

Unstable Intermediates. Part XXXVI.* The Hexamethylbenzyl Cation-radical

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Hexamethylbenzene reacts slowly with concentrated sulphuric acid to give a stable cation-radical characterised by an electron spin resonance spectrum consisting of a major triplet assigned to two equivalent protons with a hyperfine coupling constant of 5.4 gauss. Two other sets of protons cause further splitting, one coupling constant being 1.7 gauss and the other nearly twice as large. In deuteriosulphuric acid the two strongly interacting protons exchange rapidly but the remainder are unaffected. The same radical is formed from pentamethylbenzene in sulphuric acid and also by reaction with aluminium chloride. These results are interpreted in terms of the hexamethylbenzyl cation formed by oxidation of the heptamethylbenzenium cation known to be readily formed in these solutions.

REFERENCE has been made to the fact that a remarkably stable radical forms slowly in solutions of hexamethylbenzene in sulphuric acid at room temperature.^{1,2} The electron spin resonance spectrum of this radical is quite different from those assigned to the simple cations of hexamethylbenzene,^{1,2} durene,² and pentamethylbenzene.³ The purpose of the present work was to attempt to discover the nature of the radical involved and to interpret the details of its electron spin resonance spectrum. Since this work was completed our attention had been drawn to a similar study by Singer and Lewis.⁴

EXPERIMENTAL AND RESULTS

The materials used and the experimental procedures have already been described.² 2,3,4,4,5,6-Hexamethyl-1-methylene-cyclohexa-2,5-diene was prepared according to the method of Doering *et al.*⁵

Hexamethylbenzene dissolves readily in 100% sulphuric acid to give yellow solutions which have no electron spin resonance spectra. After a few hours, a deep red colour develops, together with the characteristic electron spin resonance spectrum under consideration. This spectrum consists of a basic, asymmetric triplet with a ratio of intensities approximately 1:2:1, but with the group at low-field somewhat broader than that at high-field.

Under very high amplification, 25 lines were detected in each group, and it is virtually certain that there are at least 27 lines. Under high-resolution conditions, using superheterodyne detection and very low klystron power levels, it was possible to resolve the central components of the central group into further sets, each line having a width of about 50 milligauss and a separation of about 70 milligauss. On moving away from the centre, the resolution became less, and it was not possible to resolve any of the high- or low-field components. The resolved central components appeared to consist of triplets and quartets, in accord with expectation if the hyperfine coupling due to one set of protons is close to twice that due to the other set.

In deuteriosulphuric acid the major triplet was lost, being replaced by a quintuplet (*ca.* 1:2:3:2:1) with a hyperfine splitting about one sixth that of the original. The remainder of the spectrum was unchanged, thus establishing that only the two strongly interacting protons are readily exchanged with solvent protons.

The *g*-value was measured by taking simultaneous readings of the microwave frequency and field magnitude using a proton resonance probe. The result, 2.0027, is accurate to about ± 0.0003 .

DISCUSSION

Interpretation of the Spectrum.—The major triplet splitting of 5.4 gauss is unambiguously assigned to two equivalent protons. Since these are the only protons which readily exchange with those of the solvent they cannot be two protons of a methyl group sterically constrained to a fixed orientation with respect to the ring. We therefore suggest that the radical is of the form $R\dot{C}H_2$. That the residual splitting of about 1.7 gauss is in fact composite is established by the partial resolution of the central lines. If one hyperfine coupling constant is set equal to 1.7 gauss and the other is approximately twice this value, then the central lines of each group should consist of alternating sets of three and four lines. If there is a factor of three or greater, then the maximum number of almost coincident lines is three and several are simple doublets. The results strongly suggest that two is the correct factor so we set the third coupling constant approximately equal to 3.4 gauss. There can be no further hyperfine coupling unless it is considerably less than the observed line width of about 50 milligauss.

At least 25, and probably 27 main lines have been detected in each of the three groups. This eliminates the possibility that the 1.7- and 3.4-gauss splittings stem from two pairs of two equivalent methyl groups, since this could give only 19 lines. The most likely alternative is that there is one set of six equivalent protons from two equivalent methyl groups and one set of twelve from four equivalent methyl groups. This would give 31 lines with about the correct ratio of intensities but the outer lines would be extremely weak relative to the centre and would have been lost in background noise.

The *g*-value of 2.0027 is identical to that found for other simple aromatic cations,¹ and hence oxidation to quinone-type radicals seems unlikely.

* Part XXV, S. B. Barnes and M. C. R. Symons, *J. Chem. Soc. (A)*, 1966, 66.

¹ R. Hulme and M. C. R. Symons, *Proc. Chem. Soc.*, 1963, 241.

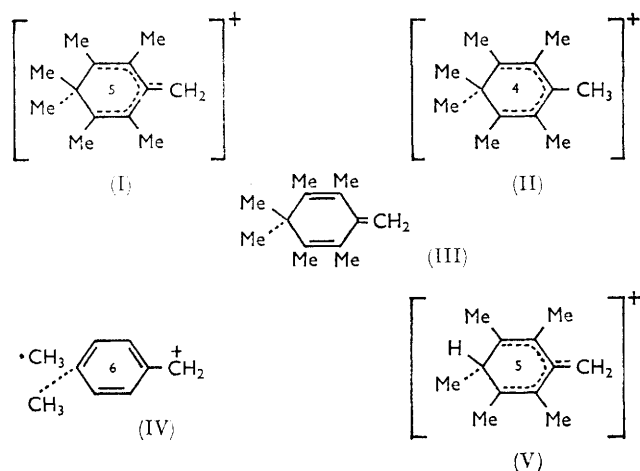
² R. Hulme and M. C. R. Symons, *J. Chem. Soc.*, 1965, 1120.

³ R. Hulme and M. C. R. Symons, *Nature*, 1965, 206, 293.

⁴ L. S. Singer and I. C. Lewis, personal communication.

⁵ W. von E. Doering, M. Saunders, H. G. Boyton, H. W. Earmart, E. F. Wadley, W. R. Edwards, and G. Laber, *Tetrahedron*, 1958, 4, 178.

Nature of the Radical.—Quite the most probable radical seems to be the hexamethylbenzyl cation (I). That protonated hexamethylbenzene in sulphuric acid can readily transfer a methyl group to give the heptamethylbenzene ion (II) is well established,⁵ and this



can then lose a proton to give (III). Oxidation of (II) or (III) could give (I), whilst an equilibrium between (II) and (III) could provide a route to exchange with deuteriosulphuric acid at the methylene groups only, provided oxidation is rapid compared with the rate of migration of the methyl group in (II). The ready oxidation of (III) to the radical under consideration is in accord with these postulates.

Perhaps the most reasonable assignment of the two small coupling constants would then be 1.7 gauss to the two aliphatic methyl groups and 3.4 gauss to the ring methyls, but other combinations of the six methyl groups are also possible.

Electronic Structure of the Radical.—If the postulated structure (I) is accepted, then the hyperfine coupling constants may be used to give information about the electronic structure of the radical.

The most remarkable result is the large hyperfine coupling to the six γ -protons of 1.7 gauss. This is reminiscent of the very large coupling to the methylene protons of the cyclohexadienyl radical,⁶ and may arise because of a strong hyperconjugative effect involving the σ -electrons joining the two methyl groups to the ring.

A strong interaction of this sort might go some way to explaining the fact that the four remaining methyl groups apparently have equal proton hyperfine coupling constants. It would also explain the relatively low spin-density of about 0.23 on the methylene carbon. Any simple theory would predict that there should be a

large positive spin-density at the positions *ortho* to the $-\text{CH}_2$ group and a small negative spin-density at the *meta*-positions. The situation envisaged is comparable with that found for the durosemiquinone anion and its conjugate acid.⁷ For the symmetrical anion all four methyl groups are equivalent, but on protonation one pair have a reduced interaction which can be shown to be negative, whilst the other pair interact more strongly, the total spin-density in the ring remaining approximately constant.

The required near-equivalence, together with the large γ -proton hyperfine coupling could be reached if structures such as (IV) contribute considerably to the actual structure.

There are alternative assignments. For example the two *ortho*-groups might be fortuitously equivalent to the two aliphatic methyl groups, and the two *meta*-groups could then give rise to the small hyperfine coupling.

Line-broadening.—The two outer sets of lines are markedly broader than the central set. Also, within each set there is a slight broadening on going away from the centre. The former effect is characteristic of radicals containing two α -protons and is due to a relaxation associated with the large hyperfine anisotropy found for α -protons which asymmetrically broadens the $M_I = \pm 1$ lines but not the central $M_I = 0$ line. This is in accord with the structure postulated since rotation of the $-\text{CH}_2$ group relative to the ring should be strongly restricted.

Stability of the Radical.—If the present assignment is accepted, then an interesting question that arises is concerned with the exclusive formation of this particular radical, and its remarkable stability. In part, its stability stems from the fact that cations are greatly stabilised by the medium, and have only a small tendency to dimerise. The contrast with the marked instability of the hexamethylbenzene cation is particularly striking. The structurally similar radical, (V) is a tautomer of the hexamethylbenzene cation and the fact that no trace of this radical is detected¹ shows either that the symmetrical cation is favoured, or that the process of decay of the hexamethylbenzene cation involves this ion as an intermediate.

We favour the latter alternative, and stress that loss of a proton followed by dimerisation is a reasonable reaction for (V) but not for (I).

We thank the D.S.I.R. for financial assistance and Shell Research Ltd. for a grant (to R. H.).

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LEICESTER. [5/883 Received, August 13th, 1965]

⁶ H. Fischer, *J. Chem. Phys.*, 1962, **37**, 1093.

⁷ T. E. Gough and M. C. R. Symons, *Trans. Faraday Soc.*, 1966, **62**, 269.