

Formation of 9-Octalin (1,2,3,4,5,6,7,8-Octahydronaphthalene) Radical Cations on Adsorption of Acyclic Dienes onto H-Mordenite

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Following the adsorption of (*Z*)- or (*E*)-piperylene (penta-1,3-diene), penta-1,4-diene or hexa-1,5-diene onto H-mordenite, EPR signals characteristic of 9-octalin radical cations **1/6** were recorded. Comparative studies of these dienes were made in solid freon matrices which indicate that a dominant mechanism involving Brønsted acid catalysis is required to explain the main molecular transformations, prior to radical cation formation.

Activated zeolites are well known as heterogeneous catalysts able to promote the transformation of adsorbed organic molecules into hydrocarbon products of industrial relevance.¹ In particular, the strongly acidic hydrogen-exchanged forms of silica-rich zeolites, such as ZSM-5, are capable of cracking simple organic molecules into well-defined mixtures of higher molecular weight hydrocarbons, which fall into the gasoline range.¹ In the conversion of methanol to gasoline on H-ZSM-5, it has been proposed that the crucial, but mechanistically enigmatic, formation of the initial C–C bond involves the coupling of surface-generated radicals,² and in other studies, the observation of EPR signals following the adsorption of unsaturated organic molecules onto zeolites has been shown to be due to the formation of primary and oligomeric substrate radical cations.^{3–16} We recently reported that the 9-octalin radical cation is formed by the adsorption of cyclopentene onto H-mordenite,^{3,4} which clearly requires a considerable structural reorganisation involving two cyclopentene molecules to yield this 'dimeric' product. The present paper concerns our continuing study of H-mordenite and reports on the additional ability of this catalyst to promote the transformation of alicyclic dienes into the octalin cation.

Experimental

H-mordenite (200 mg) was activated by being heated in air for 3 h at 873 K, followed by evacuation at 573 K in an EPR tube attached to a vacuum line, at 10^{-4} mmHg, for 2 h. The tube was cooled to 195 K and the organic sample was introduced from its storage reservoir, after being degassed by freeze–pump–thaw cycles. Typically, the weight of the organic sample was 2–5% of the catalyst. The tube was sealed-off and transferred rapidly to the precooled variable-temperature insert in the cavity of the EPR spectrometer (Bruker ER 200D), or to a Bruker finger-Dewar filled with liquid nitrogen, which was then placed in the spectrometer cavity. The adsorbate samples were obtained from Aldrich, and were not further purified other than by degassing prior to adsorption onto the catalyst. A sample of N-mordenite ($\text{SiO}_2:\text{Al}_2\text{O}_3 = 10$) was obtained from British Petroleum. A deuterium-exchanged sample of H-mordenite was prepared by evacuation and adsorption of the excess of D_2O onto the zeolite from the gas phase, followed by drying at 773 K overnight prior to air activation.

In order to carry out comparative studies of radical cations in low-temperature freon matrices, solutions (0.1–5.0%) of the organic substrates in CFCl_3 (BDH) or $\text{CF}_2\text{ClCFCl}_2$ (Aldrich) were frozen at 77 K, and then γ -irradiated to a dose of 1 Mrad using a ^{60}Co source. EPR spectra were recorded, as above, using either Bruker ER 200D or Varian E9 spectrometers.

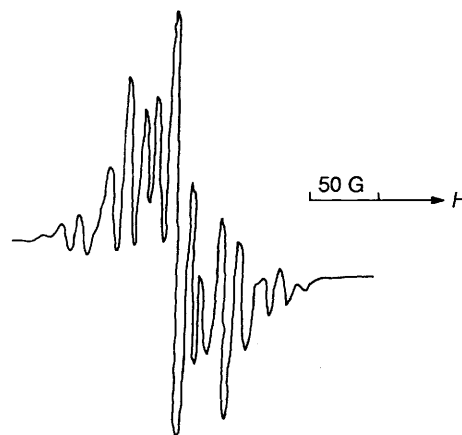
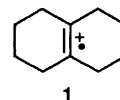


Fig. 1 EPR spectrum recorded at 77 K following adsorption of (*Z*)-piperylene on H-mordenite

Results and Discussion

Coupling constants for radicals measured in this work are collated in Table 1, along with values for related radicals which are taken from the literature.

(*Z*)- and (*E*)-Piperylene.—Following the adsorption of either diene onto H-mordenite at 195 K, weak signals developed slowly, which we were unable to assign with confidence. However, on raising the temperature to 295 K for several minutes, spectra almost identical in all respects with that shown in Fig. 1 were recorded after cooling to 77 K. As may be seen from Fig. 2, these are identical with that recorded from 9-octalin radical cations **1**, generated by γ -irradiation of an authentic



sample of 9-octalin in a CFCl_3 matrix at 77 K.^{3,4,17} Thus the situation is very similar to that of our previous investigation of the adsorption of cyclopentene on H-mordenite,^{3,4} which also formed **1**. In that study,⁴ we attempted to obtain the octalin structure *via* an ion–molecule reaction between authentic cyclopentene radical cations and cyclopentene neutral molecules in a CFCl_3 matrix by using a similar loading of cyclopentene as on the zeolite, and annealing. This procedure failed, however,

Table 1 Hyperfine coupling data for radicals discussed in the text

Radical	Couplings ^a	Medium	T/K
1	<i>a</i> (4 H) 37.0, <i>a</i> (4 H) 14.0	Mordenite	77
1	<i>a</i> (4 H) 37.3, <i>a</i> (4 H) 14.0	CFCl ₃	77
1	<i>a</i> (4 H) 37, <i>a</i> (4 H) 14	CFCl ₃ ^b	77
2	<i>a</i> (4 H) 50, <i>a</i> (2 H) 9	CFCl ₃	150
2	<i>a</i> (4 H) 50.9, <i>a</i> (13.4, <i>a</i> (3 H) 7.2	CFCl ₃	77
(<i>E</i>)-Pentadienyl	<i>a</i> (2 H) 9.69, <i>a</i> (2 H) 10.34, ^d <i>a</i> (2 H) 3.23, <i>a</i> (1 H) 11.64	Pentadiene solution	158
(<i>Z</i>)-Pentadienyl	<i>a</i> (1 H) 9.99, <i>a</i> (1 H) 10.65, ^d <i>a</i> (1 H) 12.74, <i>a</i> (1 H) 9.11, <i>a</i> (1 H) 8.43, <i>a</i> (1 H) 3.8, <i>a</i> (1 H) 3.17	Pentadiene solution	158
(<i>E</i>)-Penta-1,3-diene ⁺⁺	<i>a</i> (2 H) 7 G, <i>a</i> (3 H) 16	CFCl ₃	150
(<i>Z</i>)-Penta-1,3-diene ⁺⁺	<i>a</i> (2 H) 8, <i>a</i> (3 H) 16 <i>a</i> (3 H) 15.2, <i>a</i> (2 H) 10.4, <i>a</i> (1 H) 5.9	CFCl ₃ CF ₂ CICF ₂ Cl	150 108
Penta-1,4-diene ⁺⁺	<i>a</i> (6 H) 8	CFCl ₃	150
4	<i>a</i> (CH ₃) 13.9, <i>a</i> (2 H) 10.65, ^e <i>a</i> (1 H) 20.8, <i>a</i> (2 H) 3.6	CF ₂ CICF ₂ Cl	143
5	<i>a</i> (CH ₃) 16.4, <i>a</i> (1 H) 11.3, ^e <i>a</i> (2 H) 3.8, <i>a</i> (1 H) 14.9, <i>a</i> (1 H) 20.8	CF ₂ CICF ₂ Cl	128
Cyclohexane-1,4-diyl ⁺⁺	<i>a</i> (4 H) 11.8 ^f <i>a</i> (4 H) 11.5	CFCl ₃ CFCl ₃	77 77
Cyclohexene ⁺⁺	<i>a</i> (2 H) 54.0, <i>a</i> (2 H) 22.5 ^g <i>a</i> (2 H) 8.8 <i>a</i> (2 H) 53.6, <i>a</i> (2 H) 22.1 <i>a</i> (2 H) 8.3	CFCl ₃ CFCl ₃	77 77

^a $G = 10^{-4}$ T. ^b A. V. Vesolov, V. I. Melekhov, O. A. Anisimov, Yu. N. Molin, K. Ushida and T. Shida, *Chem. Phys. Lett.*, 1987, 133, 478. ^c C. J. Rhodes, *J. Chem. Soc., Faraday Trans.*, 1991, 3179. ^d R. Sustmann and H. Schmidt, *Chem. Ber.*, 1979, 112, 1440. ^e J. Fujisawa, T. Takayanagi, S. Sato and K. Shimokoshi, *Bull. Chem. Soc. Jpn.*, 1988, 61, 1527. ^f Q.-X. Guo, X.-Z. Qin, J. T. Wang and F. Williams, *J. Am. Chem. Soc.*, 1988, 110, 1974. ^g T. Shida, Y. Egawa and H. Kubodera, *J. Chem. Phys.*, 1980, 73, 5963.

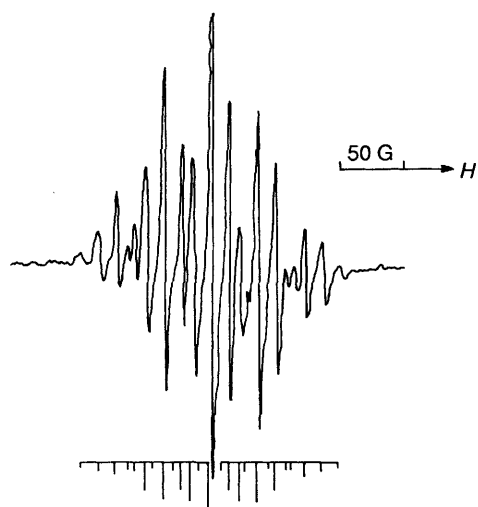
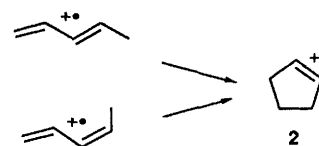


Fig. 2 EPR spectrum recorded at 77 K following γ -irradiation of a dilute solution of 9-octalin in a CFCl₃ matrix and assigned to the primary octalin radical cation

since only radicals formed by deprotonation (cyclopentenyl) or overall loss of H₂ (cyclopentadiene radical cations) were observed. Thus we conjecture that, in accord with conventional wisdom regarding the importance of Brønsted acidity in these zeolites,¹ the formation of the basic octalin structure is driven from an initial protonation of a cyclopentene molecule. At the outset, however, it must be emphasised that the physical properties of solid CFCl₃, as a matrix, must be quite different

from mordenite, and discrimination between different reaction pathways could operate through differential matrix effects which are known to affect profoundly certain radical cation transformations in different freon matrices.¹⁸ However, we can at least be sure that the primary radical cations are genuine species in an irradiated freon medium, and so such a comparative study is justified, even with this caveat.

Therefore, we have undertaken a study of the title isomeric dienes in solid CFCl₃ from which were recorded the spectra shown in Figs. 3 and 4. What is most interesting about these is the presence of wing features that can be unequivocally assigned to cyclopentene radical cations **2**, and so it appears that the



Scheme 1

reactions in Scheme 1 occur. In this regard, our results are in accord with those reported by Fujisawa *et al.*,¹⁹ but differ somewhat in that these workers observed no paramagnetic product other than **2** from either diene in a CFCl₃ matrix at 77 K, although the primary piperylene radical cations could be stabilised successfully by a CFCl₂CFCl₂ matrix at 77 K. In each of our spectra [Figs. 3(a), 4(a)] there is a considerable yield of a set of lines with a *central* feature, which are rather broad at 77 K but which sharpen on annealing to 150 K (Figs. 3(b), 4(b)). In view of the propensity of cyclopentane radical cations to deprotonate under similar conditions, we considered the

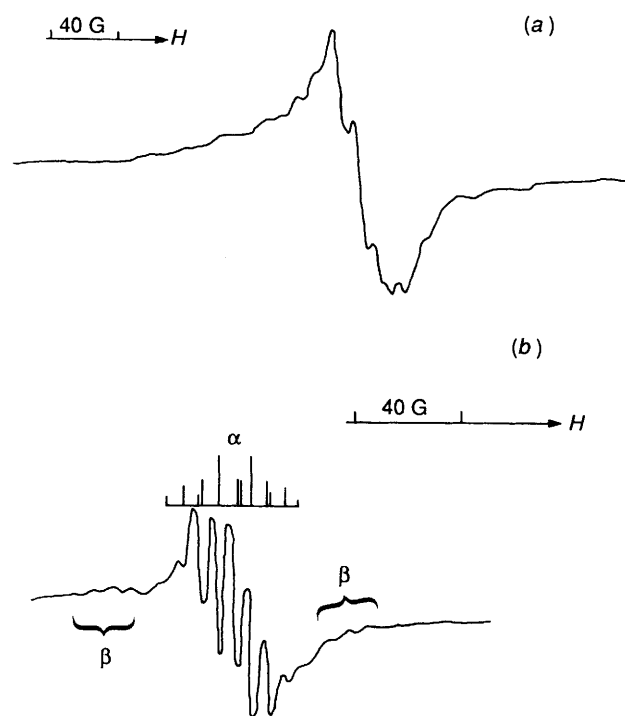


Fig. 3 EPR spectra from (*Z*)-piperylene following γ -irradiation as a dilute solution in CFCl_3 at 77 K, recorded (a) at 77 K; (b) at 150 K, showing features from (α) the primary radical cations and (β) cyclopentene radical cations

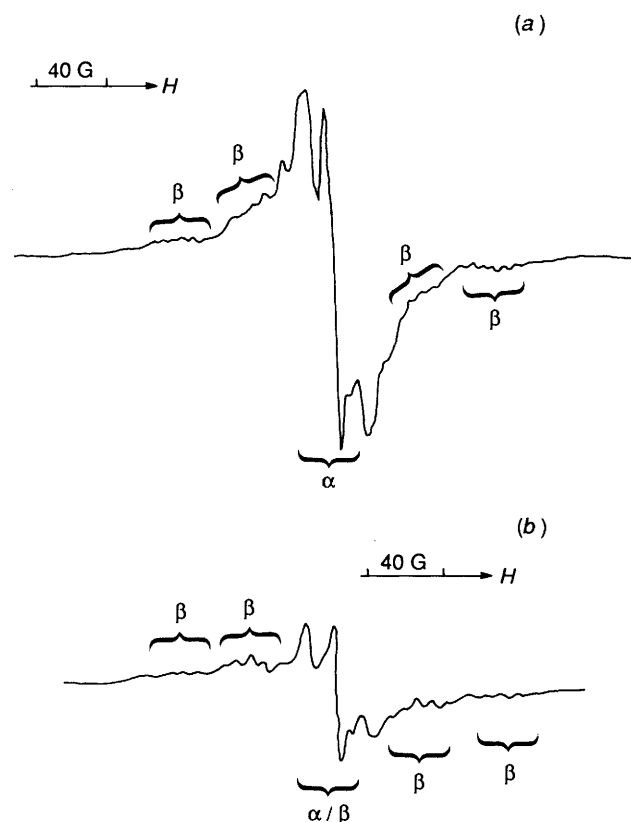
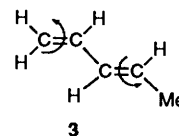


Fig. 4 EPR spectra from (*E*)-piperylene following γ -irradiation as a dilute solution in CFCl_3 at 77 K, recorded (a) at 77 K; (b) at 150 K, in each case showing features from (α) the primary radical cations and (β) cyclopentene radical cations

possibility that these features arose from *Z* and *E* pentadienyl radicals, of which the piperylene radical cations are the conjugate acids. Data for these potential candidates are

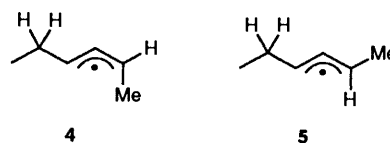
provided by the work of Sustmann²⁰ (Table 1) from which it is clear that *six-line* spectra (*i.e.* with *no* central feature) would be expected for the linewidths of *ca.* 8 G* which we anticipate from the typical anisotropies associated with α -protons in a slowly reorienting radical with the spin density distribution measured for a diene radical cation.¹⁹ Data for these species,¹⁹ as measured in a $\text{CFCl}_2\text{CFCl}_2$ matrix (Table 1) largely support our assignment, but it is apparent that the (negative) α -proton couplings are rather smaller in CFCl_3 , and this probably relates to a slightly more non-planar structure **3** which is adopted in



the latter medium, so that a (positive) hyperconjugative contribution largely cancels the spin-polarisation mechanism that gives rise to negative hydrogen (1 s) spin populations.

In view of our previous finding that cyclopentene is converted into **1** on H-mordenite, the result that piperylene radical cations are isomerised to cyclopentene radical cations **2** in a CFCl_3 matrix might suggest that at least part of **1** observed from the absorption of these dienes on the same zeolite could arise *via* a radical-cation-initiated route. However, under no conditions did we obtain any evidence for C–C bond formation from genuine cations **2** which preferred to deprotonate, and so we do not consider that this observation is of great significance to the zeolite system.

In their study of piperylene radical cations in a $\text{CFCl}_2\text{CFCl}_2$ matrix, Fujisawa et al.¹⁹ observed the initial step of a cationic polymerisation, leading to the 'chain-end' allylic radicals **4**



and **5**. Clearly we do not find this type of polymer chain propagation in the zeolite, nor in the CFCl_3 matrix. However, when a $\text{CF}_2\text{ClCFCl}_2$ matrix was used, features were detected that are consistent with the formation of these 'end' radicals. In view of the more mobile nature of this matrix, its difference in behaviour from CFCl_3 is perhaps not surprising since a combination of mobility and relatively high (5%) substrate concentration could certainly encourage the development of an extended (chain) structure: alternatively, the very rigid nature of solid CFCl_3 as a matrix may retard this.

We emphasise that in no case were we able to detect features from **1** in a freon matrix, and so the altogether contrasting behaviour of the zeolite in this respect points to the operation of a different mechanism: if it were the case that the initial event in the latter matrix is ionisation to form piperylene radical cations, then some similarity particularly with the halogenoethane matrices might be expected, given that their structures are relatively mobile as is true of the zeolite.

An alternative is that a Brønsted acid catalysed route operates to first convert piperylene to 9-octalin, which is then oxidised to **1** by an appropriate site on the zeolite surface. A possible mechanism for this is drawn in Scheme 2 for (*E*)-piperylene, and a similar route can be envisaged for the *Z* isomer. A scheme of this kind would lead to the extensive exchange of protons between the adsorbate and the zeolite, and

* 1 G = 0.1 mT.

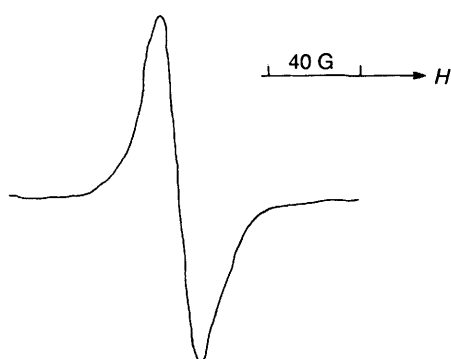
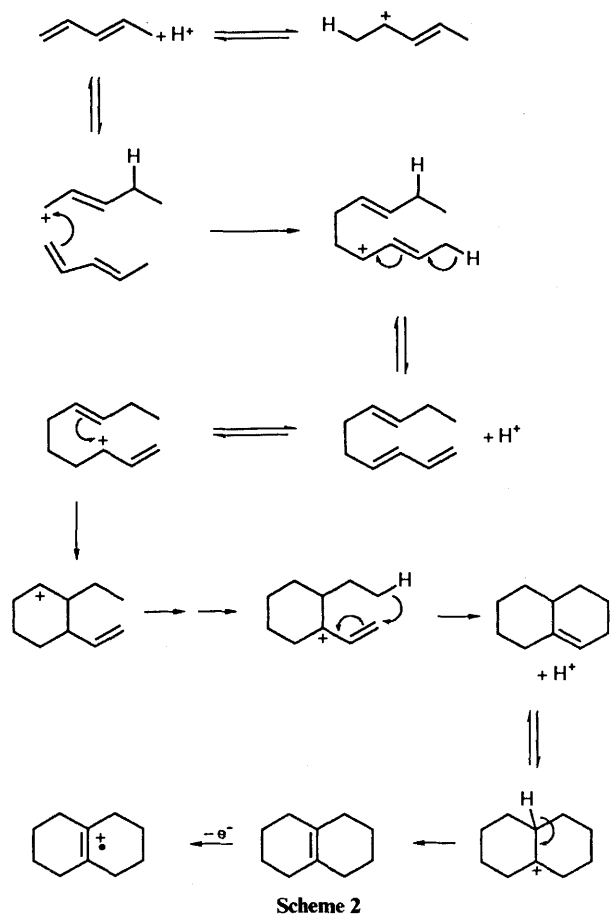


Fig. 5 EPR spectrum recorded at 77 K following the adsorption of (*E*)-piperylene onto a deuterium-exchanged sample of H-mordenite

this is confirmed by the observation of an unresolved single peak (Fig. 5) when a sample of H-mordenite was used that had previously been exchanged with D_2O , because of the reduction in the hyperfine splitting in the perdeuteriated 9-octalin radical cation. This accords with previous work on propene adsorption onto a deuterium-exchanged sample of H-mordenite, in which a single peak was similarly observed, in contrast with the well-resolved hyperfine structure developed on the unexchanged catalyst.¹⁰

1,4-Pentadiene and 1,5-Hexadiene.—Adsorption of these substrates at 195 K led to the development of weak EPR signals, but, on raising the temperature to 295 K for several minutes, these increased in intensity and the spectra taken at 77 K can again be assigned to octalin radical cations. These observations are essentially those reported by Kucherov and Slinkin,¹¹ but these workers incorrectly assigned their spectra to the primary cyclopentene radical cations (**2**). When generated in a $CFCl_3$

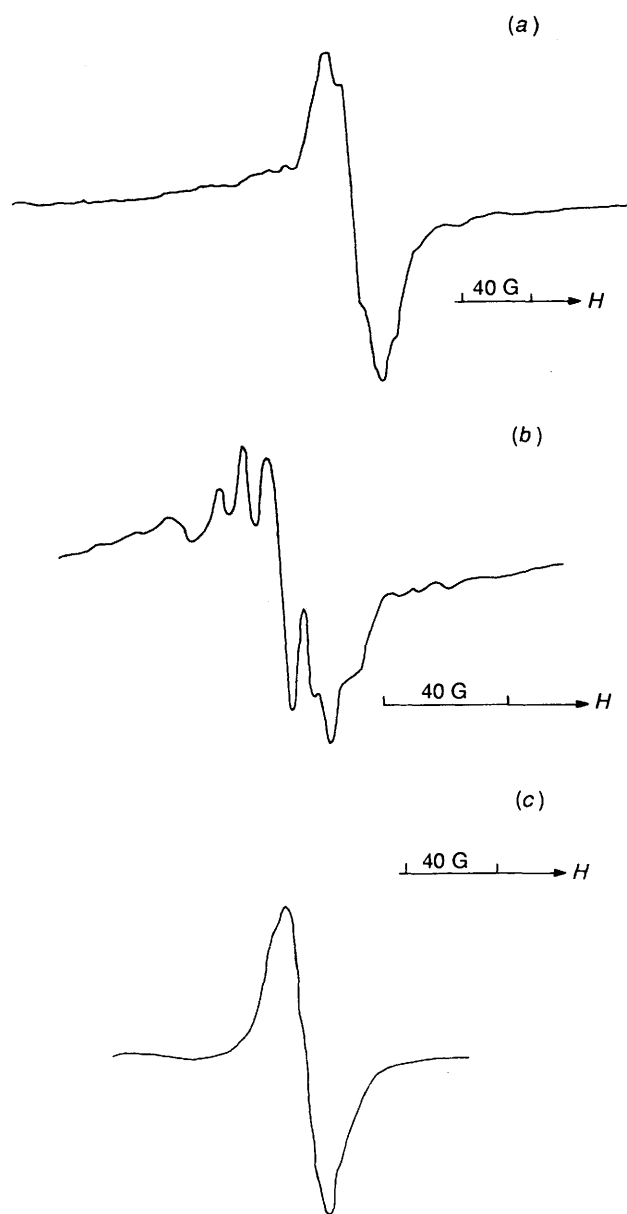


Fig. 6 EPR spectra recorded following γ -irradiation of penta-1,4-diene in a $CFCl_3$ matrix (a) at 77 K; (b) at 150 K; (c) at 77 K following the adsorption of penta-1,4-diene on deuterium exchanged H-mordenite

matrix, the radical cation of penta-1,4-diene exhibits an odd number of broad lines in its EPR spectrum [Fig. 6(a)] at 77 K, with an apparent spacing of *ca.* 10 G, but which sharpened on annealing to 150 K [Fig. 6(b)]. Again, features from cyclopentene radical cations are present at 77 K, but although these appear to increase in intensity on annealing, the additional signals from the primary cations are not lost completely. Williams *et al.*²¹ reported that they were unable to observe the cyclopentane-1,3-diyl radical cation, which might be an intermediate in the reaction **1**, by cyclization of penta-1,4-diene radical cations, but managed to trap this species from the radiolytic oxidation of bicyclo[2.1.0]pentane in freon matrices, and indeed this species was isomerised to **2** by annealing. Our results confirm the former result, but show that product **2** is formed nonetheless. The initial weak signals observed at 195 K in the zeolite matrix may reflect the early formation of penta-1,4-diene radical cations but could not be assigned with any certainty.

It is surprising that hexa-1,5-diene should also form **1** on mordenite, since this is no longer a simple 'dimer' of the

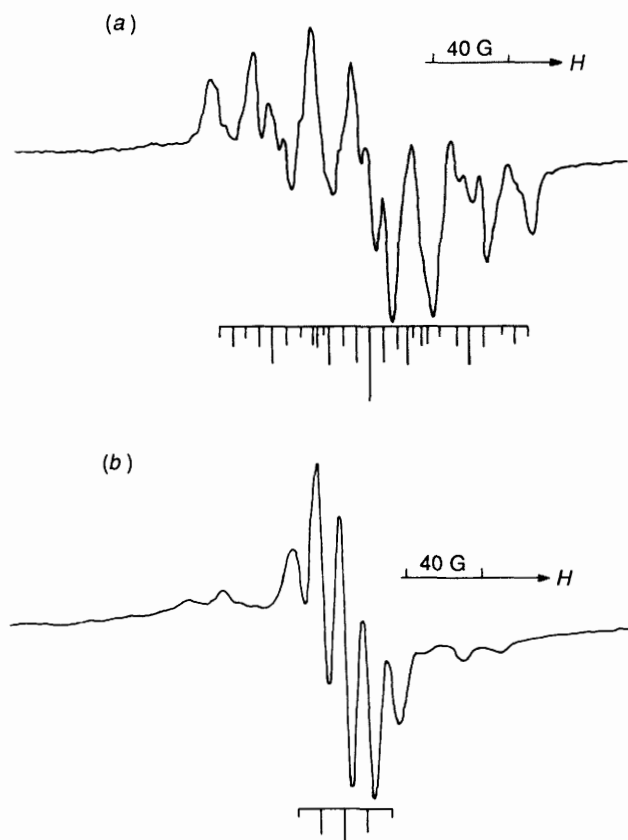
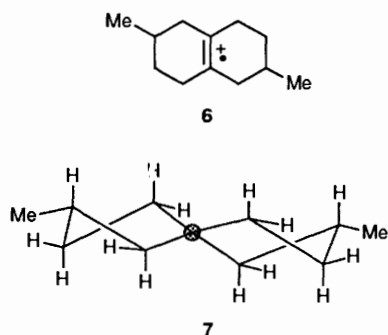


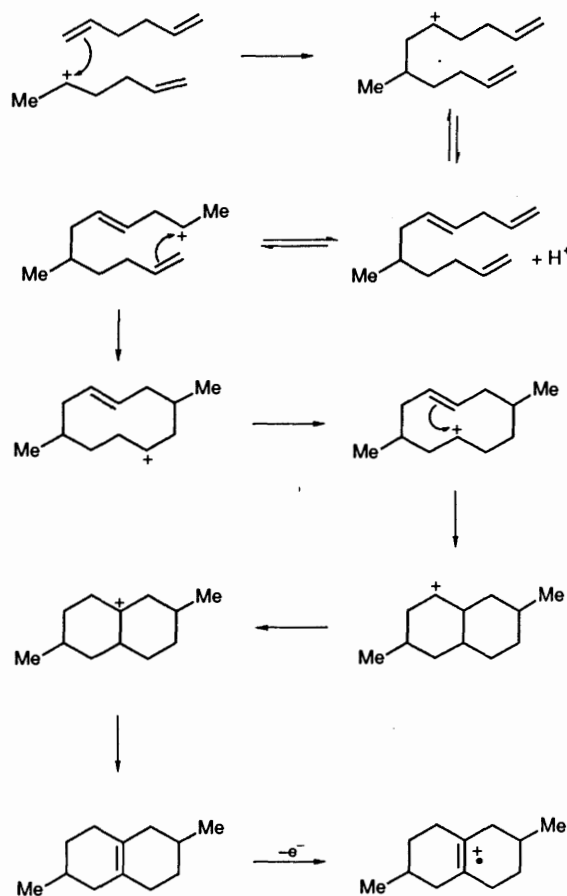
Fig. 7 EPR spectra recorded at 77 K following γ -irradiation of hexa-1,5-diene in (a) CFCl_3 and (b) $\text{CF}_2\text{ClCFCl}_2$ matrices

substrate, and it is difficult to draw a plausible mechanism that accounts for the loss of two carbon atoms and arrives at a C_{10} structure. An alternative is that there are two methyl groups present, which migrate to positions remote from the alkene-centred SOMO, as in structure 6. If these occupy pseudo-



equatorial positions, as might be imposed by the limiting channel dimensions of the zeolite, the overall ring conformation may be little affected; particularly with regard to the orientation of the C-H bond projections with respect to the density axes of the SOMO p_z orbitals 7. Therefore, very similar couplings would be expected for this and the unsubstituted derivative 1, as observed.

Comparison with the behaviour of authentic hexa-1,4-diene radical cations is once again provided by results obtained in freon matrices. The Williams group have made a very thorough study¹⁸ of the influence of the solid freon matrix on the cyclization of this cation: they find that while in matrices such as CFCl_3 only cyclohexene radical cations were detected, even at 77 K; in $\text{CF}_2\text{ClCFCl}_2$, a potential intermediate in this conversion, the cyclohexane-1,4-diy radical cation (7), was



Scheme 3

detected at 77 K, and this was indeed converted into the cyclohexene radical cation on raising the sample temperature. Even at substrate concentrations of 5%, similar to the adsorbate loading on the zeolite, we find the same behaviour, [Figs. 7(a), 7(b)] and so it appears that cyclization is preferred over deprotonation, even in the more mobile $\text{CF}_2\text{ClCFCl}_2$ matrix.

As in the previous examples, however, there is no correspondence with the results obtained with the zeolite matrix, since at no point did we detect octalin-type cations in either freon medium. We propose therefore that a Brønsted acid catalysed route is again at work, and in Scheme 3 is outlined a mechanism that leads to the dimethyloctalin structure 6. Use of the deuterium-exchanged mordenite leads to the formation of a structureless feature [Fig. 6(c)] following hexa-1,4-diene adsorption, showing that there is again extensive exchange of protons with the zeolite.

Conclusions

The behaviour of diene radical cations, generated radiolytically in low-temperature freon matrices, is quite different from that observed in H-mordenite, and provides no real evidence that the dominant chemical transformations in the latter medium are driven through the initial formation of the diene primary radical cations. Rather, we propose that the major events are proton (Brønsted acid) catalysed dimerisation, leading to 9-octalin species which are subsequently converted into their radical cations. Nonetheless, this capability of an activated zeolite to generate alkene radical cations holds the potential for further C-C bond formations, by radical combination, that are not available through a purely acid-catalysed route, and needs to be investigated further.

Acknowledgements

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