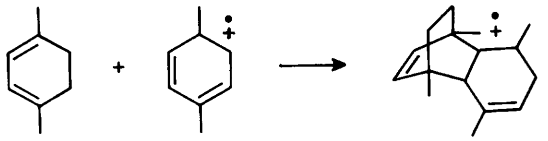
The One-electron Oxidation of Dialkylcyclohexadienes

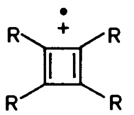
Alwyn G. Davies * **and Robyn Hay-Motherwell**
Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ

When α-terpinene, γ-terpinene, isoterpinolene, $\Delta^{3,8}$-*p*-menthadiene, or α-phellandrene is subjected to one-electron oxidation in fluid solution, either of two e.s.r. spectra can be observed, neither of which resembles the spectra of the monomer radical cations which are formed when the substrates are γ-irradiated in Freon matrices. Treatment of 1,4-dimethylcyclohexa-1,3-diene or 1,4-dimethylcyclohexa-1,4-diene with a variety of oxidising agents in fluid solution gives rise to the same e.s.r. spectrum, which is different from that of the monomer radical cations in a Freon matrix. This spectrum is assigned to the radical cation of the Diels–Alder adduct between 1,4-dimethylcyclohexa-1,3-diene (as the diene) and 2,5-dimethylcyclohexa-1,3-diene (as the dienophile), and this adduct has been isolated and characterised. It is proposed that the monomer radical cations which are first formed lose a proton which catalyses the interconversion of the various possible dimethylcyclohexadienes, and that hole-catalysed cycloaddition then occurs between the pair of isomers which provides the least sterically hindered combination.

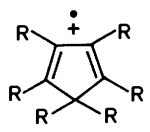


There is a great deal of current interest in the chemistry of organic radical cations, and recent improvements in experimental technique have made it possible to observe the e.s.r. spectra of many new examples of these species in fluid solution.[1] We report here a study of the radical cations derived from certain cyclohexadienes.

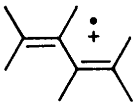
When this work was started, the e.s.r. spectra of fluid solutions of many tetra-alkylcyclobutadiene radical cations (**1**),[2–4] a few cyclopentadiene radical cations (**2**),[5,6] and one acyclic butadiene radical cation (**3**)[7] had been reported.



(**1**)



(**2**)



(**3**)

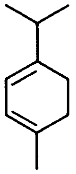
Shida and Kato and their colleagues,[8] and Tabata and Lund,[9] had observed the e.s.r. spectra of the cyclohexa-1,3- and -1,4-diene radical cations in frozen Freon matrices, and had established their major e.s.r. characteristics, but no cyclohexadiene radical cations had been observed in fluid solution. These species however have been the subject of much debate in relation to the 'hole catalysis' of the Diels–Alder reaction which has been studied extensively, particularly by Bauld.[10]

The simplest butadiene for which we have subsequently been able to observe a long-lived radical cation is 1,1,4,4-tetramethylbutadiene.[11] We therefore directed our attention initially to the 1,4-dialkylcyclohexa-1,3-dienes, in which the diene unit is terminally tetra-alkylated.

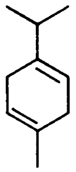
Results and Discussion

Because of their ready availability, the initial experiments were carried out on the *p*-menthadienes, namely α-terpinene (**4**), and γ-terpinene (**5**), isoterpinolene (**6**), $\Delta^{3,8}$-*p*-menthadiene (**7**), and α-phellandrene (**8**).

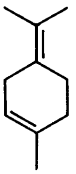
To identify the principal characteristics of the e.s.r. spectra of the radical cations, compounds (**4**)—(**8**) were first subjected to γ-radiolysis in a CCl_3F matrix at 77 K. If the solutions are sufficiently dilute, bimolecular reactions of the solute do not occur and the spectra which are observed usually relate to the



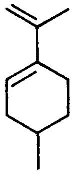
(**4**)



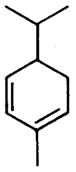
(**5**)



(**6**)



(**7**)



(**8**)

primary radical cations, although the lines are often broad, and the spectra anisotropic.[8,9,12,13]

α-Terpinene (**4**) at 132 K showed a spectrum with a line width of *ca.* 4 G, *g* 2.0027, which could be simulated using the hyperfine coupling constants *a* (2 H) 36, *a* (2 H) 24, *a* (3 H) 12, and *a* (2 H) 3 G. The values of 36 and 24 G would be reasonable for a substituted cyclohexadiene: for cyclohexa-1,3-diene itself, Shida and Kato[8] reported *a* (2 H) 31.0 and *a* (2 H) 28.0 G for the four methylene protons (see below).

γ-Terpinene (**5**) at 80 K gave a clear quintet, *a* (4 H) 58.5 G, with some further coupling at 4 G. The large quintet coupling is clearly due to the two methylene groups in the ring: for cyclohexa-1,4-diene, Shida and Kato[8] reported *a* (4 H) 68.0 and *a* (4 H) 4.8 G, and Tabata and Lund[9] reported *a* (4 H) 67.1 and *a* (4 H) 4.0 G.

Isoterpinolene (**6**) at 80 K gave a spectrum which was appreciably anisotropic but which could be simulated reasonably well using the isotropic hyperfine coupling constants *a* (2 H) 26.2, *a* (6 H) 12.75, and *a* (2 H) 9.25 G. The value of 12.75 G probably refers to the geminal methyl groups: in the radical cation of hexamethylbutadiene (**3**), the terminal methyl groups show *a* (2 Me) 10.55 and *a* (2 Me) 10.7 G.

$\Delta^{3,8}$-*p*-Menthadiene (**7**) at 156 K showed a spectrum with *a* (2 H) 27.5, *a* (4 H) 9.5, and *a* (2 H) *ca.* 2.5 G. Three of the four hyperfine couplings of 9.5 G probably refer to the terminal protons on the diene unit, and the larger coupling of 27.5 G to the methylene group within the ring at the end of the diene unit.

The spectrum obtained from α-phellandrene (**8**) was too weak to be simulated with confidence.

To summarise, although the line widths and the anisotropy of the solid-state spectra preclude a complete analysis, the major aspects of the spectra of the monomeric radical cations are apparent, and are in accord with the few data in the literature on related compounds.

Three techniques were used for generating the radical cations for e.s.r. studies in fluid solution, namely (a) dissolving the diene in a mixture of trifluoroacetic acid and dichloromethane in the presence of air at *ca.* 240 K, (b) dissolving the diene in trifluoroacetic acid and dichloromethane containing mercury(II) trifluoroacetate (Kochi's reagent) at *ca.* 250 K, and (c) treating the diene in dichloromethane with tris-(4-bromophenyl)aminium or tris-(2,4-dibromophenyl)aminium hexachloroantimonate [$(4\text{-BrC}_6H_4)_3N^{+\bullet}SbCl_6^-$ or $(2,4\text{-Br}_2C_6H_3)_3N^{+\bullet}SbCl_6^-$], at *ca.* 200 K.

Under these conditions, compounds (**4**)—(**6**) gave satisfactory persistent e.s.r. spectra, but the linewidths were 1.2—1.5 G, and although the simulations were acceptable, they are not necessarily uniquely so.

Different combinations of substrate and reagent gave only two types of spectra, the first with *a* (2 H) 15.0, *a* (4 H) 6.5, and *a* (2 H) 3.5 G, *g* 2.0028, and the second with *a* (3 H) 14.6, *a* (2 H) 4.6, and *a* (2 H) 4.25 G. The first type was obtained with the (substrate) (reagent) combinations (**4**) (a), (**4**) (c), (**5**) (a), and (**6**) (a), and the second with (**5**) (b) and (**5**) (c). Spectra from compounds (**7**) and (**8**) were too weak to be interpreted with confidence.

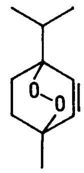
Both these spectra are clearly different from those of monomeric radical cations which we observed in the solid state. Neither do they relate to the radical cation of the endoperoxide (**9**)[14] which could be formed by aerobic oxidation of a radical cation: when (**9**) was used as the substrate, neither of the two spectra was obtained.

The nature of the chemical changes which occur in fluid solution was briefly studied by ^{1}H n.m.r. and g.l.c.–m.s.

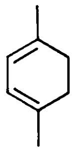
A solution of α-terpinene in dichloromethane containing trifluoroacetic acid in the presence of oxygen, which showed the e.s.r. spectrum reported above, showed by ^{1}H n.m.r. that within 5 min, *p*-cymene had been formed, together with what appeared to be a variety of the possible Diels–Alder dimers. The solution was quenched with aqueous sodium carbonate, and analysed by g.l.c.–m.s., when it showed the presence of *p*-cymene, dihydrogenated and hydrated derivatives of the dienes, and five different dimeric structures.

The equilibration of the various diterpene dienes, and the formation of *p*-cymene, under acid conditions, has been reported previously.[15,16]

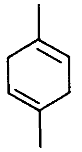
As in fluid solution the spectra did not relate to any monomeric diene, but more likely were to be associated with a dimeric structure, attention was transferred to the more symmetrical dimethylcyclohexadienes (**10**) and (**11**), which were expected to give spectra which could more readily be analysed.



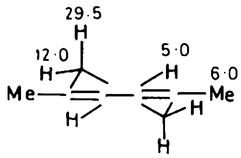
(**9**)



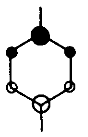
(**10**)



(**11**)



(**12**)



(**13**)

The e.s.r. spectra of the monomeric radical cations of (**10**) and (**11**), and of *p*-xylene which might be expected to be formed by aromatization, were first obtained by γ-irradiation.

1,4-Dimethylcyclohexa-1,3-diene (**10**) in CCl_3F at 77 K gave a spectrum showing *a* (2 Me) 6.0, *a* (2 H) 29.5, *a* (2 H) 12.0, and *a* (2 H) 5.0 G, *g* 2.0029 though the lines were broad. The spectrum is illustrated in our preliminary note.[17] The probable assignment of these hyperfine coupling constants is shown in (**12**). These figures correlate reasonably well with those obtained by Tabata and Lund[9] for cyclohexa-1,3-diene [*a* (2 H) 8.4, *a* (2 H_{ax}) 30.2, and *a* (2 H) 4.2 G], though their *g* value of 2.0037 is much higher than ours.

Shida and Kato[8] however reported that the methylene protons, even in conformationally equilibrating cyclohexa-1,3-diene, were slightly non-equivalent [*a* (2 H) 31.0 and 28.0 G]. We therefore repeated their experiment of the γ-radiolysis of the diene in CCl_3F. A well resolved spectrum was obtained at 140 K which could be simulated using the hyperfine coupling constants *a* (2 H) 32.5, *a* (2 H) 28.25, *a* (2 H) 7.8, and *a* (2 H) 3.75 G, Δ_{pp} 2.4 G, and no satisfactory simulation could be obtained when all four methylene protons were treated as being equivalent.

1,4-Dimethylcyclohexa-1,4-diene (**11**) gave a well resolved quintet pattern, *a* (4 H) 57.2 G, with a further splitting of *a* (8 H) 6.0 G, *g* 2.0034. This correlates with the spectra obtained for cyclohexa-1,4-diene itself by Tabata and Lund [*a* (4 H) 67.1 and *a* (4 H) 4.0 G],[9] and by Shida and Kato [*a* (4 H) 68.0 and *a* (4 H) 4.8 G].[8]

p-Xylene gave a septet spectrum, *a* (6 H) 17.5 and *a* (4 H) 2.75 G. Under similar conditions, Symons[13] reported *a* (6 H) 18.2 G, but the hyperfine coupling by the ring protons was not resolved. Electron release by the two methyl groups breaks the degeneracy of the ψ_A and ψ_S molecular orbitals, placing the unpaired electron principally in the ψ_S M.O. (**13**), with a high electron density at the 1- and 4-position.

The dimethylcyclohexadienes were then subjected to oxidation in fluid solution.

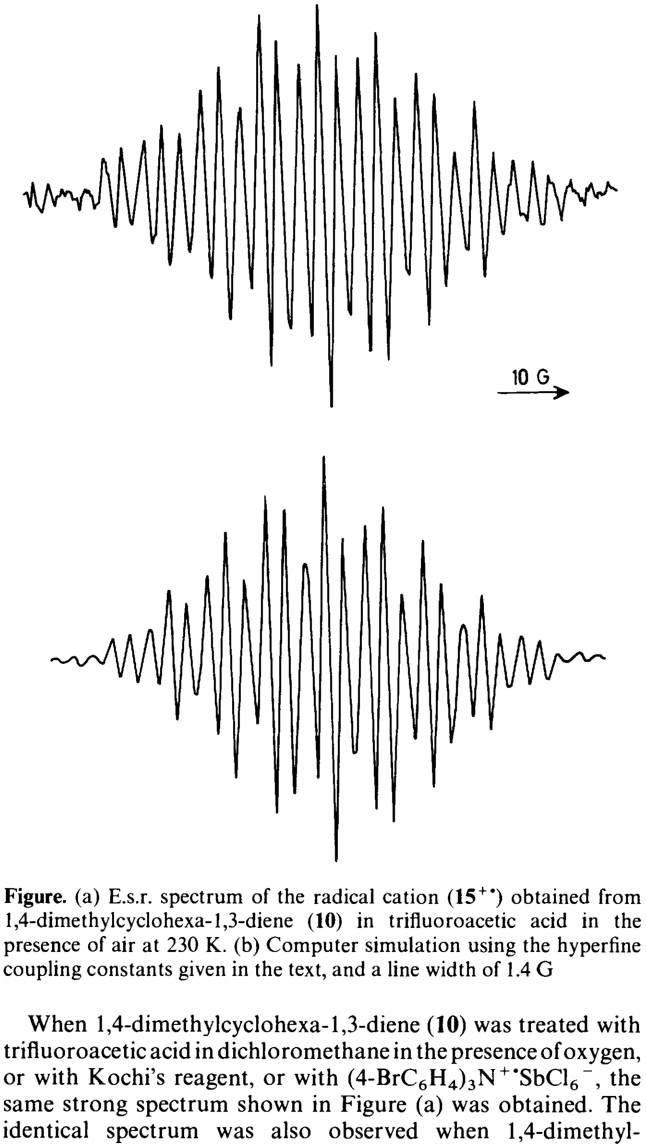


Figure. (a) E.s.r. spectrum of the radical cation ($15^{+\bullet}$) obtained from 1,4-dimethylcyclohexa-1,3-diene (**10**) in trifluoroacetic acid in the presence of air at 230 K. (b) Computer simulation using the hyperfine coupling constants given in the text, and a line width of 1.4 G

When 1,4-dimethylcyclohexa-1,3-diene (**10**) was treated with trifluoroacetic acid in dichloromethane in the presence of oxygen, or with Kochi's reagent, or with $(4\text{-BrC}_6H_4)_3N^{+\bullet}SbCl_6^-$, the same strong spectrum shown in Figure (a) was obtained. The identical spectrum was also observed when 1,4-dimethylcyclohexa-1,4-diene (**11**) was treated with trifluoroacetic acid in dichloromethane, or with $(2,4\text{-Br}_2C_6H_3)_3N^{+\bullet}SbCl_6^-$ in dichloromethane [but not $(4\text{-BrC}_6H_4)_3N^{+\bullet}SbCl_6^-$]. A satisfactory analysis of the spectrum could not be achieved by inspection, but ENDOR spectroscopy[17] provided the hyperfine coupling constants *a* (2 H) 14.8, *a* (4 H) 8.52, *a* (2 H) 6.03, *a* (2 H) 2.63, and *a* (2 H) 0.3 G, and the simulation of the spectrum is shown in Figure (b).

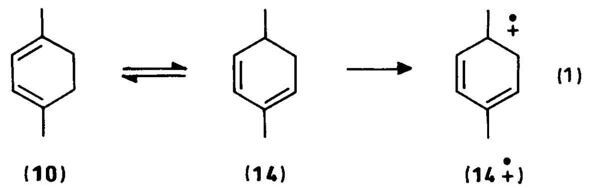
This spectrum is different from that of ($10^{+\bullet}$) or ($11^{+\bullet}$) which was obtained in a Freon matrix.

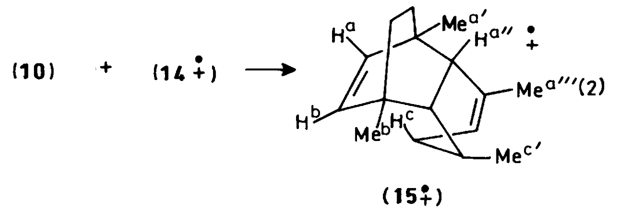
The reaction between (**10**) and 5 mol% of $(4\text{-BrC}_6H_4)_3N^{+\bullet}SbCl_6^-$ was carried out on a preparative scale, and a single (g.l.c.) dimeric hydrocarbon was isolated in 40% yield. Mass spectrometry showed the presence of the molecular ion (*m/e* 216) with the major fragment at *m/e* 108, suggesting a retro-Diels–Alder fragmentation.

When this dimer was treated with the above aminium salts, the same e.s.r. spectrum was observed as before and the dimer was recovered essentially quantitatively, and we believe that the spectrum relates to the radical cation of this dimer.

Attempts to prepare a solid derivative for single-crystal *X*-ray diffraction [Br_2, $AgNO_3$, $Hg(OAc)_2$, $3\text{-ClC}_6H_4CO_3H$] were unsuccessful, and the identification rests on spectroscopic evidence. ^{13}C N.m.r. (with off-resonance decoupling and modulated spin-echo) confirmed the presence of 16 non-equivalent carbon atoms, with four methyl groups and two double bonds, and ^1H n.m.r., with n.O.e., indicated structure (**15**). Details are given in the Experimental section.

The dimer is presumably formed by the catalysed interconversion of the dienes (**10**) and (**14**), then their hole-catalysed





Diels–Alder association. Reaction (2) is therefore similar to the dimerisation of cyclohexadiene which is catalysed by $(4\text{-BrC}_6H_4)_3N^{+\bullet}$.[10]

Gassman[18] has shown that this catalysis can involve either electron transfer or proton transfer, and that the latter mechanism can be suppressed by a base. Accordingly, diene (**10**) was treated with 50 mol% of $(4\text{-BrC}_6H_4)_3N^{+\bullet}$ in the presence of 55 mol% of 2,6-di-t-butylpyridine. The colour of the iminium salt was immediately lost. The non-polar products (35%) were isolated, and were identified as the reactant (**10**) (58%) and *p*-xylene (37%), but none of the isomer (**14**), nor of the dimer (**15**), could be detected.

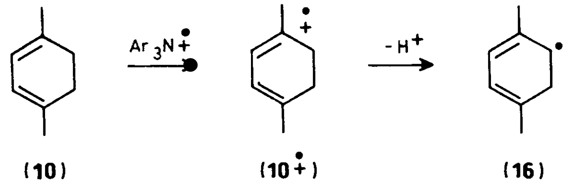
The isomerisation (**10**) ⟶ (**14**) thus appears to be dependent on acid catalysis. We propose that the diene (**10**) [or (**11**)] reacts with the aminium salt to give the corresponding radical cation, which can lose a proton [equation (3)]. In the absence of a base, this induces equilibration of the dienes [equation (4)], which now undergo a radical cation catalysed crossed Diels–Alder reaction to give ($15^{+\bullet}$) exclusively [equation (5)]. This can now accept an electron from (**10**) and only a catalytic amount of the aminium salt is necessary to induce the reaction.

If a base is present, it scavenges the proton, and stops the interconversion (**10**) ⟶ (**14**). The neutral dimethylcyclohexadienyl radical (**16**) is further oxidised to the cation (**17**), which loses a proton giving *p*-xylene (**18**) as the major product.

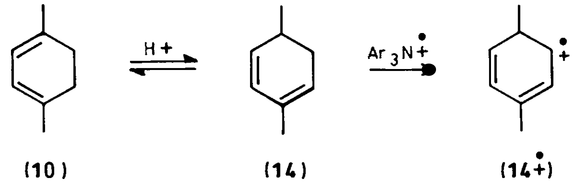
The dimerisation reaction of 1,4-dimethylcyclohexa-1,3-diene therefore differs from that of cyclohexa-1,3-diene itself, in that whereas the latter can involve either proton or electron-hole catalysis, the former requires both, the proton to induce the formation of the requisite pair of isomers (**10**) and (**14**), and the loss of the electron to induce both the release of the proton and the addition reaction. Six regioisomeric diene–dieneophile combinations are possible, but only the crossed product (**15**) is formed, presumably because this is the least sterically congested, most energetically favoured combination.

When cyclohexa-1,3-diene itself (**19**) is treated with $(4\text{-BrC}_6H_4)_3N^{+\bullet}SbCl_6^-$, the blue colour of the aminium radical cation persists in the reaction mixture, and at no time could we observe the spectrum of the monomer or dimer radical cation ($19^{+\bullet}$) or ($20^{+\bullet}$). Neither were we able to find any other conditions under which the e.s.r. spectrum of ($20^{+\bullet}$) could be detected, using pre-formed (**20**) as the substrate.

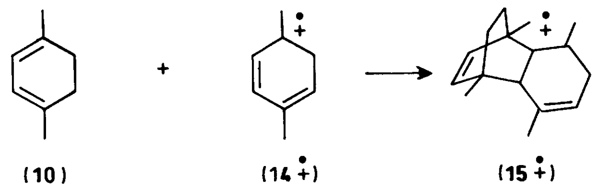
This suggests that the ionisation potential of (**15**) is lower than that of (**20**). Inspection of molecular models suggests that



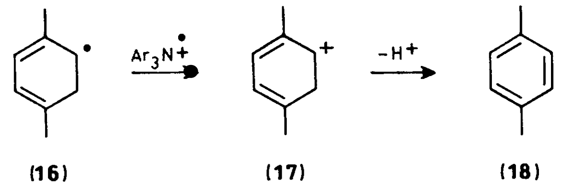
(3)



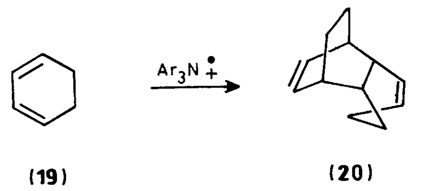
(4)



(5)



(6)



(7)

the incorporation of the four methyl groups in (**15**) may give a buttressing effect which forces the double bonds into propinquity, and permits the formation of a stable intramolecular (alkene)$_2^{+\bullet}$ complex, analogous to the (arene)$_2^{+\bullet}$ complexes which are more familiar.

Experimental

α-Terpinene (**4**), γ-terpinene (**5**), α-phellandrene (**8**), and *p*-xylene were commercial products which were purified by preparative g.l.c. Terpinolene (**6**) was prepared from the tosylhydrazone of pulegone,[19] while (**7**) was obtained by heating the reduction product of pulegone[20] with ethyl borate.[21] Ascaridole (**9**) was prepared by the published method.[14]

1,4-Dimethylcyclohexa-1,4-diene (**11**) was obtained by Birch reduction of *p*-xylene,[22] and 1,4-dimethylcyclohexa-1,3-diene (**10**) (95% pure) from the 1,4-diene by equilibration with acid[23] then separation by preparative g.l.c.

Tris-(4-bromophenyl)aminium hexachloroantimonate was a commercial sample (Aldrich), and the tris-(2,4-dibromophenyl)-aminium salt was prepared by a published method.[24]

E.s.r. Experiments.—*γ-Irradiation.* 10^{-3}M Solutions of the substrate in $CFCl_3$ (purified on an alumina column) were thoroughly degassed and sealed under vacuum. The solutions were cooled in liquid nitrogen, and irradiated with γ-rays from a ^{60}Co source with a dose of *ca.* 10^6 Rad.

Trifluoroacetic acid solutions. A mixture of dichloromethane (0.6 cm^3; purified immediately before use by passage through a silica column) and trifluoroacetic acid (0.1 cm^3) was degassed with a stream of argon, then a solution of the substrate (*ca.* 10 μl) in dichloromethane (0.3 cm^3) was added.

Kochi's reagent. Recrystallised mercury trifluoroacetate[25] (*ca.* 20 mg) was added to a mixture of dichloromethane (0.6 cm^3) and trifluoroacetic acid (0.1 cm^3), and degassed at *ca.* −30 °C with argon. A solution of the substrate (*ca.* 10 μl) in dichloromethane (0.3 cm^3) was then added, and mixed in with a stream of argon.

Aminium salts. The aminium salt $(4\text{-}BrC_6H_4)_3N^{+\bullet}SbCl_6^-$ or $(2,4\text{-}Br_2C_6H_3)^3N^{+\bullet}SbCl_6^-$ (2 mg) in dichloromethane (0.7 cm^3) at −70 °C was degassed with argon. A solution of the substrate (10 μl) in dichloromethane (0.3 cm^3) was then added, and the mixture was degassed with argon at the same temperature.

E.s.r. spectra were recorded on a Varian E4 or E109 spectrometer fitted with a 500 W high-pressure mercury arc focused on the cavity.

Preparation of the Dimer (**15**).—A solution of 1,4-dimethylcyclohexa-1,3-diene (**10**) (0.275 g) in degassed dichloromethane (5 cm^3) was added to an ice-cold degassed solution of tris-(4-bromophenyl)aminium hexachloroantimonate (0.112 g) in dichloromethane (10 cm^3). The e.s.r. spectrum of this solution was the same as that when the reaction was carried out on the small scale as described above.

After 30 min, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel with pentane as eluant, followed by molecular distillation.

The dimer (**15**) was isolated (0.11 g, 40%), *m/e* 216 ($M^{+\bullet}$) and 108 (Found: *M*, 216.1884. $C_{16}H_{24}$ requires *M*, 216.1878), δ_H ($CDCl_3$; 200 MHz) 0.80 (3 H, d, *J* 5.3 Hz, C*H*$_3$ CH), 1.14 (3 H, s, CH_3C), 1.29 (3 H, s, CH_3C), 1.80 (3 H, br s, CH_3C=), 5.40 (1 H, br d, *J* 6.9 Hz, CH=C), and 5.83 (2 H, d, *J* 1.25 Hz, C*H*=C*H*).

N.O.e. experiments established the following correlations [the labelling of the hydrogen atoms is shown on the formula (**15**)]:

Irradiated signals	Affected signals
δ 0.8 (CH_3CH)	$H_{b''}$, $H_{c'}$
δ 1.14 (CH_3b′)	H_b, $H_{b'}$
δ 1.12 (CH_3a′)	$CH_{3a'''}$, H_a, $H_{a''}$

The ^{13}C n.m.r. spectrum showed δ ($CDCl_3$; modulated spin echo, off-resonance, and decoupled) 23.07 (q, CH_3), 23.99 (q, CH_3), 25.92 (q, CH_3), 26.37 (q, CH_3), 28.16 (d, C*H*CH_3), 29.30 (t, CH_2), 36.57 (t, CH_2), 37.57 (s, C), 38.27 (t, CH_2), 38.89 (s, C), 50.58 (d, CH), 53.18 (d, CH), 122.90 (d, *C*H=C), 136.49 (s, *C*=C), 137.59 (d, *C*H=C), and 137.90 p.p.m. (d, *C*H=C).

The Effect of Base.—A solution of 1,4-dimethylcyclohexa-1,3-diene (0.200 g) in dichloromethane (3 cm^3) was added to a degassed ice-cold solution of tris-(4-bromophenyl)aminium hexachloroantimonate (0.756 g, 50 mol%) and 2,6-di-t-butylpyridine (0.195 g, 55 mol%) in dichloromethane (7 cm^3) under argon. The colour of the aminium salt was immediately lost. After 25 min, the solvent was removed under reduced pressure, and the residue was chromatographed using pentane on silica gel to give 35% non-polar products. G.l.c. showed them to consist of 1,4-dimethylcyclohexa-1,3-diene (58%) and *p*-xylene (37%); no dimer (**15**) could be detected.

Acknowledgements

We thank Drs. J. C. Evans and C. C. Rowlands, Cardiff, for recording the ENDOR spectra, and Dr. P. Clay, Imperial College, London, for providing facilities for γ-radiolysis. This work was supported by the S.E.R.C.

References

1 J. L. Courtneidge and A. G. Davies, *Acc. Chem. Res.*, 1987, **20**, 90.
2 H. Bock, B. Roth, and G. Maier, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 209.
3 Q. B. Broxterman, H. Hogeveen, and D. M. Kok, *Tetrahedron Lett.*, 1981, **22**, 173.
4 J. L. Courtneidge, A. G. Davies, E. Lusztyk, and J. Lusztyk, *J. Chem. Soc., Perkin Trans. 2*, 1984, 155.
5 J. L. Courtneidge, A. G. Davies, and S. N. Yazdi, *J. Chem. Soc., Chem. Commun.*, 1984, 570.
6 J. L. Courtneidge, A. G. Davies, P. S. Gregory, and S. N. Yazdi, *Faraday Discuss. Chem. Soc.*, 1985, **78**, 49.
7 J. L. Courtneidge and A. G. Davies, *J. Chem. Soc., Chem. Commun.*, 1984, 136.
8 T. Shida, Y. Egawa, H. Kobudera, and T. Kato, *J. Chem. Phys.*, 1980, **73**, 5963.
9 M. Tabata and A. Lund, *Chem. Phys.*, 1983, **75**, 379.
10 D. J. Bellville, D. D. Wirth, and N. L. Bauld, *J. Am. Chem. Soc.*, 1981, **103**, 718; D. J. Bellville and N. L. Bauld, *ibid.*, 1982, **104**, 2665; N. L. Bauld and R. Pabon, *ibid.*, 1983, **105**, 633; N. L. Bauld, D. J. Bellville, R. Pabon, R. Chelsky, and G. Green, *ibid.*, p. 2378; D. J. Bellville, N. L. Bauld, R. Pabon, and S. A. Gardner, *ibid.*, p. 3584; R. A. Pabon, D. J. Bellville, and N. L. Bauld, *ibid.*, p. 5158; R. A. Pabon and N. L. Bauld, *ibid.*, 1984, **106**, 1145; R. A. Pabon, D. J. Bellville, and N. L. Bauld, *ibid.*, p. 2730; D. W. Reynolds and N. L. Bauld, *Tetrahedron Lett.*, 1985, **26**, 2539.
11 J. L. Courtneidge, A. G. Davies, and S. N. Yazdi, unpublished work.
12 T. Shida, E. Haselbach, and T. Bally, *Acc. Chem. Res.*, 1984, **17**, 180.
13 M. C. R. Symons, *Chem. Soc. Rev.*, 1984, **13**, 393.
14 G. O. Schenck, K. G. Kunkel, and H. J. Mertens, *Justus Liebigs Ann. Chem.*, 1953, **584**, 125; R. W. Denny and A. Nickon, *Org. React.*, 1973, **20**, 133.
15 A. A. Newman, 'The Chemistry of Terpenes and Terpenoids,' Academic Press, London, 1972, p. 24.
16 C. M. Williams and D. Whittaker, *J. Chem. Soc. B*, 1971, 668.
17 A. G. Davies, R. S. Hay-Motherwell, J. C. Evans, and C. R. Rowlands, *J. Chem. Soc., Chem. Commun.*, 1986, 1513.
18 P. G. Gassman and D. A. Singleton, *J. Am. Chem. Soc.*, 1984, **106**, 6085.
19 W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, *J. Am. Chem. Soc.*, 1968, **90**, 4762.
20 R. H. Reitsema, *J. Am. Chem. Soc.*, 1953, **75**, 1996.
21 A. F. Thomas and B. Willhalm, *Helv. Chim. Acta*, 1964, **47**, 475.
22 E. A. Fehnel, *J. Am. Chem. Soc.*, 1972, **94**, 3961.
23 T. Brady, S. J. Norton, and J. Ko, *Synthesis*, 1985, 704.
24 W. Schmidt and E. Steckhan, *Chem. Ber.*, 1980, **113**, 577.
25 W. Lau, J. C. Huffman, and J. K. Kochi, *J. Am. Chem. Soc.*, 1982, **104**, 5515.

Received 12*th February* 1988; *Paper* 8/00535