The One-electron Oxidation of 1,4-Dimethylcyclohexa-1,3-diene

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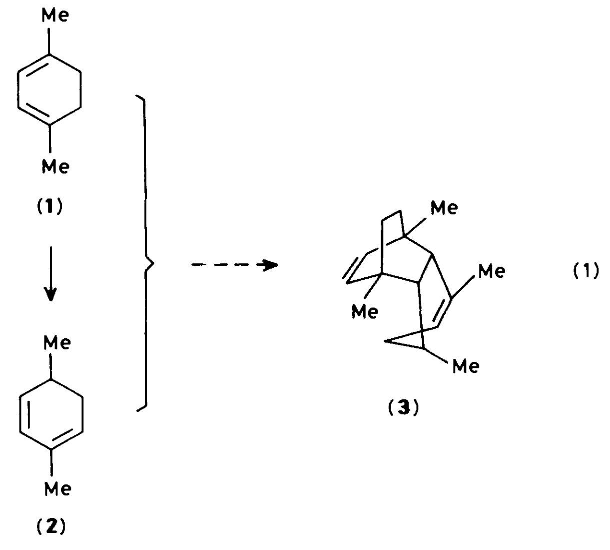
1,4-Dimethylcyclohexa-1,3-diene reacts with $(4\text{-}BrC_6H_4)_3N^{\cdot+}SbCl_6^-$ by a mechanism involving both proton and electron hole catalysis to give the product of the cyclo-addition between the parent diene and 2,5-dimethylcyclohexa-1,3-diene acting as the dienophile; the persistent e.s.r. spectrum of the adduct can be observed.

If butadienes,[1] cyclobutadienes,[2] or cyclopentadienes,[3] suitably alkylated to prevent polymerization, are subjected to one-electron oxidation, the e.s.r. spectra of the corresponding radical cations can be observed in fluid solution. Similar experiments with cyclohexadienes have as yet given spectra which are too complex to be associated with the diene radical cations, and it seemed likely that this behaviour was related to the radical cation catalysis of the Diels–Alder reaction of 1,3-dienes which has been investigated recently by Bauld and his colleagues.[4]

We report here an e.s.r. study of the one-electron oxidation of 1,4-dimethylcyclohexa-1,3-diene (**1**).

There is extensive evidence that γ-radiolysis of a solute in frozen Freon generates the derived monomeric solute radical cation. Figure 1 shows the e.s.r. spectrum which is obtained when a 10^{-3} M solution of (**1**) in $CFCl_3$ is irradiated with γ-rays at 77 K. The spectrum can be simulated using the hyperfine coupling constants a(6H) 6.0, a(2H) 29.5, a(2H) 12.0, a(2H) 5.0 G. These are in line with those which have been obtained in similar experiments with cyclohexadiene itself[5,6] and other alkylated cyclohexadienes,[6] and we ascribe the spectrum to ($\mathbf{1}^{\cdot+}$).

By way of contrast, if a fluid solution of (**1**) in CH_2Cl_2 is treated with 5 mol% tris(4-bromophenyl)aminium hexachloroantimonate, $(4\text{-}BrC_6H_4)_3N^{\cdot+}SbCl_6^-$ at 0 °C, the colour immediately changes, and the e.s.r. spectrum shown in Figure 2 can be observed. Clearly this spectrum is different from the spectrum shown in Figure 1, and ENDOR spectroscopy yields the hyperfine coupling constants a(2H) 14.8, a(4H) 8.52, a(2H) 6.03, a(2H) 2.63, and a(2H) 0.3 G, and the e.s.r. spectrum can be simulated using these values and a line width of 1.0 G.



On a preparative scale, the principal product, isolated in 40% yield, gives spectroscopic data (mass; ^1H n.m.r. with nuclear Overhauser enhancement; ^{13}C n.m.r. with off-resonance decoupling and modulated spin echo) which are entirely consistent with the crossed Diels–Alder adduct (**3**). Moreover, if (**3**) in CH_2Cl_2 is similarly treated with the aminium salt, the spectrum shown in Figure 2 is regenerated, and work up leads to essentially quantitative recovery of starting material.

We therefore assume that this spectrum should be assigned to the radical cation ($\mathbf{3}^{\cdot+}$) (equation 1); a complete assignment of the hyperfine coupling constants is not yet possible because there is no precedent for e.s.r. spectra of radical cations with a similar structure.

The formation of (**3**) is most readily rationalized in terms of the isomerization of the diene (**1**) to the diene (**2**), followed by a cyclo-addition reaction. It is interesting that none of the other possible dimers [*e.g.* (**4**)—(**6**)] could be detected.

The same spectrum (Figure 2) is observed when 1,4-dimethylcyclohexa-1,4-diene (**7**) is treated with tris(2,4-dibromophenyl)aminium hexachloroantimonate, $(2,4\text{-}Br_2C_6H_3)_3N^{\cdot+}\ SbCl_6^-$ in CH_2Cl_2.

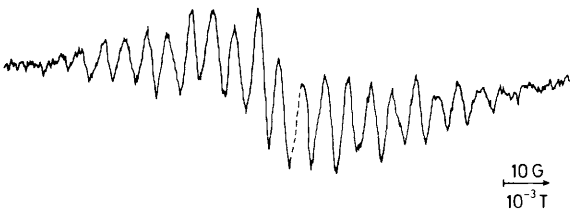


Figure 1. The e.s.r. spectrum of ($\mathbf{1}^{\cdot+}$) in $CFCl_3$ at 77 K; g 2.0029. The broken line indicates the position of contamination by a signal from the silica sample tube.

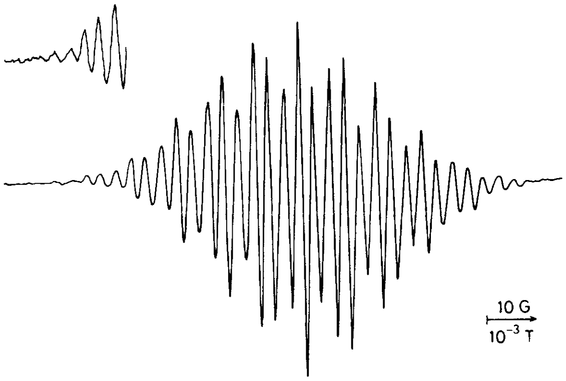
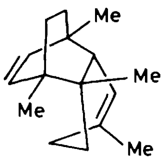


Figure 2. The e.s.r. spectrum of ($\mathbf{3}^{\cdot+}$) in CH_2Cl_2 at 192 K, counterion $SbCl_6^-$; g 2.0028.



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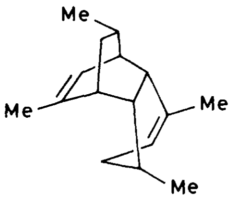

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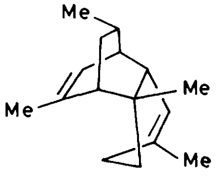

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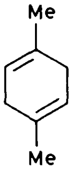

(7)

The elegant recent work of Gassman[7] has demonstrated that triarylaminium salt catalysed Diels–Alder reactions may proceed either *via* proton catalysis or *via* electron transfer catalysis, and that the former reaction may be suppressed by the addition of a further external base.

Accordingly, the diene (**1**) was treated with 50 mol% of $(4\text{-BrC}_6\text{H}_4)_3\text{N}^{\cdot +}\text{SbCl}_6^-$ in the presence of 55 mol% of 2,6-di-t-butylpyridine. The colour due to the aminium radical cation was immediately discharged, and on isolation of the non-polar products (35%) only (**1**) (58%) and *p*-xylene (37%) were identified, and no dimer (**3**) could be observed.

An interpretation of these results, consistent with the work of Bauld[4] and of Gassman[7] is as follows.

The initial reaction between (**1**) and the aminium salt involves electron transfer to give ($\mathbf{1}^{\cdot +}$) but this has a low reactivity as a dienophile, and its principal reaction is to lose a proton which can be scavenged by the base. If the base is absent the proton induces the isomerization of the diene (**1**) → (**2**), and now ($\mathbf{2}^{\cdot +}$) can act as the dienophile in the cycloaddition (equation 1). This process can then be continued as a chain reaction. Similarly the 1,4-diene (**7**) undergoes acid catalysed rearrangement to give both (**1**) and (**2**), and thence (**3**). The adduct (**3**) is preferred over any of the other possibilities presumably for steric reasons.

It is interesting to contrast these results with those obtained for the dimerization of the parent cyclohexa-1,3-diene which is generally recognised in the literature[4,7] to involve the radical cation. Reaction with $(4\text{-BrC}_6\text{H}_4)_3\text{N}^{\cdot +}\text{SbCl}_6^-$ under the same conditions as before now gives the e.s.r. spectrum of the aminium radical cation only, implying that the radical cations of both the parent diene and its dimer product are very short lived species. We speculate that in the dimer ($\mathbf{3}^{\cdot +}$), a buttressing effect between the methyl groups may contribute to the persistence of the radical cation.

These reactions provide a further caveat[7] that caution must be exercised in predicting structure and mechanism in Diels–Alder reactions performed under electron transfer conditions.

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