Free radicals from cyclic enones: an electron paramagnetic resonance investigation. Part 1. Radicals formed by hydrogen abstraction†

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Electron paramagnetic resonance has been used to characterise free radicals formed by the reaction of photochemically generated *tert*-butoxyl radicals with a range of methyl substituted cyclopentenones and cyclohexenones. The spectra have been interpreted using computer analysis and simulation and assigned to cyclic allylic and alkyl radicals formed by abstraction of a hydrogen atom. The 1-oxocyclohept-2-en-4-yl radical derived by abstraction of bromine from 4-bromocyclohept-2-enone exhibits a temperature dependent EPR spectrum attributed to ring inversion.

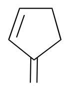
Introduction

The role of anthropogenic and natural biogenic hydrocarbons in tropospheric chemistry[1] has been the subject of much recent research. It is our aim to characterise by EPR spectroscopy radicals formed by hydrogen abstraction from and radical addition to biogenic VOCs (volatile organic compounds) implicated in atmospheric processes; we have already described some radicals derived from monoterpenes.[2] The present paper describes some radicals formed by hydrogen abstraction from cyclic enones designed to provide a set of reference data for cyclic allyl radicals. These data should be useful in interpreting the complicated, and often weak, spectra obtained from natural products.

Experimental

Materials

Cyclopent-2-enone **1**, 3-methylcyclopent-2-enone **2**, 2,3-dimethylcyclopent-2-enone **3**, 2,3,4,5-tetramethylcyclopent-2-enone **4**, 4,4-dimethylcyclopent-2-enone **5**, cyclohex-2-enone **6**, 3-methylcyclohex-2-enone **7**, 3,5-dimethylcyclohex-2-enone **8**, 3,5,5-trimethylcyclohex-2-enone **9** and 4,4-dimethylcyclohex-2-enone **10** were purchased from Aldrich, as was di-*tert*-butyl peroxide. 4-Bromocyclohept-2-enone **11** was prepared as follows.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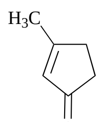
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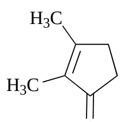
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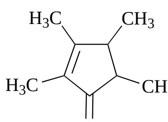
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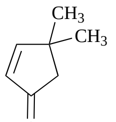
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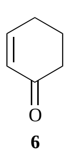
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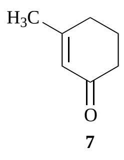
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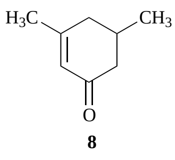
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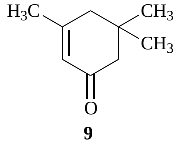
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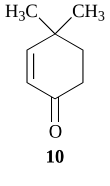
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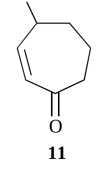
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4-Bromocyclohept-2-enone 11. Cyclohept-2-enone (Aldrich) (0.506 g, 4.53 mmol), *N*-bromosuccinimide (0.858 g, 4.82 mmol) and dibenzoyl peroxide (Fluka) (0.014 g, 0.057 mmol) were dissolved in 6 ml of carbon tetrachloride and refluxed with stirring for 90 min. The mixture was then cooled, filtered and the filtrate was evaporated under reduced pressure. The residue was chromatographed over silica gel using methylene chloride as eluent. After removing the solvent, pure 4-bromocyclohept-2-enone **11** was obtained (0.7 g, 3.7 mmol, 81%), δ_H(CDCl$_3$, internal ref. TMS, *J*/Hz) 1.7 to 2.9 (6H, m), 4.97 (1H, q, H-4, J_{4-3} 5.1, J_{4-5} 5.0), 5.88 (1H, d, H-2, J_{2-3} 12.6), 6.48 (1H, dd, H-3, J_{3-2} 12.6, J_{3-4} 5.1); *m*/*z* 190, 188 (M$^+$), 109 (M$^+$ − Br), 81 (M$^+$ − Br − CO).

EPR experiments

The spectra were recorded on Bruker ER-200D and Varian E104 spectrometers using previously described procedures.[3] The enones were mixed with di-*tert*-butyl peroxide in a ratio of 1 : 3 by volume, in quartz EPR tubes. Oxygen was removed by purging the solutions with nitrogen for between 5 and 20 min and then cooled to between −45 and −50 °C. The solutions were photolysed *in situ* by focusing ultraviolet light from a 1 kW high pressure mercury–xenon lamp into the cavity. Infrared radiation was removed by passing the light through a water-filled quartz window.

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

Radicals from cyclopentenones

Only abstraction from the 4-position in cyclopent-2-enone **1** will produce a radical that is allylic in character. Fig. 1 shows the spectrum obtained along with a simulation. The assignment is straightforward. The coupling constants of the allylic moiety are much as expected;[4] the rather small coupling to the methylene group is noteworthy and will be the subject of later discussion. An alternative description would be to regard the system as an oxapentadienyl radical but the coupling constants suggest that the radical is best regarded as carbon-centred and

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† Presented at the 30th International Meeting of the Electron Spin Resonance Group of the RSC, University of Lancaster, 6–10th April 1997.

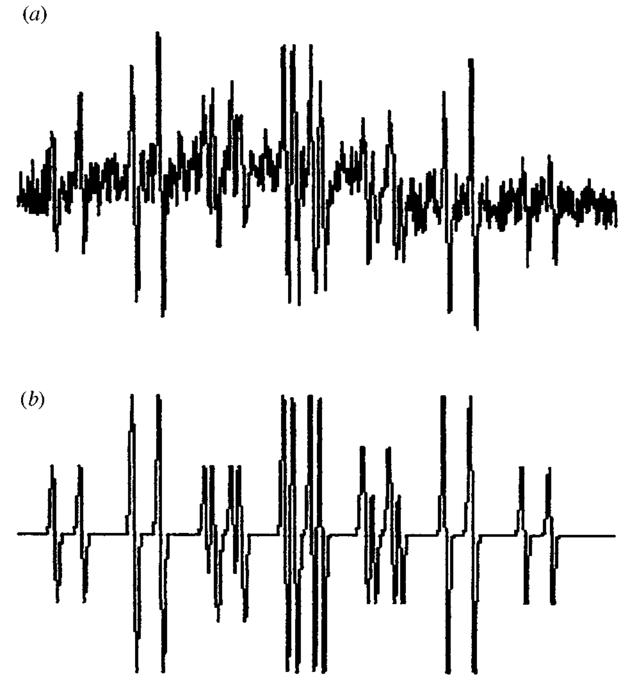
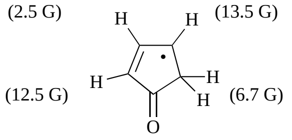
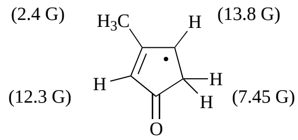


Fig. 1 The experimental EPR spectrum of the radical obtained by hydrogen abstraction from cyclopent-2-enone (*a*) and the computer-simulated spectrum of the 1-oxocyclopent-2-en-3-yl radical (*b*)

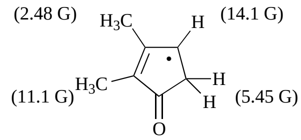
essentially allylic with some delocalisation onto the carbonyl group.



The radical formed by hydrogen abstraction from 3-methylcyclopent-2-enone **2** supports the above interpretation of the cyclopent-2-enone radical. The presence of a well resolved 2.4 G quartet in the EPR spectrum clearly indicates that abstraction has occurred from the 4-position and not from the 3-methyl group. In the case of 2,3-dimethylcyclopent-2-enone, the



introduction of a further methyl group produces some variation in the couplings.



The methyl group in the 2-position has a coupling of 11.1 G which is less than is observed for an α-hydrogen in the same position. Similarly the α-hydrogen coupling in the 4-position is slightly larger than the previous couplings. This indicates some shifting of the electron density away from the 2-position. We also note the lower (5.45 G) splitting from the methylene hydrogens. However, the couplings in the radical from 2,3,4,5-tetramethylcyclopent-2-enone are much as expected. The substrate in this case was actually a mixture of isomers in which the 4- and 5-methyl groups are *cis* and *trans* to each other but both will yield the same radical on abstraction of hydrogen from the 4-position.

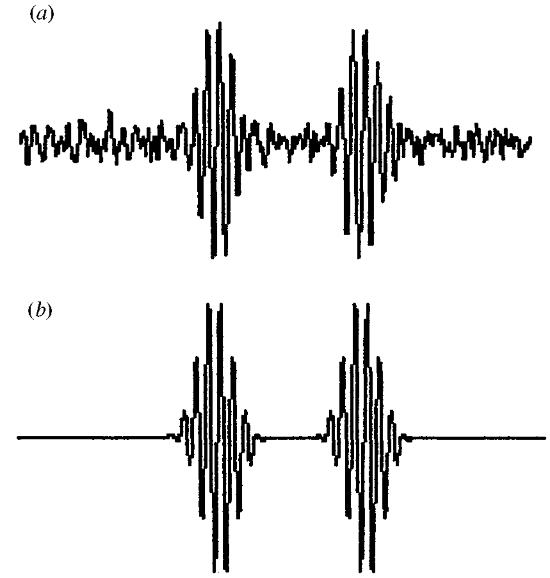
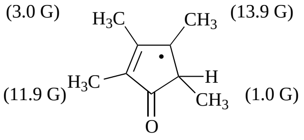
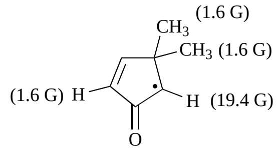


Fig. 2 Experimental EPR spectrum of the radical formed by hydrogen abstraction from 4,4-dimethylcyclopent-2-enone (*a*) and the computer-simulated spectrum of the 4,4-dimethyl-1-oxocyclopent-2-en-5-yl radical (*b*)



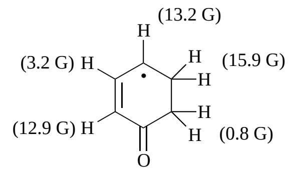
The final example containing a five-membered ring is 4,4-dimethylcyclopent-2-enone. Hydrogen abstraction in this case is distinctive since the system has no abstractable hydrogens which will form an allylic system. Fig. 2 shows the spectrum and simulation. The following parameters were assigned to the radicals as shown.



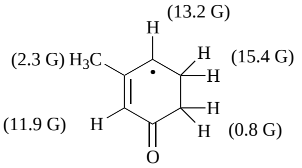
The α-proton coupling of 19.4 G is comparable with that observed in the acetonyl radical.[5]

Radicals from cyclohexenones

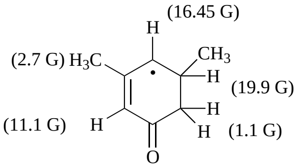
As expected, cyclohex-2-enone forms an allylic radical by abstraction of hydrogen from the 4-position. The allylic couplings are comparable with those found in five-membered rings but the methylene coupling is much larger than the 6–8 G observed in the cyclopentenone radicals. This difference is an example of the effect of orbital symmetry on methylene hyperfine couplings as was first explained by Whiffen.[6] He showed that the proton hyperfine splitting for a CH_2 group bridging two π-centres depends on $(c_1 + c_2)^2$ where c_1 and c_2 are the linear combination of atomic orbital (LCAO) coefficients of the neighbouring π-centres in the singly occupied molecular orbital (SOMO). In the cyclopentenone radicals we have a π-system over five centres with the methylene group spanning C1 and C4.



In a pentadienyl radical C1 would be at a nodal position in the SOMO. However, simple Huckel calculations show that replacing the terminal carbon in pentadienyl by oxygen leads to a SOMO in which the coefficients at positions 1 and 4 are of opposite sign, thus explaining the small coupling. An analogous situation has recently been noted in the spectra of some 1,2-indansemidiones and we refer to Strom's paper[7] for a more detailed discussion. In the six-membered ring the methylene coupling depends only on the spin density on C4 and a normal value is observed. A similar pattern of coupling constants is found for the radical derived from 3-methylcyclohex-2-enone.

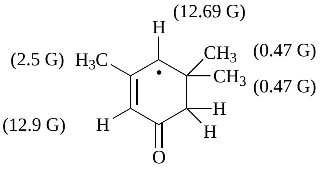


In 3,5-dimethylcyclohex-2-enone the hydrogens in the 4-position are still abstractable to form a delocalised radical.

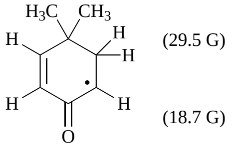


The splittings suggest that spin density has shifted away from the 2-position and towards the 4-position as illustrated by the imbalance of the couplings of the two hydrogens of 11.1 G and 16.45 G. The 2.7 G coupling from the 3-methyl group is unexceptional. The hydrogen coupling of 19.9 G in the 5-position indicates a conformation in which the hydrogen is in an out-of-plane position. The triplet of 1.1 G is comparable with that attributed to other hydrogens in the 6-position.

Isophorone, 3,5,5-trimethylcyclohex-2-enone, introduces a further methyl group in the 5-position. Computer simulation leads to the assignment shown. Enlarging the detail of the spectrum reveals the presence of a further septet splitting of 0.47 G. This splitting is assigned to the magnetically equivalent methyl groups on the 5-position carbon. The hydrogens in the 6-position do not appear to give a resolvable coupling although they might have been expected to exhibit an interaction of comparable size to the methyl groups. We report no coupling for the two hydrogens as the seven line group of intensities 1 : 6 : 15 : 20 : 15 : 6 : 1 fits considerably better than a group of nine lines with ratios 1 : 8 : 28 : 56 : 70 : 56 : 28 : 8 : 1 that would be produced by eight protons.



Finally we consider the six-membered ring analogue of 4,4-dimethylcyclopent-2-enone. 4,4-Dimethylcyclohex-2-enone gives a simple six line spectrum consisting of a doublet of triplets. As expected the β-hydrogens are producing the largest coupling.



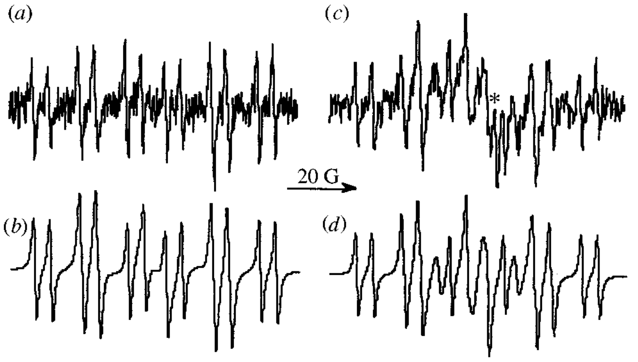
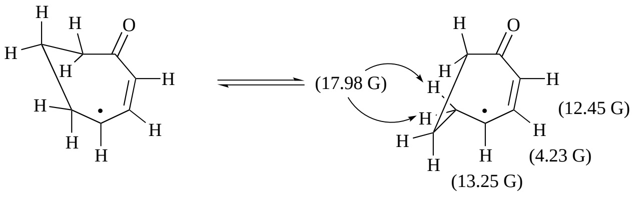


Fig. 3 Experimental EPR spectra obtained by bromine abstraction from 4-bromocyclohept-2-enone at −40 °C (*a*) and at room temperature (*c*) and computer-simulated spectra of the 1-oxocyclohept-2-en-4-yl radical [(*b*) and (*d*)]. The line marked with an asterix in spectrum (*c*) is due to an impurity of the sample tube.

Radical from cycloheptenone

Photolysis of a deoxygenated di-*tert*-butyl peroxide solution of cyclohept-2-enone in the temperature range −50 to 0 °C failed to afford any detectable EPR signal. On the other hand, photolysis of argon purged *tert*-butylbenzene solutions of 4-bromocyclohept-2-enone containing some hexabutylditin led to spectra whose pattern varied drastically with temperature (see Fig. 3) and which, although very weak, could be attributed to the cyclic allyl radical resulting from bromine abstraction.



The room temperature spectrum results from coupling of the unpaired electron with the protons in positions 2, 3 and 4 and with the two protons in position 5 which appear to be equivalent, owing to inversion of the cycloheptenyl ring at a rate which is fast compared with the difference in hyperfine coupling constants. At lower temperatures the inversion process slows down and the *ca.* 18 G triplet is replaced by a *ca.* 36 G doublet. This new doublet is in fact the sum of the couplings of the two protons in positions 5 when the rate of inversion is not fast enough to make them equivalent and yet not slow enough to make them completeley inequivalent. The computer simulation of the spectra at the different temperatures would allow the determination of the energy barrier to inversion, provided the couplings of the two exchanging atoms are known for the slow exchange limit. Unfortunately such determination was impossible. In fact, further lowering of the temperature resulted in the disappearance of the spectrum, and it proved impossible to reach a situation when the inversion is completely frozen out thus allowing the determination of the couplings of the two individual hydrogens. However, we were able to obtain spectra at 263, 273, 300 and 313 K and simulate them, assuming that the coupling constants exchange between values of 0 and 36 G. An Arrhenius plot then leads to an activation energy of *ca.* 7 kcal mol^{-1}. This procedure yields the correct barrier but not the preexponential factor provided the spectra are in the fast exchange region where the broadening is proportional to Δa^2.

There do not seem to be any comparable systems containing seven-membered rings in which ring inversion has been investigated; it may be worth noting that the cycloheptyl radical is much more flexible,[8] owing to the absence of the C=C double bond. The closest analogy is with the cyclohex-3-enyl radical where studies of line-width alternation have yielded a barrier for ring inversion of about 30 kJ mol^{-1}.[9,10] In that case the allylic system is essentially rigid and the hydrogen atoms in positions 4 and 6 are rendered magnetically equivalent by inversion of the methylene group in the 5-position through the C1–C2–C3 plane.

Conclusions

We have shown that it is possible to observe and analyse EPR spectra from primary radicals formed by hydrogen abstraction from a series of cyclic enones. In general the single species observed is an allylic radical stabilised by electron delocalisation. In the absence of allylic hydrogen atoms acetonyl radicals are formed. A subsequent paper will describe a study of radical addition reactions to cyclopentenones and cyclohexenones.

Acknowledgements

We thank Dr R. A. Jackson and Dr Marco Lucarini for the use of their computer programmes, the EPSRC for the award of a research studentship to D. W., the University of Bologna for the award of a training grant to M. A. D. B., and CNR for the award to A. H. of a short-term mobility fellowship.

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Paper 7/02510F
Received 11*th April* 1997
Accepted 9*th July* 1997