Temperature-controlled Addition *vs.* Abstraction by Methylthiyl Radical with Cyclopentene

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Summary Both the radical adducts of addition to and hydrogen abstraction from cyclopentene by methylthiyl radical (MeS•) have been detected by e.s.r. spectroscopy.

It has been observed by e.s.r. spectroscopy that alkylthiyl radicals (RS•) add to double bonds[1,2] whereas alkoxyl radicals (RO•) usually abstract hydrogen.[3] There is, however, chemical evidence[4] that alkylthiyl radicals, like alkoxyl radicals, can abstract hydrogen. We report here an unusual case where it is possible unambiguously to detect both the addition of the methylthiyl radical to a double bond and hydrogen abstraction from the same molecule, by appropriate temperature changes.

Photolysis in the cavity of an e.s.r. spectrometer of a cyclopropane solution of dimethyl disulphide (MeSSMe) and cyclopentene yields, at −100 °C, the radical whose spectrum is shown in Figure 1(a). The spectrum has been interpreted as being due to the radical (**2**) resulting from addition of MeS• to the double bond of cyclopentene.

The experimental hyperfine splitting (h.f.s.) constants (G) reported here were assigned in the following way. First,

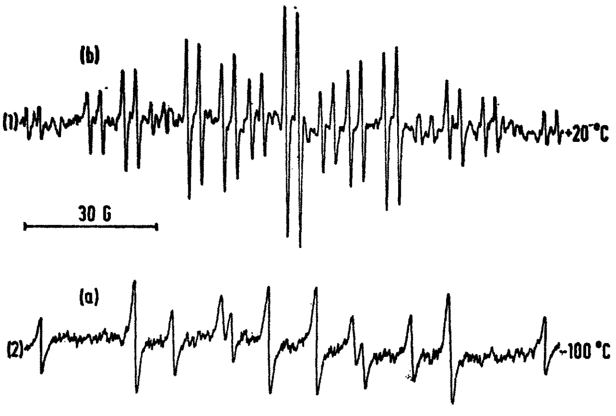
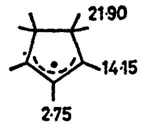
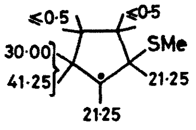


Figure 1. E.s.r. spectra of the radicals (**1**) ($g = 2{\cdot}0029$) at +20 °C and (**2**) ($g = 2{\cdot}0030$) at −100 °C (line width 0·5 G) obtained by photolysis of MeSSMe and cyclopentene in cyclopropane. Second order features (ref. 3) for the cyclopentenyl radical (**1**) were also detected when a smaller modulation was applied.

the modifications of the h.f.s. constants of alkyl radicals caused by an MeS– substituent were estimated by comparing the values of ethyl and isopropyl radicals[5] with those of β-mercapto-ethyl and -isopropyl radicals.[1] Then the h.f.s. constants of the cyclopentyl radical in solution[5] and in solid matrix[6] were modified accordingly: the resulting values matched satisfactorily the experimental values observed for (**2**). It is noteworthy that, to the best of our knowledge, this is the first direct observation of a radical resulting from addition to cyclopentene.



(1)



(2)

As for the conformation of (**2**), it has been suggested[7,8] that five-membered radicals exist in two rapidly interconverting 'half-chair' conformations; the sum of their pseudo-axial and -equatorial splittings being given by a $B\cos^2\theta$ type of relationship (B = 50 G, θ = 10 or 50°).[8]

The sum computed in this way (70 G) agrees with the experimental values of (**2**) (71·25 G); in addition the largest experimental splitting (41·25 G) is close to the value expected (49 G) for a pseudo-axial and the smallest (30·00 G) to that expected (21·00 G) for a pseudo-equatorial splitting.

An –SR substituent is known to reduce the splitting of a β-hydrogen by 11—13 G with respect to the corresponding hydrocarbon;[1,5] the experimental value of 21·25 G thus corrsponds to a pseudo-equatorial and the –SMe group to a pseudo-axial position. The conformation of (**2**) shown in Figure 2 thus seems preferable to the alternative half-chair having the –SMe group in the pseudo-equatorial position.

On raising the temperature to −60 °C the radical (**2**) disappears and between 0 and +20 °C the spectrum of the cyclopentenyl radical (**1**) due to hydrogen abstraction by MeS• is observed [Figure 1 (b)]. Weak signals due to (**1**) were observed between −60 and 0 °C. The experimental h.f.s. constants of (**1**) are almost identical to those reported for cyclopentenyl radical generated by means of alkoxyl radicals.[3]

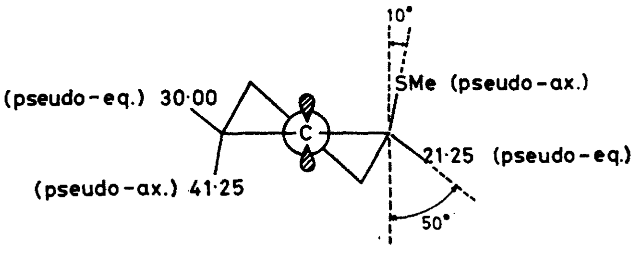


Figure 2

Radical (**2**) is only observed at temperatures ≤ −60 °C. This indicates that the addition of MeS• to cyclopentene has a low activation energy. It also suggests that (**2**) decomposes readily, presumably by the loss of MeS•, since alkylthiyl additions to olefins are known to be reversible. The hydrogen abstraction reaction which yields (**1**) must have a higher activation energy than the addition reaction.

Although our observations merely represent the two routes by which an alkylthiyl radical can react with an olefin, the observation of both reactions with the same substrate is remarkable. That is, for the majority of olefins one pathway will be much more strongly favoured than the other and so reaction will proceed either by addition or by abstraction at all readily accessible temperatures. For example, with cyclohexene we could detect only hydrogen abstraction, whereas with acyclic alkenes only addition has been reported.[1,2]

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