Free radicals from cyclic enones: an electron paramagnetic resonance investigation. Part II.[1] Radical additions

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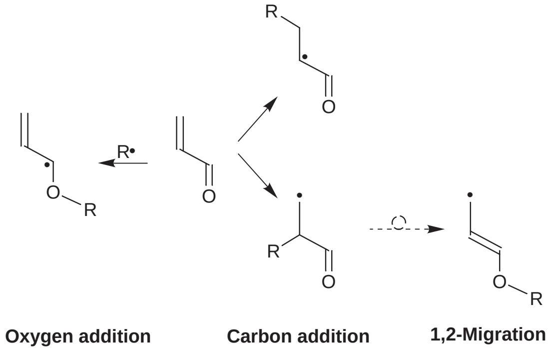
The addition of silyl and germyl radicals to a series of substituted cyclopentenones and cyclohexenones has been investigated using EPR spectroscopy. At low temperatures the 3-position is the preferred site for addition unless it is substituted or sterically hindered in which case addition occurs at the carbonyl oxygen. The latter process is also favoured at higher temperatures but no evidence has been obtained for either addition at the 2-position or for an intramolecular migration following initial attack at the 3- or 2-position.

Introduction

In Part I of this series we showed that cyclic α,β-enones readily undergo hydrogen abstraction to give free radicals detectable by EPR.[1] We now report on an investigation of the addition of silyl and germyl radicals to the same series of compounds. Three possible pathways for addition to an enone are shown below.



If one pathway is not significantly favoured over the other two, then overlapping spectra of two or three species may be observed. Numerous studies have reported on trialkylsilyl radical additions to carbonyl groups and to carbon–carbon double bonds.[2] Owing to the different π contributions to the bond strength of C=C and C=O double bonds, carbon addition has a lower activation energy and is kinetically preferred and so occurs initially; on the other hand, the oxygen–silicon bond is significantly stronger than the carbon–silicon bond and oxygen addition is therefore thermodynamically favoured. It is therefore predicted that carbon addition is more favourable at low temperatures and that oxygen addition is more favoured at higher temperatures. It has also been proposed that 1,3-intramolecular carbon to oxygen shifts can occur within the adducts: that is to say, initial addition will occur at the carbon–carbon double bond but the organometallic moiety then shifts to the carbonyl oxygen, although the rearrangement would not be a radical process.[3]

Depending on the time scale of the shift, it may be that addition to carbon will not be observed in an EPR experiment and only the oxygen adduct is seen. In theory, cooling a system may stabilise the carbon-adduct and warming will destabilise it causing the radical to shift and form the oxygen adduct. Because the shift occurs *via* a four-membered cyclic intermediate, migration can only occur when the silicon is β to the involved carbonyl carbon.[4] 1,4 Oxygen to oxygen migration within radicals derived from compounds containing adjacent carbonyl groups was also observed in the adducts between benzil and tri-*n*-butylgermyl radicals,[5] and between other MR_3 radicals and some *ortho*-quinones.[6] The negative activation entropies characterising these processes were explained by assuming the migration to proceed through a cyclic transition state where the Group 14 metal is simultaneously bound to both oxygens; besides, the rather low activation energies were thought to be indicative of a weakening of the oxygen–metal bond in the initial state, due to partial coordination of the metal by the second oxygen atom.[5,6]

Experimental

Materials

Cyclopent-2-en-1-one, 3-methylcyclopent-2-en-1-one, 2,3-dimethylcyclopent-2-en-1-one, 2,3,4,5-tetramethylcyclopent-2-en-1-one, 4,4-dimethylcyclopent-2-en-1-one, cyclohex-2-en-1-one, 3-methylcyclohex-2-en-1-one, 3,5-dimethylcyclohex-2-en-1-one, 3,5,5-trimethylcyclohex-2-en-1-one, 4,4-dimethylcyclohex-2-en-1-one and cyclohexanone were purchased from either Aldrich or Fluka, as were di-*tert*-butyl peroxide and all of the organometallic hydrides.

EPR Experiments

EPR spectra were recorded using previously described procedures[7] on Bruker ER-200D and Varian E104 spectrometers equipped with an NMR-gaussmeter for field calibration and a frequency counter for the determination of *g*-factors. Triphenylsilyl, tris(trimethylsilyl)silyl and triphenylgermyl radicals were generated *via* hydrogen abstraction from the parent silanes or germane by *in situ* generated *tert*-butoxy radicals. The triphenylgermane samples were prepared by putting a small quantity of the hydride on the bottom of a quartz EPR tube (i.d. 4 mm). The enone and peroxide were then added in concentrations 2:1 by volume (added drop-wise from a pipette, one drop is sufficient for the peroxide). The sample was subsequently diluted to make up the necessary volume with *tert*-butylbenzene (~500 μl), which acts as a non-reactive solvent.

While a similar procedure was successfully used with tris(trimethylsilyl)silane, triphenylsilane adducts proved more difficult to observe and a variety of techniques were employed to try to optimise the spectra. The most productive protocol involved using the peroxide in a greater quantity, in fact substituting the *tert*-butylbenzene as a solvent, but keeping the silane and enone at similar low quantities to the germane samples.

Oxygen was removed by purging the solutions with argon for between 15 and 20 minutes. The solutions were photolysed *in situ* by shining onto the cavity ultra-violet light from a 1 kW high pressure mercury–xenon lamp, whose infrared component was removed by inserting a water-filled quartz window in the optical path. Unless otherwise stated all the spectra were recorded in the temperature range −30 to 0 °C.

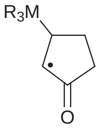
The EPR spectrometers were coupled to computers and the results were digitised and recorded using a spectral manipulation program. This allowed the spectra to be Fourier filtered and smoothed, if necessary, before interpretations were carried out.

Results and discussion

Triphenylgermyl and tris(trimethylsilyl)silyl radicals provided detectable adducts with most of the investigated enones but we had less success with triphenylsilyl radicals. For the sake of simplicity, we shall consider the results for each enone in turn.

Radicals from cyclopentenones

Cyclopent-2-en-1-one. Triphenylgermyl addition to cyclopent-2-en-1-one gives a spectrum consisting of four sets of triplets which we assign to the adduct **Ia** ($MR_3 = GePh_3$).



Ia-c

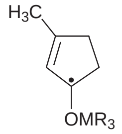
	MR_3	$a(H^2)$	$a(H^3)$	$a(2H^5)$	g
Ia	$GePh_3$	15.9	33.1	3.0	2.0043_0
Ib	$SiPh_3$	15.9	36.0	3.7	2.0043_5
Ic	$Si(SiMe_3)_3$	15.8	37.4	3.8	2.0044_4

The two large doublets indicate that addition to position 3 has occurred, in line with the g-factor of 2.0043, characteristic of a radical centre adjacent to a carbonyl group. The assignment of the triplet splitting to the hydrogen atoms in position 5 is consistent with partial delocalisation of the unpaired electron onto the carbonyl group, and has been confirmed by INDO calculations. However any such delocalisation must be small as the 15.9 G coupling in position 2 is similar to that in normal allyl radicals. The large splitting (33 G) from position 3 indicates a conformation in which the hydrogen is in a near axial position. Upon replacement of the germanium hydride with triphenylsilane or tris(trimethylsilyl)silane, cyclopent-2-en-1-one also leads to analogous adducts (adducts **Ib** and **Ic**, respectively) exhibiting weaker but similar spectra.

In all cases, upon warming the system, the spectra decreased in intensity until only noise remained. If migration of the organometallic units occurred a build up of secondary signals would be expected as the primary signals decreased, but nothing was observed. In order to check whether this had to be attributed to depletion of the original samples over time, the experiments were repeated by warming identical new samples to 60–70 °C before beginning photolysis. Even under these conditions no signals were detected, so no evidence of either the occurrence of carbon to oxygen migration or the direct formation of oxygen adducts can be reported.

3-Methylcyclopent-2-en-1-one. The presence of a methyl group in the 3-position is of interest as that seems to be the favoured point for addition. The spectra obtained were fairly noisy but the lines were narrow and the spectral structure was clearly visible.

The hyperfine couplings determined for the three adducts were as expected for an allylic system, and the spectra have been assigned to radicals **IIa**–**c** resulting from oxygen addition. The lower values of the g-factors exhibited by these adducts with respect to **Ia**–**c** reflect a lower spin density on oxygen, and are therefore consistent with the structure proposed for the former adducts. The assignment of the two triplet splittings of *ca.* 18 G is consistent with molecular orbital calculations but could well be reversed.

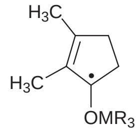


IIa-c

	MR_3	$a(H^2)$	$a(3H^3)$	$a(2H^4)$	$a(2H^5)$	g
IIa	$GePh_3$	2.7	15.4	18.0	18.0	2.0028_7
IIb	$SiPh_3$	2.9	15.0	18.5	17.7	2.0029_0
IIc	$Si(SiMe_3)_3$	2.3	15.3	18.1	18.0	2.0029_4

The observation of the oxygen adducts suggests that the presence of a methyl group in the 3-position has prevented the addition that was favoured for the unsubstituted species. Because of steric hindrance redirection of the addition to the 2-position might have been anticipated, and it could be thought that radicals **IIa**–**c** resulted from a rearrangement of such adducts. On this basis we would expect that sufficient cooling might allow the latter carbon adduct to be detected. However, the above spectra were observed at −30 °C, and when the system was further cooled to around −90 °C the oxygen adducts were still observed. It would thus appear that the system shows no tendency for carbon-2 addition.

2,3-Dimethylcyclopent-2-en-1-one. Quite surprisingly, we only obtained rather poor spectra upon reaction of triphenylgermyl radicals with this compound, and their interpretation was questionable. On the other hand, much better and unambiguously interpretable spectra were obtained with silyl radicals, which were assigned to adducts **IIIb** and **IIIc**.



IIIa-c

	MR_3	$a(3H^2)$	$a(3H^3)$	$a(2H^4)$	$a(2H^5)$	g
IIIa	$GePh_3$	2.6	14.8	18.6	17.6	2.0029_0
IIIb	$SiPh_3$	2.9	15.2	19.5	17.9	2.0029_0
IIIc	$Si(SiMe_3)_3$	2.8	15.1	18.9	17.6	2.0028_5

The close similarity between the hfs constants measured for radical adducts **IIa**,**c** and **IIIb**,**c** suggests that also in the latter cases addition has occurred at the carbonyl group. Of course the presence of a second methyl group in the 2-position made the oxygen attack easily foreseeable. The value in the Table also supports the tentative identification of the species resulting from germyl addition as adduct **IIIa**.

4,4-Dimethylcyclopent-2-en-1-one. This system, which is of interest in terms of the effect that the steric hindrance exerted by two adjacent methyl groups may have on addition to the 3-position, behaved differently from the three pentenones dealt

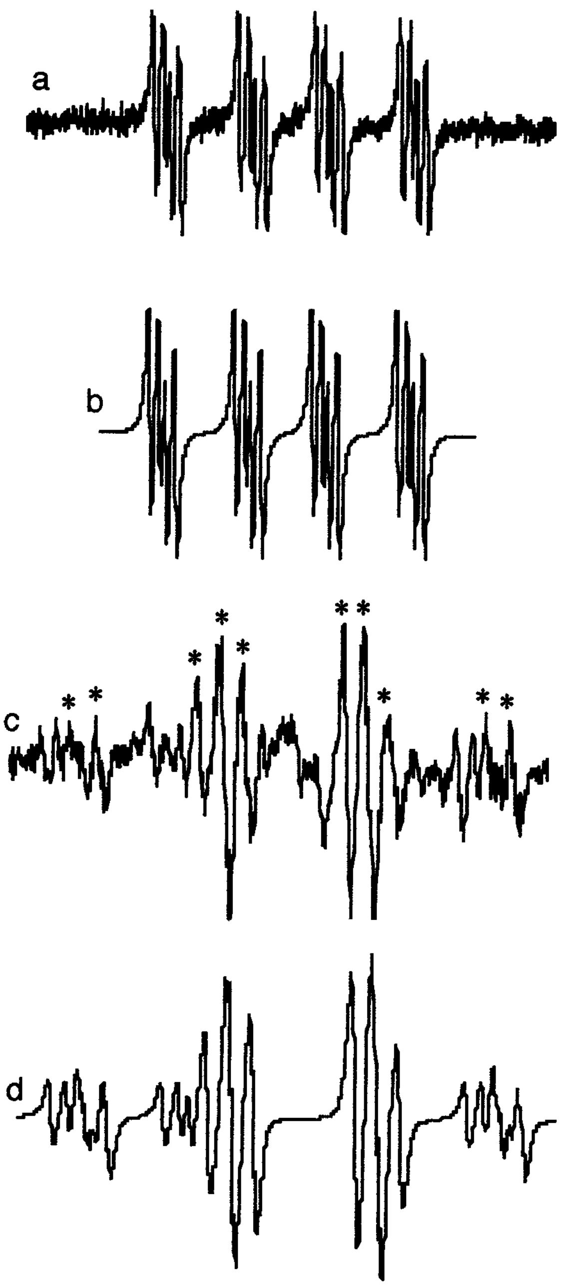
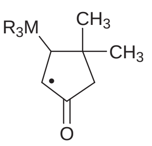
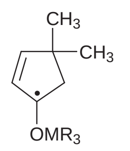


Fig. 1 Experimental and simulated spectra of the adducts formed by addition of triphenylgermyl radicals to 4,4-dimethylcyclopent-2-en-1-one at −30 °C (a, b) and at 75 °C (c, d). The starred lines are due to adduct **Va**.



IVa,b



Va-c

	MR$_3$	$a(\mathrm{H}^2)$	$a(\mathrm{H}^3)$	$a(6\mathrm{H}^4)$	$a(2\mathrm{H}^5)$	g	T/°C
IVa	GePh$_3$	16.2	30.8	—	1.9, 3.1	2.0043_0	−30
IVa	GePh$_3$	13.1	35.5	—	2.0, 3.2	2.0043_0	75
IVb	SiPh$_3$	14.0	34.9	—	2.0, 3.1	2.0043_5	−30
Va	GePh$_3$	2.4	14.2	0.4	17.1	2.0027_0	75
Vb	SiPh$_3$	2.6	14.0	n.r.[a]	17.6	2.0027_6	75
Vc	Si(SiMe$_3$)$_3$	2.5	14.4	n.r.[a]	16.9	2.0029_5	25

[a] Not resolved.

with so far. Actually, while $[(CH_3)_3Si]_3Si^{\bullet}$ added exclusively to the oxygen atom of the carbonyl group to give adduct **Vc**, $Ph_3Ge^{\bullet}$ and $Ph_3Si^{\bullet}$ radicals exhibited a marked temperature dependent selectivity of the site of attack. In fact, at the lower temperature (*ca.* −30 °C) their radical adducts exhibited hfs constants and *g*-factor values typical of species resulting from addition to the 3-position of the carbon–carbon double bond (adducts **IVa** and **IVb**), whereas the room temperature spectra were dominated by signals centred at higher field (lower *g*-factors) and conceivably due to the oxygen adducts (adducts **Va** and **Vb**, see Fig. 1). It should also be noted that the two larger hfs constants exhibited by adducts **IVa** and **IVb** proved very temperature dependent, probably because of different conformational preferences at different temperatures.

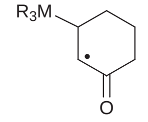
Although the amount of the ring adducts **IVa** and **IVb** decreases and that of **Va** and **Vb** increases as the temperature is raised, the oxygen adducts cannot originate from a rearrangement of the former adducts, because a 1,4 intramolecular migration of the MR$_3$ fragment would involve a five-membered cyclic transition state. As was the case for adducts **II** and **III**, there is also no evidence that adducts **Va**,**b** should be formed through a rearrangement *via* a 1,3 migration of the MR$_3$ fragment in the undetected adducts resulting from addition of the organometallic radicals to the 2-position of the ring, the rearrangement being too fast to allow the detection of the initially formed ring adducts.

The present results, instead, further substantiate that addition to the carbon–carbon double bond is easier than that to the carbon–oxygen double bond, although the latter is thermodynamically favoured. At the lower temperatures the addition is kinetically controlled, and only occurs at position 3 despite the presence of two methyl groups in the 4-position. As the temperature is raised, addition to the carbonyl oxygen becomes increasingly competitive and the formation of adducts **Va**,**b** is favoured. The two methyl groups in the 4-position seem, however, a large enough obstacle to the addition of the $[(CH_3)_3Si]_3Si^{\bullet}$ radical to the adjacent 3-position, which is in fact redirected to the carbonyl oxygen.

2,3,4,5-Tetramethylcyclopent-2-en-1-one. Strong, very broad and asymmetric spectra were obtained, no matter what the nature of the attacking species. They could not be successfully explained but they are certainly not straightforward adducts of the organometallic radicals.

Radicals from cyclohexenones

Cyclohex-2-en-1-one. The addition of triphenylgermyl radicals to cyclohex-2-en-1-one leads to the observation of a spectrum confirming that addition to the 3-position is favoured for an unsubstituted enone.



VIa-c

	MR$_3$	$a(\mathrm{H}^2)$	$a(\mathrm{H}^3)$	g
VIa	GePh$_3$	17.9	38.7	2.0043_0
VIb	SiPh$_3$	16.2	38.9	2.0043_9
VIc	Si(SiMe$_3$)$_3$	15.0	39.3	2.0044_0

The addition of triphenylsilyl and tris(trimethylsilyl)silyl radicals to cyclohex-2-en-1-one was less facile but was achieved by recording the spectrum extremely quickly after initial photolysis. Warming of the sample led to no change except depletion of the primary signal. In all cases the spectra exhibited rather broad lines, this being probably due to an unresolved splitting from the two hydrogen atoms in the 6-position.

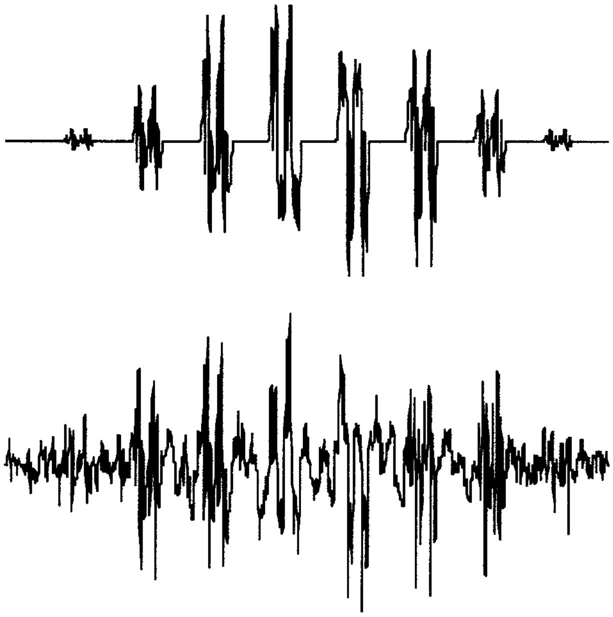
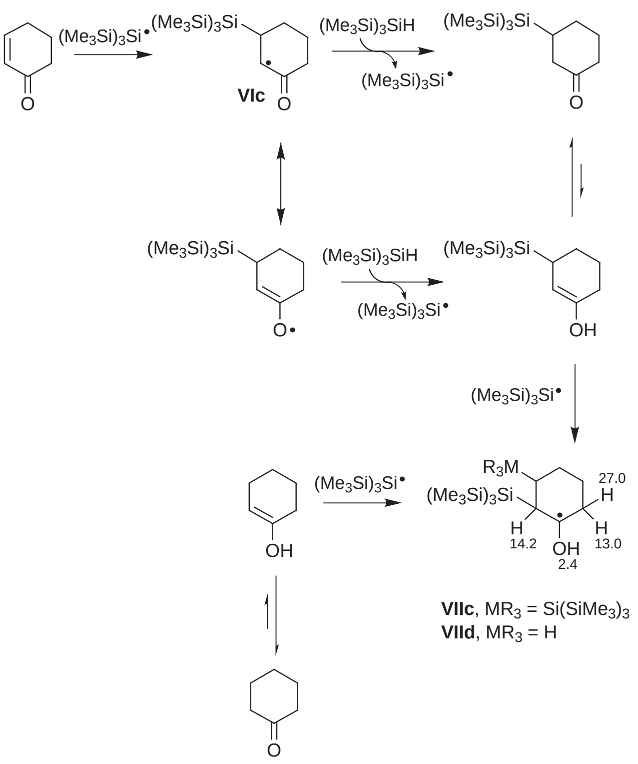


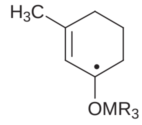
Fig. 2 Experimental spectrum and simulation of adduct **VIIIa** obtained by the addition of triphenylgermyl radicals to 3-methylcyclohex-2-en-1-one at −50 °C.



The prolonged reaction of cyclohex-2-enone with tris(trimethylsilyl)silane eventually led to the replacement of the first observed spectrum by a new one which could be interpreted in terms of the coupling of the unpaired electron with four different hydrogen atoms ($a_H = 2.4$ G, $a_H = 13.0$ G, $a_H = 14.1$ G, $a_H = 27.0$ G) and with a low *g*-factor (2.0028_0). Although the *g*-factor suggests oxygen addition, the measured hfs splitting constants can hardly be reconciled with the oxygen adduct of cyclohex-2-enone.

In view of the fact that tris(trimethylsilyl)silane is known to be a very efficient radical-based reducing agent,[8–10] cyclohexanone was allowed to react with the organometallic hydride under similar conditions. Interestingly, a spectrum was observed which was characterised by spectral parameters very similar to those of the radical observed at the end of the reaction of cyclohex-2-enone, and consistent with an adduct having structure **VII**. 3-[Tris(trimethylsilyl)silyl]cyclohex-1-enol can be formed by hydrogen abstraction from tris(trimethylsilyl)silane by the mesomeric form of radical adduct **VIc** formally bearing the unpaired electron on the oxygen atom. Although it is known that the keto–enolic tautomerism in cyclohexanone is largely shifted towards the ketonic form,[11] the silyl radicals might also react with the small fraction of the enolic form present at each time in order to afford radicals **VII**.

3-Methylcyclohex-2-en-1-one. The presence of a methyl group in the 3-position of the six-membered ring leads, upon addition of triphenylgermyl radicals, to the observation of a considerably more complex EPR signal than observed with the unsubstituted derivative (see Fig. 2). Despite the fact that it is fairly weak, the spectrum could be nicely simulated using hyperfine coupling constants consistent with addition of the germyl moiety to the carbonyl oxygen.

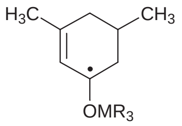


VIIIa-c

	MR_3	$a(H^2)$	$a(3H^3)$	$a(2H^4)$	$a(2H^5)$	$a(2H^6)$	*g*
VIIIa	$GePh_3$	3.1	14.5	14.6	0.9	14.6, 15.0	2.0029_0
VIIIb	$SiPh_3$	Weak and asymmetric—not interpreted					
VIIIc	$Si(SiMe_3)_3$	3.3	14.7	14.7	0.9	15.0	2.0028_0

The identification of the adduct as radical **VIIIa** is further supported by the low *g*-factor, a value which is in fact very close to those exhibited by the corresponding oxygen adducts of the cyclopentenones. We were unable to interpret the weak and asymmetric spectrum which was obtained on adding triphenylsilyl radicals to 3-methylcyclohex-2-en-1-one. A well defined and resolved spectrum of adduct **VIIIc** was instead obtained with tris(trimethylsilyl)silyl radicals.

3,5-Dimethylcyclohex-2-en-1-one. When triphenylgermane was added to 3,5-dimethylcyclohex-2-en-1-one, a strong complex spectrum was observed which exhibited coupling of the unpaired electron with virtually all the hydrogens present in the enone, with the exception of those in the 5-position. Once again, its spectral parameters indicated that the radical adduct derived from oxygen addition and was therefore identified as adduct **IXa**. It should be noticed that in this adduct the six-membered ring deviates significantly from planarity, the hyperfine splittings of the pairs of hydrogens in the 4- and 6-positions being indicative of pseudo-equatorial and pseudo-axial arrangements.



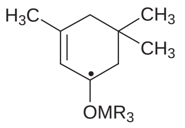
IXa-c

	MR_3	$a(H^2)$	$a(3H^3)$	$a(2H^4)$	$a(2H^6)$	*g*
IXa	$GePh_3$	3.1	14.7	7.3, 21.2	6.6, 22.6	2.0029_0
IXb	$SiPh_3$	Weak and asymmetric—not interpreted				
IXc	$Si(SiMe_3)_3$	Weak and asymmetric—not interpreted				

The couplings from the protons in positions 4 and 6 could be interchanged.

As was the case with 3-methylcyclohex-2-enone, the reaction with silyl radicals only led to very weak, asymmetric and uninterpretable spectra. Although the apparent *g*-factors of these radicals suggest we are still dealing with oxygen adducts, a definite identification of adducts **IXb** and **IXc** was not possible. As might have been anticipated, it is evident that the introduction of a further methyl group on carbon-5 has little effect on the stability of the adducts.

3,5,5-Trimethylcyclohex-2-en-1-one. Although the presence of a further methyl group in the 5-position did not greatly affect the spin density distribution within the adducts, as could be inferred by comparing the spectral parameters for adducts **IXa** and **Xa**, it led to more intense spectra for the silyl adducts **Xb** and **Xc**.



Xa-c

	MR_3	$a(H^2)$	$a(3H^3)$	$a(2H^4)$	$a(2H^6)$	g
Xa	$GePh_3$	3.0	14.6	21.6, 7.7	22.6, 7.0	2.0029_0
Xb	$SiPh_3$	3.2	14.4	22.5, 7.7	22.9, 6.5	2.0028_3
Xc	$Si(SiMe_3)_3$	3.1	14.8	14.7	15.0	2.0028_2

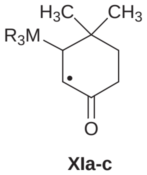
The couplings from the protons in positions 4 and 6 could be interchanged.

The spectrum from **Xc** was however rather peculiar, as, at variance with those from **Xa** and **Xb**, it exhibited a marked linewidth alternation and could only be rationalised by assuming that the hydrogens in the 4- and 6-positions exchanged from the pseudo-axial to the pseudo-equatorial position with a frequency comparable to the difference of the splittings of the limiting situations.

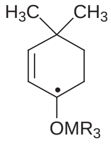
Because the slow inversion region where the two hydrogens were clearly differentiated could not be attained, several pairs of couplings and an appropriate exchange rate could be used to satisfactorily reproduce the experimental spectrum. We therefore report for adduct **Xc** the average value of the two splittings.

4,4-Dimethylcyclohex-2-en-1-one. While the site-selectivity of the addition of triphenylgermyl and triphenylsilyl radicals to this compound proved extremely temperature dependent, only one radical adduct could be detected in the reaction with tris(trimethylsilyl)silyl radicals.

Thus at low temperature the spectra of the $Ph_3Ge^•$ and $Ph_3Si^•$ adducts consisted of only four lines and were characterised by g-factor values close to 2.0040. They were in fact very similar to those of adducts **VIa**,**b** observed in the reaction of the same organometallic radicals with the unsubstituted cyclohex-2-enone, thus indicating that addition had occurred to the ethylenic double bond. It may be worth noting that the β splitting in adducts **XIa** and **XIb** is 13 to 14 G lower than that observed in **VIa** and **VIb**, while the α splittings are very similar in the four adducts.



XIa-c



XIIa-c

	MR_3	$a(H^2)$	$a(H^3)$	$a(6H^4)$	$a(2H^6)$	g	T/°C
XIa	$GePh_3$	15.7	24.5	—	—	2.0040_1	−40
XIb	$SiPh_3$	16.01	25.8	—	—	2.0040_3	−40
XIc	$Si(SiMe_3)_3$			Not observed			
XIIa	$GePh_3$	3.9	14.1	0.6	31.6, 0.1	2.0029_4	75
XIIb	$SiPh_3$	3.4	14.2	0.7	31.8, 0	2.0029_3	75
XIIc	$Si(SiMe_3)_3$	3.2	14.3	0.7	30.0, 0	2.0029_0	75

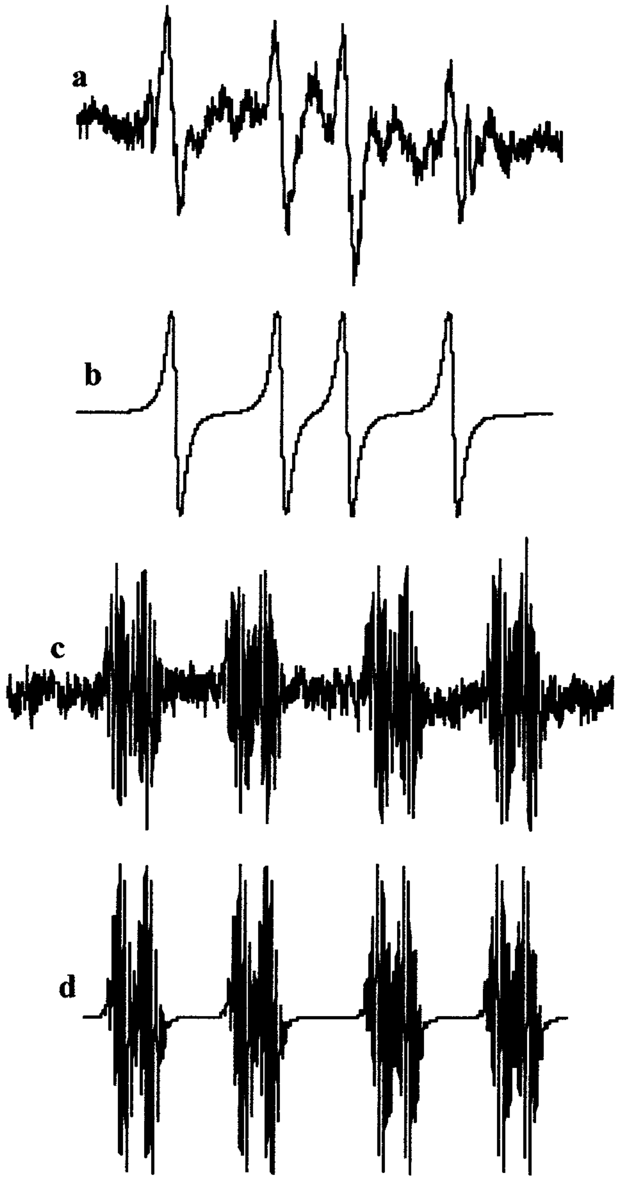


Fig. 3 Experimental spectra and simulations obtained by the addition of triphenylsilyl radicals to 4,4-dimethylcyclohex-2-en-1-one at low (a, b) and high temperature (c, d).

This different conformational preference must be the consequence of the presence of the two methyl groups on carbon-4, which push the bulky organometallic groups towards an axial position, thus compelling the β-hydrogen to adopt a more equatorial arrangement.

The reaction of 4,4-dimethylcyclohex-2-enone with the three organometallic radicals at or above room temperature resulted in the detection of more complex spectra, characterised by much lower g-values. The spectra, which were very similar for the three attacking radicals, were assigned to radical adducts **XIIa**–**c** resulting from oxygen addition. The spectra of the triphenylsilyl adducts **XIb** and **XIIb** are shown in Fig. 3 along with their computer simulations. The spectra are made up of eight main groups that are accounted for by a large (30 G) doublet and two smaller (3 and 14 G) ones. The latter are typical of an allylic system, while the *ca.* 30 G doublet is attributed to one of the hydrogens of the methylene group in the 6-position, the other having a vanishingly small splitting.

General remarks

All of the investigated cyclopentenones and cyclohexenones led to the observation of rather weak spectra. This is probably because these compounds are readily photodegraded by reactions such as fragmentation of the carbon–carbon bond adjacent to the carbonyl group which is not involved in the enonic system. Actually, the presence of the double bond conjugated to the carbonyl group may somewhat slow down the Norrish 1 fragmentation of these molecules with respect to saturated cycloalkanones. The possibility of hydrogen abstraction by the excited triplet state of the enone from the organometallic hydrides cannot be discounted but we were unable to observe any EPR spectra of the hydrogen adducts when we photolysed mixtures of the enone and a silane or germane in the absence of di-*tert*-butyl peroxide. Since the latter was generally present in excess in our experiments we do not feel that the contribution of the triplet state is very significant.

At the lower temperatures, as might have been anticipated, the 3-position is the preferred site of addition of the attacking radicals, unless it is substituted or sterically hindered. At higher temperatures, on the other hand, attack occurs at the carbonyl oxygen indicating that the addition reaction switches to a thermodynamic control. The carbonyl oxygen is also the favoured site of attack when position 3 is substituted or hindered. No evidence of addition occurring at the 2-position of the carbon–carbon double bond could be obtained with any of the investigated substrates, nor of the oxygen adducts being formed *via* an intramolecular migration following initial attack at the 3- or 2-position.

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