Reactions of the Methylthiyl Radical with Unsaturated Cycloalkanes: Abstraction, Addition, and Rearrangement

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The methylthiyl radical (MeS·) generated by photolysis of dimethyl disulphide (MeSSMe) is shown to give three types of reactions with cyclic molecules containing carbon–carbon double bonds. E.s.r. spectra corresponding to radicals formed by addition of MeS·, by hydrogen abstraction, and by a rearrangement (possibly involving 1,4-hydrogen shift between SMe and the radical centre) have been detected. In the case of cyclopentene, all three types of radicals were observed. In the case of cyclohexene, only radicals due to abstraction and rearrangement were detected. With methylenecycloalkanes there was no evidence for hydrogen abstraction but radicals from addition and rearrangement were identified.

PHOTOLYSIS of dialkyl disulphides (RSSR) produces alkylthiyl radicals (RS·) which, depending on the experimental conditions, can either abstract a hydrogen atom from a suitable hydrocarbon or add to a carbon–carbon double bond.[1] The first reaction is unusual and has been only recently reported,[1] whereas addition to double bonds is well known.[2,3] Under steady state conditions the e.s.r. spectra of radicals obtained from such processes can be detected.[1-3] Methylenecycloalkanes have been reported [4] to add silyl radicals. The present work is concerned with the radicals formed by addition of methylthiyl radical to these molecules, as well as to cyclic alkenes. Both classes of compounds also displayed radicals due to a rearrangement which we tentatively interpret as a 1,4-hydrogen shift.

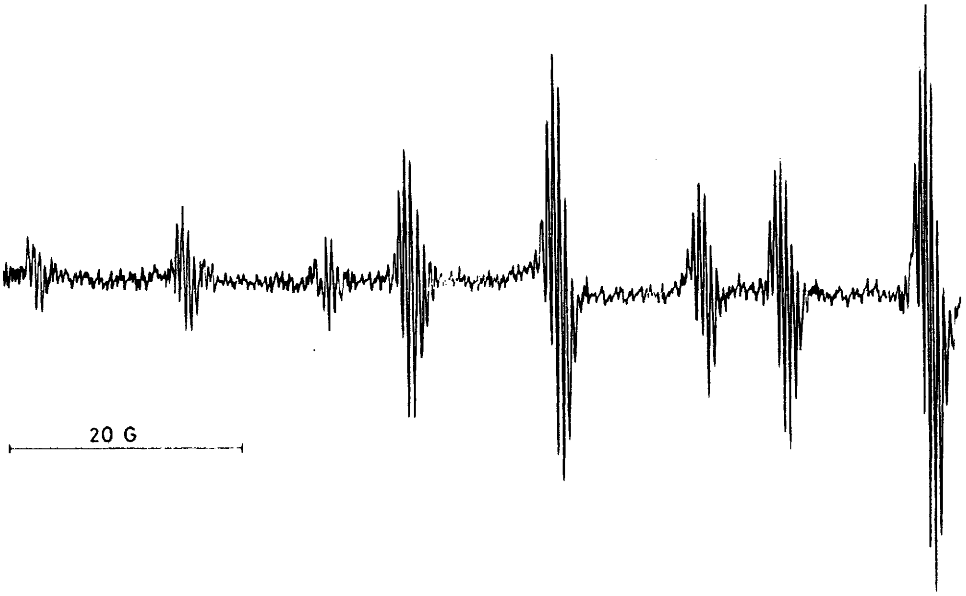
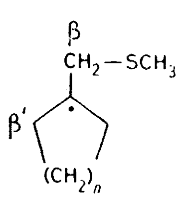


FIGURE 1 Half e.s.r. spectrum of radical (2) from methylenecyclopentane at −50°

RESULTS AND DISCUSSION

Dimethyl disulphide (MeSSMe) was photolysed directly in an e.s.r. cavity in the presence of methylenecyclo-propane, -butane, -pentane, and -hexane using cyclopropane as solvent. In the case of the four-, five-, and six-membered methylenecycloalkanes, addition of MeS· occurred and the spectra corresponding to radicals (1)—(3) were observed (Figure 1). Their hyperfine splitting constants are reported in Table 1.

With these derivatives hydrogen abstraction by MeS· does not occur; this contrasts with the behaviour of RO·, which yields the corresponding allylic radicals.[5]



(1) $n = 1$
(2) $n = 2$
(3) $n = 3$

In the case of methylenecyclopropane the radical due to addition was not observed: it seems that the strained three-membered ring opens up giving other species, as reported in other cases.[2,4,5]

In radicals (1)—(3) there are two kinds of β-protons, those on the ring and those of the methylene group bridging the ring to the sulphur. Their hyperfine splittings are known to depend upon the conformational arrangement.

TABLE 1

Hyperfine coupling constants (G) of radicals (1)—(3) obtained by addition of MeS· to methylenecycloalkanes

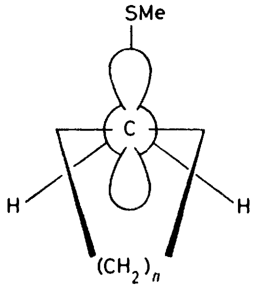
Radical	a_H^{SMe}	$a_{\beta,2H}$	$a_{\beta',4H}$	a_γ
(1)	0.5	13.00	33.62	1.12
(2)	0.45	12.62	32.00	0.45
(3)		12.12	$a_{\beta'ax} + a_{\beta'eq} = 45.12$	

Conformational Studies.—The hyperfine splittings of the ring hydrogens can give an indication of the ring shape, by means of the relationship $a_{H\beta} = A + B\cos^2\theta$. Values of A and B (3.8 and 37.2 G) were recently obtained for a similar class of compounds.[4] In the case of (1) an assumption of planarity (*i.e.* θ 25°) gives a computed splitting (34.3 G) not too different from the experimental value (33.56 G); the cyclobutyl derivative should thus be planar or only slightly puckered. In the case of (2) the value computed for a half-chair (θ 10°, a_H 32.75 G) is closer to experiment (a_H 32.0 G) than the value for a planar conformation (θ 28°, a_H 30.8 G), in agreement with the known non-planarity of five-membered rings.[4-6] Finally, in the case of the cyclohexyl radical (3) we could not identify the individual axial and equatorial splittings, since at the temperature at which ring reversal is slow another radical appears (see below). However the sum $a_{ax} + a_{eq}$ could be measured (43.1 G) and compared with the value expected for a chair or a half-chair conformation (35.5 and 54.1 G, respectively). The value, although not equal, is closer to that for the chair: a distorted chair seems therefore the most likely conformation.[4,5]

The β-splittings of the sulphur-bonded methylene decrease with an increase in the ring size. The values in Table 1 had to be taken at different temperatures and the CH_2S splittings are known[3,7] to have a positive temperature dependence. The values extrapolated to −50°, taking into account the observed temperature effect (*ca.* 10 mG degree^{-1}) would give the following trend: 13.1_5, 12.6, and 11.9 G for (1), (2), and (3), respectively. In order to rationalize this small, but certainly real difference, the conformation of C–SMe has to be considered.

The order of magnitude of the β-CH_2 splitting we observed is considered[7] to be typical of conformations with SMe in an eclipsed position relative to the C_α $2p_z$ orbital [structure (A)]. In this situation, if ϕ is the dihedral angle between the $2p_z$ orbital and the C–SMe bond, the two methylene hydrogens have identical a_H values, since they have equal angles θ (θ = 60 − ϕ).

In some cases, however, spectra taken at very low temperature showed[8] that these hydrogens are not equivalent (*i.e.* their angles are different) and have, therefore, ϕ different from 0°. The single CH_2 splitting, observed at higher temperature, could be due to the fast exchange between the two sites, with a low interconversion barrier. Recently we confirmed[9] this finding for a similar radical ($MeS{-}CH_2{-}\dot{C}H{-}CH_2{-}SMe$) where two different a_β splittings were detected below −130° (6.0 and 19.2_5 G). Accordingly, if in the present case the methylene splitting is also the result of an averaging process, a modification of the angle ϕ in radicals (1)—(3) would explain the observed differences. To check, albeit approximately, this hypothesis, let us assume* that $a_{H\beta} = A + B\cos^2\theta$. Since for this situation A and B are not known with sufficient accuracy, we considered as a first approximation $A = 0$ and $B = 48$ G.[1,7,9] When $\phi = 0$ (*i.e.* C–SMe eclipsed with respect to the p orbital of the sp^2 carbon) the computed averaged methylene splitting is 12 G, as observed for radical (3); when ϕ is 9 and 12° the calculated values become 12.6 and 13 G, respectively, as in (2) and (1). This approach thus accounts for the observed variation of the CH_2 splittings in (1)—(3). The larger the ring, the smaller is expected to be the splitting: the angle is in fact reduced by the steric hindrance of the larger rings that force SMe to move from its preferred, slightly staggered conformation, toward an eclipsed arrangement. Obviously, because of the imperfect knowledge of A and B, the angles ϕ are only indicative of a trend and do not represent the exact conformation of these radicals.



(A)

Reaction Mechanism.—When methylenecycloalkanes are photolysed in the presence of MeSSMe and the modulation of the spectrometer is raised, the sharp lines due to radicals (1)—(3) broaden considerably and eventually become barely detectable. In these conditions a weaker signal, with a broader linewidth, is now observed.

This second spectrum is formed by four lines of equal intensity and is independent of the methylenecycloalkane employed: the hyperfine splitting constants are reported in Table 2. The g factor (2.0051 ± 0.0002) and the two a_{CH} splittings are typical[10,11] of radicals of general formula $R_3C{-}S\dot{C}H_2$, which are known to display two non-

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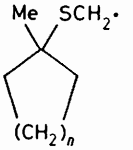
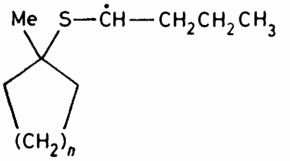
* Kochi and Krusic suggested[2,3] that sulphur radicals of this type might not obey this relationship. However, they could not perform the INDO calculations that, according to their claim, would have checked this hypothesis. We carried out these calculations[9] and found that sulphur radicals of this type do obey the relationship.

equivalent hydrogens below —80°. Structures (4)—(6) would thus account for the e.s.r. spectra as well as for the invariance with the ring size.



(4) $n = 1$
(5) $n = 2$
(6) $n = 3$

To check this hypothesis n-butyl disulphide was photolysed at $-100°$ in the presence of the same methylenecycloalkanes; under these conditions we should detect the spectra of radicals (4′)—(6′). Radicals of this type (RS-CH-CH_2CH_2R′) have e.s.r. spectra with equal[11] ($a_{CH} = a_{CH_2} = 16.8$ G) or almost equal[12] (a_{CH} 16.9, a_{CH_2} 17.2 G) α- and β-splittings. The spectra of (4′)—(6′) are quartets with a splitting of 16.8 G; the relative heights of the lines are not, however, 1 : 3 : 3 : 1 since the two inner signals are broader than the outer. This feature proves that the quartet is due to near-degeneracy of the CH and CH_2 splittings, thus confirming the proposed structures. We also ruled out the possibility that the observed radicals are $MeSSCH_2$ or Bu^n-S-S-$\dot{C}H$-$CH_2CH_2CH_3$, generated by hydrogen abstraction from the parent disulphide. Photolysis of MeSSMe alone did not produce any e.s.r. spectrum; furthermore the radical $MeSS\dot{C}H_2$ (obtained *via* Bu^tOOBu^t)[2,3] does not have different methylene hydrogens, and thus cannot be mistaken for radicals (4)—(6). Photolysis of di-n-butyl disulphide alone yields a spectrum with a quartet similar to that of radicals (4′)—(6′) but with a splitting larger by 0.7 G. This radical is Bu^n-S-S-$\dot{C}H$-Pr which is known[12] to have a splitting larger by this amount than the corresponding sulphide.



(4′) $n = 1$
(5′) $n = 2$
(6′) $n = 3$

TABLE 2

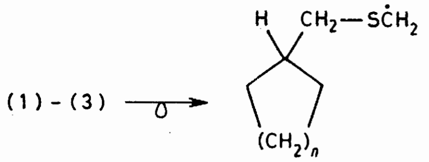
Hyperfine coupling constants (G) of radicals (4)—(6), (12), and (13) (g 2.0051 ± 0.0002)

Radical	a_H^H	$a_H^{SCH_2}$	$a_{H'}^{SCH_2}$
(4)		16.00	17.25
(5)		15.75	17.00
(6)		15.87	16.87
(12)	3.5	16.12	17.25
(13)	2.0	16.12	17.25

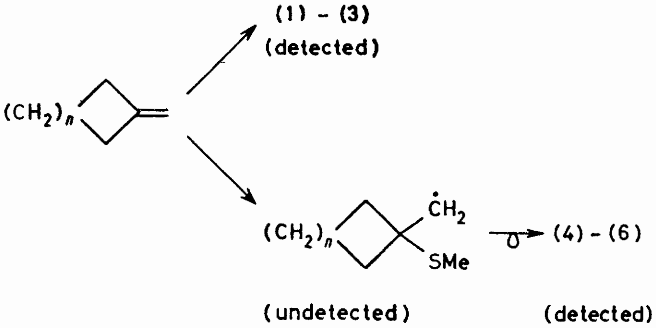
The mechanism of the generation of these species requires a rearrangement involving the carbon bearing the unpaired electron and the adjacent SR group. If we assume that the radicals (1)—(3) formed by normal addition rearrange *via* a 1,4-hydrogen shift, the resulting radicals would have structures (7)—(9).

These types of radicals, however, are known to have a rather large methylene splitting for R-CH_2-S-,[10,11] thus allowing us to eliminate this possibility. There is also the possibility that, besides the normal addition, a reverse addition takes place. Although not frequently encountered, both inter-[13] and intra-molecular[14] reverse additions have been observed. The radical formed in this way (Scheme 1), an unconjugated primary radical, might be expected to form the more stable alkylthiomethyl radicals (4)—(6) which we have detected by e.s.r.

Although invoked by Krusic and Kochi[3] to explain the formation of $\cdot CH_2OCH_2CH_3$ from $CH_3OCH_2CH_2\cdot$, 1,4-hydrogen shifts are quite unusual rearrangements.[15] Alternative pathways for the formation of radicals (4)—(6) were thus considered. For instance the radical $>$C(SMe)$\dot{C}H_2$, formed by reverse addition of MeS•, could, in principle, abstract a hydrogen atom from the environment to give a neutral molecule $>$C(SMe)CH_3. Subsequently either MeS• or $>$C(SMe)$CH_2\cdot$ itself, still present in solution, might abstract a hydrogen atom from the SMe moiety of this molecule to give radicals (4)—(6). Alkyl[16] and thiyl[1] radicals can in fact abstract hydrogen atoms from suitable substrates. To check whether SMe is one of these substrates we allowed dimethyl sulphide (MeSMe) to react, under the same conditions, either with MeS• (generated from photolysis of MeSSMe) or with Me• (generated from photolysis of MeCOO-COOMe). No radicals due to intermolecular hydrogen abstraction were detected: this contrasts with the behaviour observed when alkoxyl radicals were employed.[10] To check further that radicals (4)—(6) are not derived from a neutral molecule generated by photolysis, the following experiment was carried out. The spectrometer was tuned on the top of one line of the spectrum of (4) and the field sweep was shut off. Then a new sample, not previously photolysed, was introduced: once photolysis is applied radical (4) builds up faster than we could measure (*i.e.* in <1 s). This proves that (4) does not derive from a product due to the decay of the initial radical, but appears simultaneously with



(7) $n = 1$
(8) $n = 2$
(9) $n = 3$



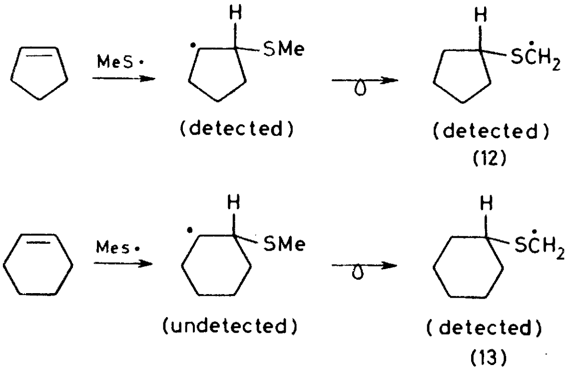
SCHEME 1

radical (1). The same result is observed even in absence of the solvent (cyclopropane). Although we realize that a mechanism based on a 1,4-hydrogen shift is quite unlikely, it is nonetheless difficult to dismiss such an hypothesis in the present case, in view of the results so far obtained. A point worthy of consideration concerns the failure to detect radicals of the same type (*i.e.* C–S$\dot{C}H_2$) when linear unsubstituted olefins are employed. In these cases, in fact, only addition was reported.[2] We suggest that rearrangement is favoured when SMe and $\dot{C}H_2$ have a suitable spatial arrangement. Apparently this is not the case with linear unsubstituted alkenes, whereas this situation exists in cyclic derivatives. If so, other cyclic olefins should also experience this rearrangement: to check this possibility we photolysed MeSSMe in the presence of cyclopentene and cyclohexene.

As already reported, the reaction which occurs near room temperature is hydrogen abstraction to give the corresponding allylic radicals (10) and (11). In principle hydrogen abstraction could be caused, rather than by direct reaction of methylthiyl radical (MeS·), by the alkyl radical due to addition of MeS· to the double bond. However, when we photolysed a source of alkyl radicals (MeCOO–COOMe) in the presence of cyclopentene, the e.s.r. signal of the allylic radical was much weaker; furthermore the allylic radical produced by Me· was detectable only in a narrow temperature range around 0°, as opposed to the wide range (−30 to +50°) when MeSSMe was used. As already pointed out in ref. 2 this fact seems to imply that the rate of hydrogen abstraction by alkyl radicals is too slow to produce the same steady state concentration of allylic radicals given by methylthiyl. At *ca.* −100° the same sample containing MeSSMe and cyclopentene shows the radical due to addition of methylthiyl;[1] the corresponding addition radical is not observed, however, in the case of cyclohexene. Again if the modulation is raised and the lines of the addition radical partially saturated a second radical, formed by eight lines, is observed for both cyclohexene and cyclopentene (Figure 2a). In the latter case the spectrum is superimposed on that due to addition,* thus suggesting that radicals (12) and (13) are derived from a rearrangement, according to Scheme 2.


(10)


(11)



SCHEME 2

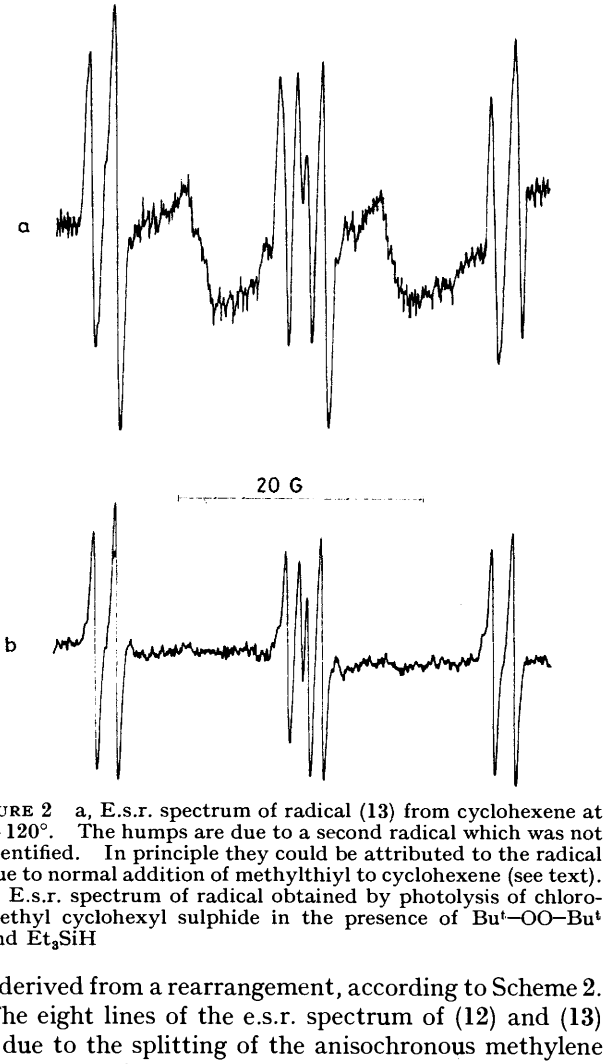


FIGURE 2 a, E.s.r. spectrum of radical (13) from cyclohexene at −120°. The humps are due to a second radical which was not identified. In principle they could be attributed to the radical due to normal addition of methylthiyl to cyclohexene (see text). b, E.s.r. spectrum of radical obtained by photolysis of chloromethyl cyclohexyl sulphide in the presence of Bu^t–OO–Bu^t and Et_3SiH

The eight lines of the e.s.r. spectrum of (12) and (13) are due to the splitting of the anisochronous methylene hydrogens and to the methine hydrogen which is not present in (4)—(6). To produce unambiguous proof of the structure of radical (13) we generated it in a completely independent way, according to Scheme 3. The radical obtained in this way shows a spectrum equal to that of (13): the *g* factor (2.0050 ± 0.0002) is also the same within experimental error (Figure 2b). It seems therefore that this rearrangement is not peculiar to

$$Bu^tOOBu^t + Et_3SiH \xrightarrow{h\nu} Et_3Si\cdot$$

$$Et_3Si\cdot + C_6H_{11}{-}SCH_2{-}Cl \longrightarrow \underset{(13)}{C_6H_{11}{-}SCH_2\cdot}$$

SCHEME 3

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* In the case of cyclohexene a weak signal (Figure 2a) is observed, which in principle could be assigned to the addition radical: its weakness, however, prevents an unambiguous identification.

methylenecycloalkanes (where reverse addition is also required) but also occurs when only one type of addition is feasible.

A final point concerning the structure of (**13**) also needs to be clarified. In contrast to (**12**), radical (**13**) should give, in principle, two e.s.r. spectra corresponding to the axial and equatorial conformers, since ring reversal of cyclohexyl is much slower ($\Delta G^\ddagger$ 10.5 kcal mol^{-1}) [17] than that of cyclopentyl. Careful inspection of the spectrum of (**13**) shows that some lines are more intense than others, although the linewidth is the same: in addition the weaker lines were not as symmetrical as the more intense lines. There is thus the possibility that the spectrum is formed by two superimposed spectra, with the differences in *g* factor and hyperfine splitting constants too small to show separate lines. Some of them, however, are probably exactly coincident whereas others are slightly displaced, thus giving rise to unequal intensities. We estimated that the observed difference can be accounted for by the presence of 5—10% of the minor conformer. This conclusion is supported by ^{1}H and ^{13}C n.m.r. spectra of a similar molecule, cyclohexyl methyl sulphide. At −100° (in CD_2Cl_2 or Freon) we observed two n.m.r. spectra corresponding to the axial (*ca.* 5%) and equatorial (*ca.* 95%) conformers.

EXPERIMENTAL

Unless otherwise indicated all compounds employed in this study were reagent grade commercial samples, most of which were used without further purification; methylenecyclohexane however was distilled and the disulphides were passed through neutral alumina prior to use. Chloromethyl cyclohexyl sulphide was prepared as reported by Walter *et al.*[18] and was purified by distillation. Cyclohexyl methyl sulphide was prepared as follows. Cyclohexanethiol (5.2 g) was mixed with methyl iodide (6.5 g) in benzene (40 ml) and aqueous 1.5N-sodium hydroxide (50 ml) as solvent. Triethylbenzylammonium chloride (100 mg) was added as phase transfer catalyst. The reaction was carried out at room temperature for 15 min.[19] The products were checked by n.m.r. spectroscopy. The low temperature n.m.r. spectra of cyclohexyl methyl sulphide were recorded at 100 (^{1}H) and 25.16 MHz (^{13}C) in the Fourier transform mode, using as solvent either CD_2Cl_2 or $CHF_2Cl-CF_2Cl_2$.

E.s.r. Measurements.—The samples were prepared as follows. A small amount of alkyl disulphide was introduced into a Suprasil sample tube, followed by the desired amount of olefin. The contents were thoroughly degassed on a vacuum system and, when required for low temperature measurements, cyclopropane was added as solvent. The radicals were generated photolytically by methods previously reported.[5] The spectra were recorded on a Varian E-104A e.s.r. spectrometer provided with a variable temperature controller. Diphenylpicrylhydrazyl (*g* 2.0037) was used as standard in the *g* factor measurements.

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