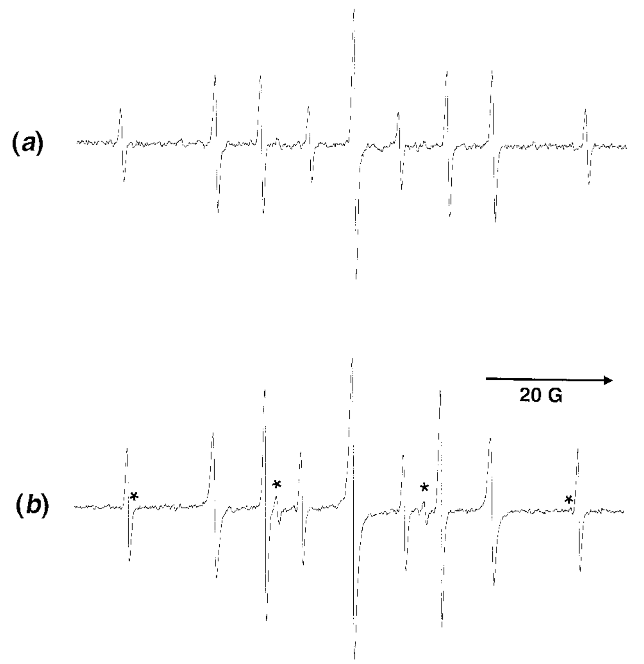


Fig. 1 EPR spectra of the β-methylthioethyl radical **10** produced by chlorine-atom abstraction from the chloroethyl sulfide **7** in cyclopropane at (a) 200 K and (b) at 163 K. The positions of the lines from the methyl radical are marked with asterisks.

Table 2 Relative rates of chlorine-atom abstraction from alkyl chlorides by metalloidal radicals in cyclopropane

Chloride	$k_{rel.}$[a]($Me_3N\rightarrow\dot{B}HBu$) at 200 K	$k_{rel.}$[a]($Et_3Si^\bullet$) at 180 K
$MeCH_2CH_2CH_2Cl$ **6**	0.17 (0.18)[b]	(0.67)[b]
$MeSCH_2CH_2Cl$ **7**	3.1[c]	5.7
$MeOCH_2CH_2Cl$ **8**	1	1

[a] Estimated error ±5%. [b] Values reported previously in ref. 4. [c] By direct competition, **7** was found to be 16 ± 2 times more reactive than **6**.

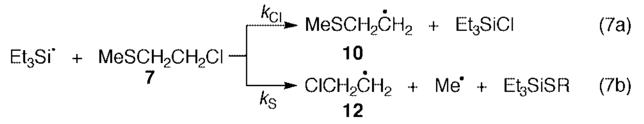
β-Alkylthioalkyl radicals undergo β-scission relatively readily (*i.e.* the addition of alkylthiyl radicals to alkenes is easily reversible[23]) and the possibility that cleavage of **10** to give $MeS^\bullet$ and ethene might occur under the conditions of the EPR experiments was therefore investigated. This process would provide another route for the removal of **10** and would lead to an apparent reactivity of **7** towards chlorine abstraction that is too low. At 180 K, the value of k_1/k_2 derived from eqn. (6) for the competition between **7** and 2-chloroethyl methyl ether **8** was not significantly influenced by the presence of ethene (*ca.* 2.0 mol dm^{-3}).§ However, at 200 K in the presence of ethene (*ca.* 2.0 mol dm^{-3}), the apparent relative reactivity of **7** was slightly greater (by 6–10%, just outside the experimental error) than in its absence, while at higher temperatures the increase in the apparent reactivity of **7** observed in the presence of ethene was significantly greater (by up to *ca.* 30% at 240 K), although no further change was found when the ethene concentration was increased to *ca.* 5.5 mol dm^{-3}. We conclude that fragmentation of **10** does indeed influence the relative concentration of the radical **10** to a small extent at 200 K and above, but that ethene at a concentration of *ca.* 2.0 mol dm^{-3} is sufficient to suppress the reversible β-scission to a point where its effect on the kinetic measurements becomes negligible.

Alkyl bromides are much more reactive than alkyl chlorides towards halogen abstraction by $Me_3N\rightarrow\dot{B}HBu$.[18] To confirm that chlorine abstraction from **7** by alkyl radicals is unimportant under the EPR conditions, a cyclopropane solution containing DTBP, TMBB, 1-bromobutane (0.6 mol dm^{-3}) and **7** (0.8 mol dm^{-3}) was UV irradiated at temperatures up to 240 K. Only the EPR spectrum of the butyl radical was observed, showing that no detectable abstraction of chlorine from **7** occurs under the reaction conditions. It has been shown previously that similar abstraction of halogen from 2-chloroethyl methyl ether by alkyl radicals can also be neglected.[4]

The relative reactivities of the chlorides **6**–**8** towards $Me_3N\rightarrow\dot{B}HBu$ were determined at 200 K in cyclopropane in the presence of ethene (*ca.* 2.0 mol dm^{-3}) and the values of k_1/k_2 obtained using eqn. (6) were independent of the halide concentration ratio, when this was varied by a factor of two. At 200 K, the chloroethyl sulfide **7** is 3.1 times more reactive towards halogen-atom abstraction by the amine-boryl radical than the chloroethyl ether **8**, which in turn is 5.9 times more reactive than 1-chlorobutane **6**; the results are summarised in Table 2.

The relative Arrhenius activation parameters for chlorine abstraction from **7** and **8** were determined from measurements between 180 and 240 K in the presence of ethene (2.0 mol dm^{-3}); the values obtained for [E_a(**8**) − E_a(**7**)] and [A(**7**)/A(**8**)] were 1.9 kJ mol^{-1} and 1.0, respectively. We have reported previously[4] that [E_a(**6**) − E_a(**8**)] and [A(**8**)/A(**6**)] are 3.2 kJ mol^{-1} and 0.82, respectively, and hence the activation energy difference [E_a(**6**) − E_a(**7**)] is 5.1 kJ mol^{-1} and the A-factor ratio [A(**7**)/A(**6**)] is 0.82.

The reaction of triethylsilyl radicals with the chloroethyl sulfide **7** was studied in cyclopropane alone as solvent and a high concentration of triethylsilane was used to ensure that attack on **7** by the *tert*-butoxyl radical would be minimised. Thus, UV irradiation of a solution containing **7** (*ca.* 1.0 mol dm^{-3}), Et_3SiH (40% v/v) and DTBP (15% v/v) at 200 K afforded the EPR spectrum shown in Fig. 2, which consists of overlapping signals from **10** and the β-chloroethyl radical **12**; a very weak signal from the methyl radical is also present, but the complexity of the spectrum makes quantitative determination of its relative concentration difficult. Triethylsilyl radicals are known to displace alkyl radicals readily from dialkyl sulfides[24] and evidently S_H2 attack at sulfur is significantly faster than abstraction of chlorine for their reaction with **7** [eqns. (7a) and (7b)].



Careful double integration and simulation of the composite spectrum obtained at 180 K, when β-scission of **10** can be safely neglected, showed that [**10**]/{[**12**] + [$Me^\bullet$]} (=k_{Cl}/k_S) is *ca.* 0.26; the value of [**12**]/[$Me^\bullet$] is *ca.* 12.5.¶ Although S_H2 dealkylation of **7** by attack of $Me_3N\rightarrow\dot{B}HBu$ at sulfur does take place to a very minor extent, only the methyl radical was detectable and thus [**12**]/[$Me^\bullet$] is evidently much smaller in this case than for attack at sulfur by $Et_3Si^\bullet$ [reaction (7b)]. Inclusion of the chloroethyl ether **8** in the reaction mixture enabled the relative reactivities of **7** and **8** towards chlorine-atom abstraction by $Et_3Si^\bullet$ to be estimated and the value of k_{Cl} for **7** is 5.7 times greater than that for **8**. Combining our present and previous[4] results, the relative rates of chlorine-atom abstraction by the triethylsilyl radical from **6**, **7** and **8** are 0.67 : 5.7 : 1 at 180 K. At the same temperature the relative reactivities of **6**, **7** and **8** towards chlorine-atom abstraction by $Me_3N\rightarrow\dot{B}HBu$ are 0.14 : 3.6 : 1.

Investigation of the proposed 1,4-hydrogen-atom transfer reaction

In 1971 Krusic and Kochi reported that a weak EPR spectrum

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§ No addition of **10** or of **11** to ethene was detectable under these conditions.

¶ The ^{35}Cl- and ^{37}Cl-containing variants of **12** are present in natural abundance (75.8 : 24.2).

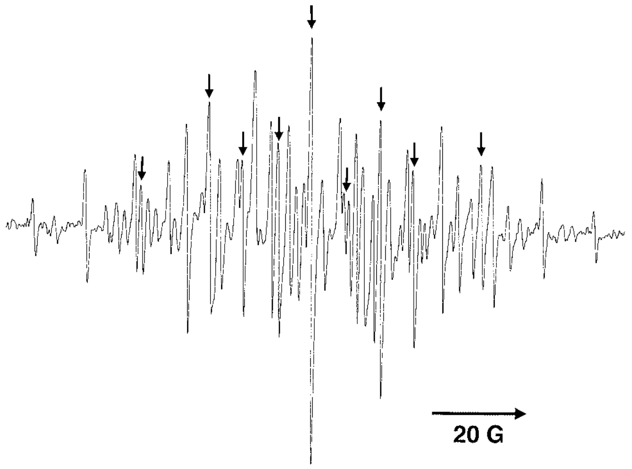


Fig. 2 EPR spectrum obtained from the reaction of triethylsilyl radicals with the chloroethyl sulfide **7** at 200 K in cyclopropane. The arrows indicate the positions of the lines from the β-methylthioethyl radical **10**; the remaining visible lines are from the β-chloroethyl radical.

of the ethoxymethyl radical **13** was apparent alongside that of the β-methoxyethyl radical **11** when the latter was generated by UV photolysis of the diacyl peroxide **14**.[10] These authors considered the possibility that **13** might be formed from **11** by an intramolecular 1,4-H-atom migration, but also pointed out that it could be produced as a result of induced decomposition of the peroxide **14**. In our earlier work on the nature of the β-oxygen substituent effect[4] we found no evidence for the rearrangement of **11** when this radical was generated by halogen-atom abstraction from $MeOCH_2CH_2Hal$ and we assumed, therefore, that the second route proposed by Krusic and Kochi accounted for the detection of **13** in their experiments.

$$\underset{\mathbf{13}}{{}^{\bullet}CH_2OCH_2CH_3} \qquad \underset{\mathbf{14}}{[MeOCH_2CH_2C(O)O]_2}$$

However, the published evidence for the analogous 1,4-H-atom migration in β-alkylthioalkyl radicals appeared to be much stronger,[11,12] and we expected to detect the ethylthiomethyl radical **15** together with the β-methylthioethyl radical **10** as the product of the rearrangement process shown in eqn. (8). In the event, this proved not to be the case and so we were led to re-examine the evidence for the occurrence of reaction (8) and for similar 1,4-rearrangements of other β-alkylthioalkyl radicals.

$$\underset{\mathbf{10}}{CH_3SCH_2\dot{C}H_2} \longrightarrow \underset{\mathbf{15}}{{}^{\bullet}CH_2SCH_2CH_3} \qquad (8)$$

$$MeSSMe \xrightarrow{h\nu} 2\ MeS^{\bullet} \qquad (9)$$

$$MeS^{\bullet} + CH_2{=}CH_2 \longrightarrow MeSCH_2\dot{C}H_2 \qquad (10)$$

Casarini *et al.*[11] reported that UV photolysis of dimethyl disulfide in a mixture of ethene and cyclopropane as solvent affords the EPR spectrum of **10** [eqns. (9) and (10)], along with that of another radical presumed to be **15**. The spectrum ascribed to **15** was relatively *stronger* at lower temperatures and this was explained on the basis of the reversibility of the addition process (10), although we would question the validity of the arguments that were advanced in support of this hypothesis. It was stated by Casarini *et al.* that their published spectrum had been obtained at 133 K. However, we have found that the spectrum of **10** exhibits temperature-dependent line-shape effects, such that the lines associated with $M_I(2\ H_\beta) = 0$ broaden selectively below *ca.* 190 K (see Fig. 1b), presumably as a consequence of restricted rotation about the S–CH_2 bond or torsional oscillation about the C_α–C_β bond. Close examination of their published spectrum indicates that it was probably recorded at a temperature appreciably above 133 K, perhaps as a result of neglecting to account for the heating effect of irradiating the sample. Repetition at 163 K of the experiment reported by Casarini *et al.* afforded the EPR spectrum shown in Fig. 3a, which is quite similar to that reproduced in ref. 11. We confirmed the report[11] that at lower temperatures than this the spectrum ascribed to the 'rearranged' radical was relatively stronger. Conversely, at temperatures above *ca.* 220 K the spectrum of this second radical was almost undetectable. Significantly, a small amount of a pale yellow solid came out of solution during UV irradiation of these samples. Because of the very small quantity of this solid formed in each experiment, its amorphous nature (it gave no powder X-ray diffraction pattern) and purification difficulties, it was not possible to identify this material conclusively although, based on its appearance, we believe it to be poly(thioformaldehyde).[25]

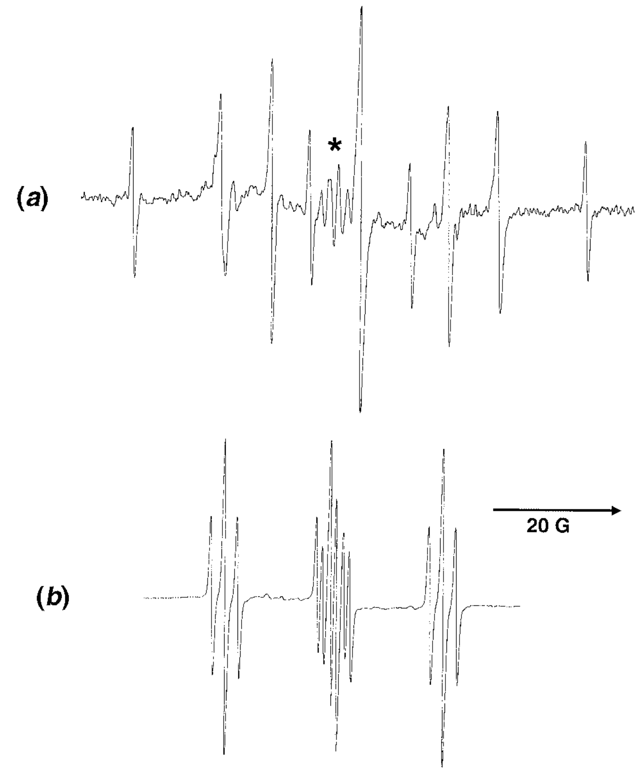


Fig. 3 EPR spectra at 163 K in cyclopropane (a) recorded during the photolysis of dimethyl disulfide in the presence of ethene and, (b) of the ethylthiomethyl radical **15** produced by chlorine-atom abstraction from the chloromethyl ethyl sulfide **16**. The asterisk in (a) indicates the central six-line multiplet of the spectrum assigned to the radical **17**, although the splittings between lines 2 and 3 of this multiplet and between lines 4 and 5 are barely discernible [*cf.* radical **15** in (b)].

The authentic ethylthiomethyl radical **15** was generated independently by abstraction of chlorine from chloromethyl ethyl sulfide[26] **16** using either $Me_3N{\rightarrow}\dot{B}HBu$ or $Et_3Si^{\bullet}$. Thus, UV irradiation of a cyclopropane solution containing **16** (1.1 mol dm^{-3}), TMBB (0.9 mol dm^{-3}) and DTBP (15% v/v) yielded the EPR spectrum shown in Fig. 3b and comparison with Fig. 3a shows clearly that, although the spectrum of **15** is *similar* to that of the weaker signal in Fig. 3a, it is not the same (see Table 1). In particular, the values of $a(2\ H_\gamma)$ are appreciably different for the two radicals. When dimethyl disulfide was photolysed in the presence of ethene, TMBB (0.8 mol dm^{-3}) and 2,2,5,5-tetramethyltetrahydrofuran (15% v/v, to mimic the solvent properties of DTBP), a spectrum essentially indistinguishable from that shown in Fig. 3a was obtained, confirming that a medium effect is not responsible for the differences between the EPR parameters of **15** and those of the radical present along-

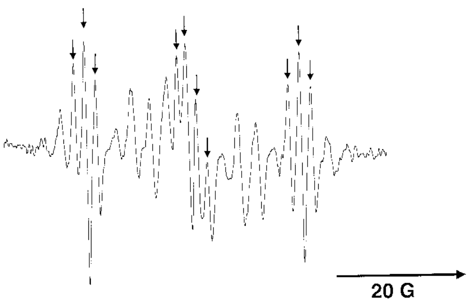


Fig. 4 EPR spectrum recorded during photolysis of DTBP in the presence of 2,5-dithiahexane in cyclopropane at 240 K. The lines indicated with arrows are from the radical **17**, the remaining lines (some of which are obscured) are from the isomeric radical **23**. Under conditions of high resolution, splitting from the δ-CH_3 protons was detected on the wing lines.

side **10** in Fig. 3a. We conclude that the latter is not **15** and propose that it is the (2-methylthioethyl)thiomethyl radical **17**, the spectrum of which would be expected to be very similar to that of **15**. Strong support for this assignment was obtained by generating the authentic radical **17** by abstraction of hydrogen from 2,5-dithiahexane **18**, using photochemically-produced *tert*-butoxyl radicals,[27] and the EPR parameters of **17** were indistinguishable from those of the 'rearranged' radical (see Table 1 and Fig. 4). In no experiment did we ever detect **15** or **17** alongside **10** when the latter was generated by chlorine-atom abstraction from the chloroethyl sulfide **7**.

Casarini *et al.* also reported that when diethyl disulfide was photolysed in the presence of ethene a spectrum which they ascribed to the 'rearranged' radical **20** was apparent alongside that of the β-ethylthioethyl radical **19**. It was further reported that signals from *both* these radicals were detected when **19** was generated independently by abstraction of bromine from 2-bromoethyl ethyl sulfide **21** by trimethylstannyl radicals. However, in our hands, UV irradiation of cyclopropane solutions containing **21** and $Me_3SnSnMe_3$, with or without added DTBP, did not afford the spectrum of **20** (or of a radical with similar EPR parameters) in addition to that of **19**, which was relatively strong in the presence of DTBP. Authentic **20** was generated by photolysis of DTBP in the presence of diethyl sulfide, as described previously;[28] competitive abstraction from the methyl groups was not observed at 200 K ([**20**]/[**19**] ≥ 15).‖

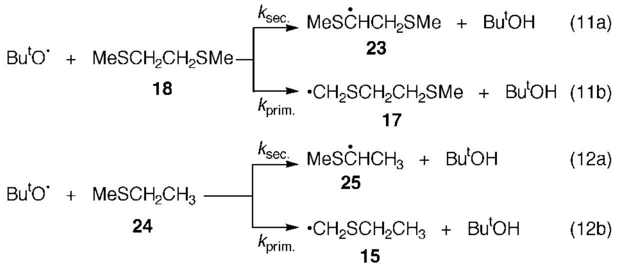
$ClCH_2SCH_2CH_3$ **16** $MeSCH_2CH_2S\dot{C}H_2$ **17** $MeSCH_2CH_2SMe$ **18**

$MeCH_2SCH_2\dot{C}H_2$ **19** $Me\dot{C}HSCH_2CH_3$ **20** $MeCH_2SCH_2CH_2Hal$ **21** Hal = Br, **22** Hal = Cl

When we repeated the photolysis of diethyl disulfide in the presence of ethene, as described by Casarini *et al.*,[11] we could not detect the spectrum of the rearranged radical **20** alongside that of the primary adduct **19**, although some weak lines which might derive from $EtSCH_2CH_2S\dot{C}HMe$, were indeed present.** In any event, when DTBP was photolysed in the presence of 2-chloroethyl ethyl sulfide **22** and TMBB between 180 and 240 K, in experiments similar to those carried out with the methyl analogue **7**, no trace of the radical **20** or of a similar alkylthiomethyl radical could be detected alongside the radical **19**.

Reactions of *tert*-butoxyl radicals with dialkyl sulfides

We were intrigued by the report of Griller *et al.*[27] that UV irradiation of a solution of 2,5-dithiahexane **18** in neat DTBP as solvent at 240 K gave rise *only* to the EPR spectrum of the radical **17** and that the isomeric radical **23**, which would be produced by abstraction of hydrogen from the SCH_2 groups of **18** [see eqn. (11b)], was not detected. It was suggested that rapid β-scission of **23**, to give MeS• and methyl vinyl sulfide, might account for this surprising observation. However, when we repeated the experiment described by Griller *et al.*, the EPR spectrum of **23** was clearly evident alongside that of **17** and the appearance of the spectrum was unaffected when less DTBP (15% v/v) was used together with cyclopropane as a solvent (see Fig. 4). However, *some* loss of **23** by β-scission would be expected under these conditions and, indeed, in the additional presence of ethene (2.0 mol dm^{-3}) a very weak EPR signal from $MeSCH_2\dot{C}H_2$ **10** was apparent alongside the spectra of **17** and **23**. Ethene at this concentration should be sufficient to trap all the methanethiyl radicals produced by fragmentation of **23** and thus the concentration of **10** may be used as a quantitative measure of the amount of **23** lost by β-scission. At 240 K the concentrations [**17**], [**23**] and [**10**] were in the ratio 34:60:6 and the rate constant ratio $k_{sec.}/k_{prim.}$, taken as equal to {[**23**] + [**10**]}/[**17**], is 1.9 ± 0.2.



For comparison, we examined the reaction of *tert*-butoxyl radicals with ethyl methyl sulfide **24** [eqn. (12)] under the same conditions in cyclopropane–ethene at 240 K and the corresponding value of $k_{sec.}/k_{prim.}$, taken as equal to [**25**]/[**15**], is 3.0 ± 0.2. Assuming that the α-alkylthioalkyl radicals are produced by direct transfer of hydrogen from the CH groups to the *tert*-butoxyl radical and that the steric effect of the second methylthio group in **18** is negligible, these results indicate that a β-MeS group slightly retards hydrogen-atom abstraction from C_α by $Bu^tO^\bullet$.

Molecular orbital calculations

To aid the interpretation of the experimental results, a number of *ab initio* molecular calculations were carried out, using the GAUSSIAN 94 and 98 packages of programs.[29] In essence, the G2(MP2) method of Pople and co-workers[30] was used since this has been shown to give reliable enthalpy changes for a wide variety of organic reactions. Geometries were first optimised at the Hartree–Fock level using the gradient method, in conjunction with the 6-31G(d,p) basis set, usually without any symmetry constraints. Spin-restricted calculations were performed for closed-shell molecules and spin-unrestricted calculations for radicals; the values of $\langle S^2 \rangle$ were in the range 0.75–0.79 for the open-shell species (the highest value was for the transition state **27**). The set of normal harmonic frequencies was computed for each structure, first in order to confirm it as a local minimum or as a transition state and then, after scaling by a factor of 0.893,[30] to obtain the zero-point vibrational energy (ZPVE) and thermal contribution ($H_{298} - H_0$) to the enthalpy at 298.15 K. Geometries were then re-optimised including electron correlation using Møller–Plesset perturbation theory taken to second-order and including the core electrons [(U)MP2(full)/6-31G(d,p) level]. Single-point calculations were next carried out for each structure at the QCISD(T)/6-311G(d,p) level [which also gives the energy at the (U)MP2(frozen core)/6-311G(d,p) level] and at the (U)MP2(frozen core)/6-311+G(3df,2p) level.

‖ However, the ethyl radical, presumably arising from attack by $Bu^tO^\bullet$ at sulfur,[28c] was detected in very low concentration.

** This radical would be formed by addition of **19** to thioacetaldehyde.

Table 3 Energies and enthalpies obtained from *ab initio* calculations

Molecule	Electronic energy/Hartree[a] (U)MP2/ 6-31G(d,p)[b]	QCISD(T)/ 6-311G(d,p)	ΔMP2	QCISD(T)/ 6-311+G(3df,2p)	ZPVE[c]/ kJ mol^{-1}	E_0/ Hartree	$H_{298} - H_0$[c,d]/ kJ mol^{-1}	H_{298}/ Hartree
$CH_3SCH_2CH_3$ **24-a**	−516.313089	−516.502606	−0.122035	−516.624641	263.3	−516.524355	19.0	−516.517119
$CH_3SCH_2CH_3$ **24-g**	−516.313074	−516.503026	−0.121797	−516.624823	263.3	−516.524537	18.8	−516.517377
$CH_3SCH_2\dot{C}H_2$ **10-a**	−515.653602	−515.833856	−0.120086	−515.953942	225.8	−515.867939	19.8	−515.860398
$CH_3SCH_2\dot{C}H_2$ **10-g**	−515.654569	−515.835217	−0.120214	−515.955431	225.8	−515.869428	19.6	−515.861963
$H_2\dot{C}SCH_2CH_3$ **15-a**	−515.662221	−515.843848	−0.122243	−515.966091	227.1	−515.879593	19.3	−515.872242
$H_2\dot{C}SCH_2CH_3$ **15-g**	−515.663118	−515.845145	−0.121672	−515.966817	227.3	−515.880243	19.0	−515.873006
Transition state **27**	−515.612007	−515.798155	−0.119644	−515.917799	218.2[e]	−515.834691	15.8[e]	−515.828673
$CH_3SCH_2\overset{+}{C}H_2$ (*anti*)[f]	—	−515.524444	−0.116944	−515.641388	—	—	—	—
$CH_3SCH_2\overset{+}{C}H_2$ (*gauche*)[f]	—	−515.541118	−0.116890	−515.658008	—	—	—	—
Thiiranium ion **28**	−515.448484	−515.617534	−0.118033	−515.735567	237.7	−515.645032	16.6	−515.638709
$H_2\overset{+}{C}SCH_2CH_3$ (*anti*)[f]	—	−515.595276	−0.114779	−515.710055	—	—	—	—
$H_2\overset{+}{C}SCH_2CH_3$ (*gauche*)[f]	—	−515.595480	−0.114562	−515.710042	—	—	—	—
Cation **29**	−515.433805	−515.607734	−0.115172	−515.722906	234.9	−515.633437	17.8	−515.626658
$CH_3OCH_2CH_3$ **26-a**	−193.691477	−193.886120	−0.125089	−194.011209	273.3	−193.907115	17.3	−193.900525
$CH_3OCH_2CH_3$ **26-g**	−193.689264	−193.884125	−0.125041	−194.009166	273.3	−193.905072	17.4	−193.898444
$CH_3OCH_2\dot{C}H_2$ **11-a**	−193.029267	−193.214176	−0.123771	−193.337947	234.8	−193.248516	18.3	−193.241546
$CH_3OCH_2\dot{C}H_2$ **11-g**	−193.029498	−193.214439	−0.123175	−193.337614	235.8	−193.247803	17.9	−193.240985
CH_3CH_3	−79.503969	−79.615778	−0.049366	−79.665144	187.0	−79.593919	11.8	−79.589425
$CH_3\dot{C}H_2$	−78.844664	−78.946626	−0.047864	−78.994490	148.5	−78.937929	13.0	−78.932978
$CH_3\overset{+}{C}H_2$[f]	—	−78.636777	−0.043761	−78.680538	—	—	—	—
Bridged ethyl cation[g]	−78.561449	−78.654706	−0.045227	−78.699933	151.1	−78.642382	12.0	−78.637811

[a] 1 Hartree = 2625.5 kJ mol^{-1}. [b] Geometrically-optimised structures. [c] To obtain these values, frequencies were scaled by a factor of 0.893 to account for their overestimation at this level of theory (see ref. 30). [d] Low frequencies (<500 cm^{-1}) were treated as molecular vibrations, rather than internal rotations. [e] One negative vibrational frequency, ignored in the calculation. [f] At the equilibrium geometry of the corresponding radical. [g] Relaxed ethyl cation (see ref. 34).

Table 4 Selected geometrical parameters for structures optimised at the (U)MP2(full)/6-31G(d,p) level

Molecule	Bond lengths/Å, bond angles/° and dihedral angles/°
$CH_3SCH_2CH_3$ **24-a**[a]	1.805 (Me–S), 1.812 (S–CH_2), 1.522 (CC), 110.0 (CCS), 98.8 (CSC)
$CH_3SCH_2CH_3$ **24-g**	1.806 (Me–S), 1.812 (S–CH_2), 1.522 (CC), 114.6 (CCS), 99.8 (CSC), 68.9 (CSCC)
$CH_3SCH_2\dot{C}H_2$ **10-a**[a]	1.807 (Me–S), 1.833 (S–CH_2), 1.483 (CC), 110.4 (CCS), 98.4 (CSC), ±82.5 (SCCH)
$CH_3SCH_2\dot{C}H_2$ **10-g**	1.810 (Me–S), 1.835 (S–CH_2), 1.491 (CC), 114.5 (CCS), 101.0 (CSC), 65.4 (CSCC), −94.8 ($SCCH_{cis}$), 69.9 ($SCCH_{trans}$)
$H_2\dot{C}SCH_2CH_3$ **15-a**	1.522 (CC), 1.815 (Et–S), 1.717 (S–$\dot{C}H_2$), 110.0 (CCS), 100.6 (CSC), 26.4 ($CSCH_{cis}$), −175.5 ($CSCH_{trans}$)
$H_2\dot{C}SCH_2CH_3$ **15-g**	1.521 (CC), 1.814 (Et–S), 1.717 (S–$\dot{C}H_2$), 113.5 (CCS), 100.5 (CSC), 68.8 (CCSC), 29.3 ($CSCH_{cis}$), −173.6 ($CSCH_{trans}$)
Transition state **27**[b]	1.841 (S–CH_2), 1.784 (S–CH_2H*), 1.347 (SCH_2–H*), 1.341 (CH_2CH_2–H*), 91.9 (CSC), 95.8 (SCH*), 138.2 (CH*C), 96.6 (H*CC), 106.0 (CCS)
Thiiranium ion **28**[a]	1.810 (Me–S), 1.834 (SC), 1.471 (CC), 102.9 (MeSC), 47.3 (H_2CSCH_2), 66.4 (SCC)
Cation **29**	1.525 (CC), 1.821 (Et–S), 1.613 (S–$\overset{+}{C}H_2$), 109.8 (CCS), 105.7 (CSC), 120.7 (CCSC), 1.0 ($CSCH_{cis}$), −178.9 ($CSCH_{trans}$)
$CH_3OCH_2CH_3$ **26-a**[a]	1.414 (Me–O), 1.419 (O–CH_2), 1.512 (CC), 107.8 (CCO), 111.5 (COC)
$CH_3OCH_2CH_3$ **26-g**	1.416 (Me–O), 1.422 (O–CH_2), 1.520 (CC), 113.3 (CCO), 113.0 (COC), 73.9 (COCC)
$CH_3OCH_2\dot{C}H_2$ **11-a**	1.415 (Me–O), 1.419 (O–CH_2), 1.483 (CC), 108.5 (CCO), 111.4 (COC), −27.6 ($OCCH_{cis}$), 166.4 ($OCCH_{trans}$)
$CH_3OCH_2\dot{C}H_2$ **11-g**	1.418 (Me–O), 1.422 (O–CH_2), 1.489 (CC), 112.9 (CCO), 111.9 (COC), 70.3 (COCC), 35.4 ($OCCH_{cis}$), −160.9 ($OCCH_{trans}$)

[a] Effective C_s symmetry, although the geometry was optimised without symmetry constraints. [b] H* is the hydrogen atom being transferred.

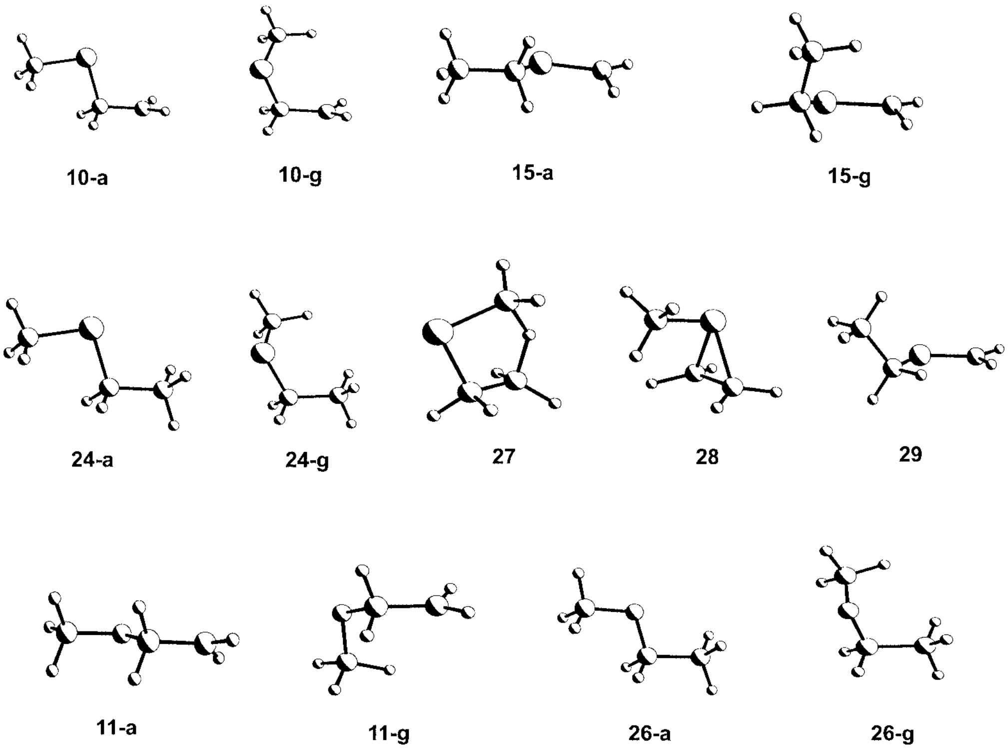


Fig. 5 Computed structures obtained from molecular orbital calculations.

Combination of these results, according to eqns. (13) and (14),

$$E[\text{QCISD(T)/6-311+G(3df,2p)}] \approx E[\text{QCISD(T)/6-311G(d,p)}] + \Delta\text{MP2} \quad (13)$$

$$\Delta\text{MP2} = E[\text{(U)MP2/6-311+G(3df,2p)}] - E[\text{(U)MP2/6-311G(d,p)}] \quad (14)$$

gives the energy effectively at the QCISD(T)/6-311+(3df,2p) level.[30] The total energy at 0 K (E_0) and the enthalpy at 298 K (H_{298}) were calculated as indicated in eqns. (15) and (16) and all

$$E_0 = E[\text{QCISD(T)/6-311+G(3df,2p)}] + \text{ZPVE} \quad (15)$$

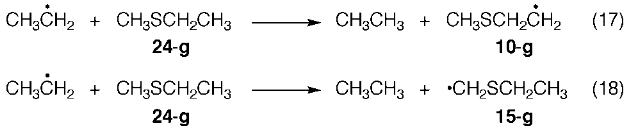
$$H_{298} = E_0 + (H_{298} - H_0) \quad (16)$$

the results are collected in Table 3; selected geometrical parameters are given in Table 4 and the computed structures are shown in Fig. 5. The complete G2(MP2) treatment includes an empirical correction to account for remaining basis set deficiencies:[30] however, this correction cancels out for the isodesmic reactions considered here.

Although the *gauche* conformation of ethyl methyl sulfide **24-g** is calculated to be slightly more stable than the *anti* conformation **24-a**, the difference is negligible (<1 kJ mol^{-1}). The enthalpy difference is larger for the corresponding conformations of the β-methylthioethyl radical and **10-g** is calculated to be more stable than **10-a** by 4.1 kJ mol^{-1}. For the isomeric ethylthiomethyl radical, the *gauche* conformation **15-g** is more stable than **15-a** by 2.0 kJ mol^{-1} and **15-g** is more stable than **10-g** by 29.0 kJ mol^{-1}.

The C–H bond dissociation enthalpies for ethyl methyl sulfide **24-g** were estimated relative to D*H*(C–H) for ethane by consideration of the isodesmic reactions (17) and (18) for which the computed enthalpy changes are −2.7 and −31.7 kJ mol^{-1}, respectively. If the value of DH_{298}(Et–H) is taken to be 423.0 ± 1.7 kJ mol^{-1},[31] the dissociation enthalpies for the $MeSCH_2CH_2$–H and H–CH_2SCH_2Me bonds in the sulfide would be 420.3 and 391.3 kJ mol^{-1}, respectively.

The *anti* conformation of the β-methoxyethyl radical **11-a** was calculated to be slightly more stable (by 1.5 kJ mol^{-1}) than



$$\mathrm{CH_3\dot{C}H_2} + \underset{\textbf{24-g}}{\mathrm{CH_3SCH_2CH_3}} \longrightarrow \mathrm{CH_3CH_3} + \underset{\textbf{10-g}}{\mathrm{CH_3SCH_2\dot{C}H_2}} \quad (17)$$

$$\mathrm{CH_3\dot{C}H_2} + \underset{\textbf{24-g}}{\mathrm{CH_3SCH_2CH_3}} \longrightarrow \mathrm{CH_3CH_3} + \underset{\textbf{15-g}}{\mathrm{\cdot CH_2SCH_2CH_3}} \quad (18)$$

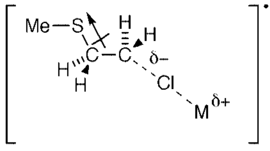
the *gauche* conformation **11-g**. The *anti* conformation of ethyl methyl ether **26-a** is more stable than the *gauche* form **26-g** by 5.5 kJ mol^{-1} and the dissociation enthalpy for the MeOCH$_2$-CH$_2$–H bond (**26-a**→**11-a**) is computed to be 429.6 kJ mol^{-1}, 6.6 kJ mol^{-1} stronger than a C–H bond in ethane and 9.3 kJ mol^{-1} stronger than the MeSCH$_2$CH$_2$–H bond in the sulfide.

The activation enthalpy for rearrangement of the β-methylthioethyl radical **10-g** to the ethylthiomethyl radical **15** *via* the transition state **27** is computed to be 87.4 kJ mol^{-1} and addition of *RT* at 298 K gives an Arrhenius activation energy[32] of 89.9 kJ mol^{-1}. If the *A*-factor for the intramolecular 1,4-hydrogen-atom transfer is taken to be $10^{11.1}$ s^{-1} (the best value for the corresponding rearrangement of the 1-pentyl radical[13]), then the rate constant for the rearrangement of **10-g** to **15** would be *ca.* 4×10^{-13} s^{-1} at 200 K and *ca.* 3×10^{-5} s^{-1} at 300 K. For a significant concentration of a rearranged radical to be detectable alongside its precursor, under the conditions of typical EPR experiments and when neither radical is persistent, the rate constant for rearrangement would have to be in the region of 10^3 s^{-1},[33] more than 15 orders of magnitude larger than the calculated value for the 1,4-hydrogen-atom transfer at 200 K!

To facilitate the discussion of polar effects, radical ionisation energies were calculated. Vertical ionisation energies were estimated as the difference between the QCISD(T)/6-311+G(3df,2p) energy of the radical and that of the corresponding cation at the equilibrium geometry of the radical. The adiabatic ionisation energies were computed as the difference in enthalpies of the radical and the relaxed cation at 298 K. The differences in higher level corrections,[30] which arise because a cation has one less electron than the radical from which it is derived, are negligible in this context. The vertical ionisation energy of the β-methylthioethyl radical **10-g** is calculated to be 8.1 eV, while the adiabatic value is only 6.1 eV. The relaxed cation has the symmetrically-bridged thiiranium ion structure **28**, accounting for the large difference between the two ionisation energies. As expected, the vertical (7.0 eV) and adiabatic (6.7 eV) ionisation energies of the ethylthiomethyl radical **15-g** are not very different, in accord with the basically similar structures of the radical and the relaxed cation **29**. The EtS–CH$_2$ bond is significantly shorter (1.613 Å) in the latter than in the parent radical (1.717 Å), reflecting the stronger 2-centre: 2-electron S–C π bond in the cation, associated with delocalisation of the positive charge onto sulfur, as compared with the 2-centre : 3-electron S–C π bond in the radical where the unpaired electron occupies an antibonding π orbital. For comparison, the computed vertical ionisation energy of the ethyl radical is 8.5 eV at this level of theory, while the adiabatic value is 8.0 eV. The relaxed ethyl cation is also symmetrically bridged[34] and the experimental value of the adiabatic ionisation energy is 8.13 eV.[35]

Discussion

At 200 K, the amine-boryl radical Me$_3$N→$\dot{\mathrm{B}}$HBu abstracts chlorine 3.1 times more rapidly from 2-chloroethyl methyl sulfide **7** than from 2-chloroethyl methyl ether **8** and 16–18 times more rapidly than from 1-chlorobutane **6**. These differences in reactivity are attributable almost completely to activation energy differences. As judged from the computed α-C–H bond strengths, the β-methylthioethyl radical is slightly stabilised (by 2.7 kJ mol^{-1}) with respect to the ethyl radical, while the β-methoxyethyl radical is destabilised by 6.6 kJ mol^{-1}, as might be expected on the basis of the abilities of the β-C–Y bonds to enter into hyperconjugation with the unpaired electron formally centred on C$_\alpha$ (see Introduction section). In the transition state **30**, the β-MeS group is optimally positioned to exert this small stabilising influence on the developing radical centre, as well as stabilising the transition state by an electrostatic field (inductive) effect. Thus, the higher reactivity of the chloroethyl sulfide **7** compared with 1-chlorobutane is probably the result of a cooperative combination of enthalpic and polar factors. For halogen abstraction from the chloroethyl ether **8** the polar effect of the β-MeO group is favourable, while its enthalpic effect will disfavour abstraction from C$_\alpha$.†† The C–S bond moment has been estimated to be 0.9 D, significantly larger than that of a C–O bond (0.74 D).[37a] Presumably the greater length of the C–S bond more than compensates for the lower electronegativity of sulfur compared with oxygen. Although the reported values of the inductive parameters (σ_I) for the MeO and MeS groups are both 0.30, the Hammett σ_{meta} constant for MeS (0.14) is greater than that for MeO (0.10),[37b] implying greater inductive electron withdrawal by the sulfur substituent. With these comparisons in mind, it would not be surprising if the polar accelerating effect of the β-MeS group on chlorine-atom abstraction by metalloidal radicals were to be similar to or even greater than that of the β-MeO group.



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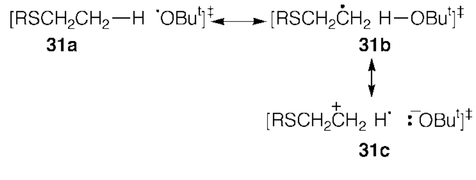
The triethylsilyl radical is less nucleophilic than the amine-boryl radical Me$_3$N→$\dot{\mathrm{B}}$HBu and is also less reactive in halogen abstraction from alkyl chlorides.[4] However, it is *less selective* than the more reactive amine-boryl radical in chlorine-atom abstraction from **6** and **8** and this breakdown in the usual parallel between reactivity and selectivity is in accord with the dominance of polar effects.[4] The relative reactivity of MeSCH$_2$-CH$_2$Cl **7** compared with MeOCH$_2$CH$_2$Cl **8** towards chlorine abstraction by Et$_3$Si$^•$ is somewhat greater than for abstraction by Me$_3$N→$\dot{\mathrm{B}}$HBu. Here it is difficult to separate the influences of enthalpic and polar factors and the relative importance of the two effects could well be different for abstraction by these two metalloidal radicals which differ appreciably in reactivity.

Because of the well-known ability of a β-RS group to stabilise positive charge on C$_\alpha$ by thiiranium ion formation in heterolytic reactions,[38] we considered it plausible that this substituent might also accelerate abstraction of hydrogen from C$_\alpha$ by electrophilic *tert*-butoxyl radicals, because of a significant contribution to the transition state from structure **31c**. However, as judged by EPR spectroscopy, Bu^{t}O$^•$ abstracts hydrogen exclusively from the CH$_2$S groups of diethyl sulfide and the β-ethylthioethyl radical **19** was not produced to a detectable extent. Although adiabatic ionisation of the β-methylthioethyl radical **10** to give the bridged thiiranium ion **28** is certainly a low-energy process (E_i = 6.1 eV), the vertical ionisation energy of **10** is much higher (8.1 eV) and similar to that of the ethyl



$$[\mathrm{RSCH_2CH_2{-}H\ {}^\bullet OBu^t}]^\ddagger \longleftrightarrow [\mathrm{RSCH_2\dot{C}H_2\ H{-}OBu^t}]^\ddagger \longleftrightarrow [\mathrm{RSCH_2\overset{+}{C}H_2\ H^\bullet\ {:}\bar{O}Bu^t}]^\ddagger$$

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†† Making the assumption that D*H*(R–Cl) parallels D*H*(R–H) for **6**–**8**.[36]

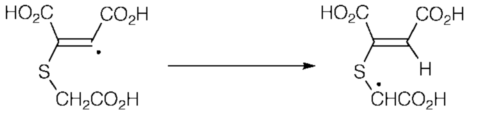
radical, suggesting that the sulfur non-bonding electrons are unlikely to participate in stabilising the transition state **31** which is electrically neutral overall. On the contrary, the results obtained for abstraction of hydrogen from $\mathrm{MeSCH_2CH_3}$ and $\mathrm{MeSCH_2CH_2SMe}$ indicate that hydrogen transfer from $\mathrm{SCH_2}$ groups to the electrophilic $\mathrm{Bu^tO^\bullet}$ is *retarded* in the presence of a β-MeS substituent in the latter molecule.

Despite the expected C_α–H bond-weakening effect of a β-MeS group in 2,5-dithiahexane, which could be rather larger than the same effect in $\mathrm{MeSCH_2CH_3}$,‡‡ an $\mathrm{SCH_2}$ group in $\mathrm{MeSCH_2CH_2SMe}$ is *less* reactive than the $\mathrm{SCH_2}$ group in $\mathrm{MeSCH_2CH_3}$, relative to abstraction from the MeS groups in these molecules. The inductive electron-withdrawing effect of the β-MeS group in $\mathrm{MeSCH_2CH_2SMe}$ increases the activation energy for abstraction of hydrogen from C_α by reducing the extent of charge-transfer stabilisation of the transition state (*cf.* structure **31c**). For hydrogen-atom abstraction by $\mathrm{Bu^tO^\bullet}$ the enthalpic and polar effects of a β-MeS group act in opposition and the latter effect evidently out-weighs the former.§§

1,4-Hydrogen-atom transfer

No experimental evidence was found to support the proposed[11] rearrangement of the β-alkylthioalkyl radicals **10** and **19** to the isomeric α-alkylthioalkyl radicals **15** and **20**, respectively, by intramolecular 1,4-H-atom transfer. Although the rearrangement of **10** is calculated to be exothermic by 29 kJ mol^{-1}, the conjugative stabilisation of **15** by delocalisation of the unpaired electron onto sulfur will not be available in the transition state **27**, because the higher-energy sulfur lone pair is in an orbital that is nearly orthogonal to the developing singly-occupied 2p orbital on the attached carbon atom. Not surprisingly, the computed activation energy for such hydrogen-atom transfer in **10** is similar to that found by experiment for the analogous rearrangement of the 1-pentyl radical to the 2-pentyl radical,[13] and is much too large for the rearrangement of **10** to proceed at a detectable rate at moderate temperatures.

It has been reported that rearrangement of the vinylic radical **32** to the α-vinylthioalkyl radical **33** can be detected by EPR spectroscopy in aqueous solution at room temperature.[39] However, the thermodynamic driving force for this rearrangement is likely to be appreciably greater than that for **10**→**15** and, significantly, it was reported that the α-carboxy group in **32** was necessary for the rearrangement to occur even at room temperature. The conjugative stabilisation of the developing radical centre by the attached $\mathrm{CO_2H}$ group should be available in the transition state for 1,4-H-atom transfer.



32 **33** (19)

The 'other' radical detected by Casarini *et al.*[11] during the UV photolysis of MeSSMe in the presence of ethene (Fig. 3a) is not the isomeric radical **15**, but is almost certainly the α-alkylthioalkyl radical **17**. It is known that UV photolysis of MeSSMe,[40a] like its pyrolysis,[40b] leads to the formation of thioformaldehyde, which polymerises readily to give poly(thioformaldehyde) as a pale yellow solid that is insoluble in hydrocarbon solvents.[25] Thioformaldehyde could arise from the disproportionation of methanethiyl radicals [eqn. (20)],[41] especially at very low temperatures when competing addition of $\mathrm{MeS^\bullet}$ to the alkene is relatively slow.

$$2\,\mathrm{MeS^\bullet} \longrightarrow \mathrm{H_2C{=}S} + \mathrm{MeSH} \qquad (20)$$

$$\underset{\mathbf{10}}{\mathrm{MeSCH_2\dot{C}H_2}} + \mathrm{H_2C{=}S} \longrightarrow \underset{\mathbf{17}}{\mathrm{MeSCH_2CH_2S\dot{C}H_2}} \qquad (21)$$

Thiocarbonyl compounds are excellent traps for carbon-centred radicals[41,42] and, in competition with its oligomerisation and polymerisation, thioformaldehyde could react with the radical **10** to give the alkylthiomethyl radical **17** [eqn. (21)]. This scenario would account for the observation that **17** is more readily detectable at very low temperatures, when more $\mathrm{H_2C{=}S}$ would be formed and its removal by polymerisation would be slower.¶¶

We conclude that the substituent effect of a β-MeS group on atom abstraction from C_α arises from a combination of thermodynamic stabilisation of the incipient β-methylthioalkyl radical, which is always rate enhancing, together with a polar effect that operates in the transition state and can accelerate or retard the abstraction, depending on the nature of the particular reaction.

Experimental

EPR spectra were recorded during continuous UV irradiation of samples positioned in a standard variable temperature insert in the microwave cavity of a Varian E-109 or a Bruker ESP-300 spectrometer operating at 9.1–9.4 GHz.[17] The light source was a 500 W mercury discharge lamp (Osram HBO 500 W/2) and the optical system has been described previously.[17] Samples were prepared using a vacuum line and were sealed in evacuated Suprasil quartz tubes (4 mm od, 3 mm id). Mixtures of halides for the determination of relative reaction rates were made up in bulk by weight and aliquots of these mixtures were used for sample preparation. To reduce the possibility of any reaction between the reagents prior to photolysis, samples were kept in liquid nitrogen and thawed and mixed by repeated inversion in a solid $\mathrm{CO_2}$–ethanol bath immediately before insertion into the EPR spectrometer. The temperature of the sample during photolysis was determined, using the method described previously,[17] by careful measurement of the value of $a(\mathrm{H}_\beta)$ for the isobutyl radical in cyclopropane; the heating effect at full light intensity varied between 5 and 7 K depending on conditions.

Relative radical concentrations were determined by double integration of appropriate lines in the composite spectrum and were confirmed by computer simulation; concentration ratios were extrapolated to zero UV irradiation time when necessary to overcome the effects of sample depletion and care was taken to avoid selective saturation of the spectra. Computer simulations of spectra were obtained using a modified version of ESRSPEC2,[43] extended to handle composite spectra from up to four radicals with different centres, second-order shifts for coupling to single nuclei with $I > \frac{1}{2}$, and line-shapes continuously variable between 100% Gaussian and 100% Lorentzian.

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‡‡ The radical $\mathrm{MeSCH_2\dot{C}HSMe}$ may benefit from captodative stabilisation, with electron delocalisation from the +R α-MeS group into the MeS–C_β σ* orbital *via* the singly-occupied C_α–$2p_\pi$ orbital.

§§ It has been proposed that the overall abstraction of hydrogen by alkoxyl radicals from CH groups attached to sulfur in dialkyl sulfides may occur by an indirect mechanism involving initial addition to sulfur to form a sulfuranyl radical, followed by loss of alcohol to give the α-alkylthioalkyl radical.[27] Although attack of alkoxyl radicals at sulfur does take place to some extent,[28c] this appears to be a process that occurs *in competition* with direct abstraction from α-CH groups, at least in solvents of low polarity.

¶¶ Although we consider it much less likely, we cannot exclude the possibility that the second radical arises by addition of photo-excited monomeric thioformaldehyde to ethene, followed by selective trapping by $\mathrm{MeS^\bullet}$ at the less-stabilised end of the diradical so formed to give **17**, or its trapping by another radical to give a species of the type $\mathrm{XCH_2CH_2S\dot{C}H_2}$ which has EPR parameters indistinguishable from those of **17**.

The experimental methods for determination of relative rate constants using the EPR method have been described in detail previously.[4,17]

Materials

Di-*tert*-butyl peroxide (98%, Aldrich) was washed repeatedly with 5% w/v aqueous sodium iodide containing 2% w/v sulfuric acid, until no more iodine was liberated. It was then washed successively with water, saturated aqueous sodium hydrogen carbonate, and saturated brine, before being dried ($MgSO_4$), passed down a column of basic alumina (activity 1) and finally distilled (bp 46–47 °C/76 Torr); it was stored under argon at 4 °C. Cyclopropane (Union Carbide) and ethene (Aldrich) were used as received. Chloromethyl ethyl sulfide[26] **16** and 2,5-dithiahexane[44] **18** were prepared as described in the literature. 2-Chloroethyl methyl sulfide, 2-chloroethyl methyl ether and 1-chlorobutane (all Aldrich) were distilled under argon before use, but all other sulfides and disulfides (Aldrich) were used as received. Trimethylamine-butylborane was prepared by the method of Hawthorne;[17b,45] triethylsilane (Lancaster) and hexamethylditin (Aldrich) were distilled before use and stored under argon.

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