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THE BENZOCYCLOBUTENE AND 1,2-BISMETHYLENECYCLOBUTANE ANION RADICALS.

A REVISED ASSIGNMENT

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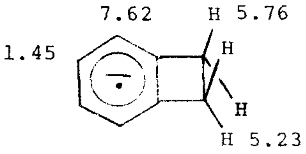
The reductions of the title compounds have recently been reported. (1,2) On the basis of their rather exceptional esr spectra and theoretical considerations, it was proposed that the anion radicals of both substrates had undergone valence isomerization and that the anion radicals actually observed were those of o-xylylene and tetramethyleneethane, respectively. Subsequent evidence, summarized below, requires us to withdraw this proposal and to identify the observed anion radicals as those of the unrearranged starting substrates, despite the several unexpected features of their esr spectra.

Benzocyclobutene. - Two particular features of the esr spectrum earlier suggested the o-xylylene, as opposed to the benzocyclobutene, structure: (i) the spectrum requires four magnetically different pairs of protons. The benzocyclobutene structure would qualify only if the methylene protons were differentiated, e.g., by conformational effects or ion pairing. Referring to the first possibility, the structure of benzocyclobutene seems not to have been determined, but cyclobutene is thought to be planar. (3,4) Moreover, the small difference in what would then have to be the methylene hfs (5.76 vs. 5.23) would reflect such a small degree of puckering that conformational rigidity at -60^0 would be difficult to conceive. As to the second possibility, that of ion pairing, a contact ion pair would seem necessary to explain the nonequivalence. This would normally lead one to expect a metal splitting, but none was observed at -60^0 to -80^0 in either THF or DME in the initial phase of this work. Further, if the methylene protons are differentiated by their proximity to the metal ion, the disparity between the methylene hfs would be expected to be profoundly solvent and temperature dependent, according as the contact ion pair is loosened or tightened. This was not observed (e.g., the difference was 0.50 G in DME vs. 0.53 G in THF): (ii) the second aspect of the spectrum which seemed to support the o-xylylene structure was the anomalously large methylene splittings. Presumably 1 should have a spin distribution similiar to that of the o-xylene anion radical (2). The experimental hfs



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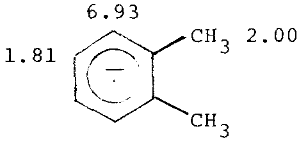

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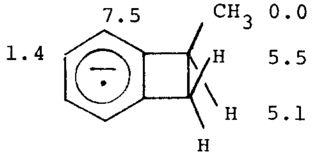
would roughly accord with this expectation so far as the ring protons are concerned, but the methylene hfs in 1 are far larger than the methyl hfs in 2. Allowance for the $\langle\cos^2\theta\rangle_{av}$ dihedral angle dependence of beta hfs lifts the expected a_{CH_2} to about 2.00 x 3/2 = 3.0 G. This follows from that fact that $\langle\cos^2\theta\rangle \simeq 3/4$ for planar 1 (only approximately because, although the H-C-H angle of benzocyclobutene is unknown, it is undoubtedly somewhat larger than that for a methyl group, upon which the estimate is based) and only 1/2 for the freely rotating methyl group. Puckering would lower the predicted value of a_{CH_2}. It also follows that the unattainable maximum beta hfs would be 2.00 x 2 = 4.0 G (assuming $\langle\cos^2\theta\rangle_{max} = 1$), still considerably smaller than the observed values. Calculations using the ring hfs of 1 and 2 indicate the juncture positions of 1 to have less, rather than more, spin density than 2, so that a larger value of a_{CH_2} could not be attributed to an augmented spin density interacting with the methylene protons. In contrast, the o-xylylene structure seemed nicely consonant with all of the above data.

The esr results for the anion radical of 3 are wholly inconsistent with the o-xylylene structure 4. The latter should have a large (ca. 5 G) methyl hfs, whereas no methyl splitting at all was resolved for 3, a fact inconsistent



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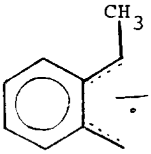

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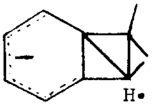
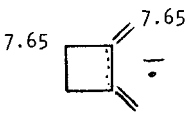
with the rearranged structure. The similarity of the observed splittings in 3 to those of 1 make it equally clear that the cyclobutene ring of the latter is also intact. Further, the esr spectrum of 1 in tetraglyme-glyme (-80°) showed equivalent methylene protons at an averaged hfs (5.60 G) and no appreciable changes in the ring splittings.

The reason(s) for the anomalously large methylene hfs in 1 are still not clear to us. An interesting possibility is a long range γ hfs of the type shown below, which might be especially favorable in the cyclobutane system, where the 1,3 carbon-carbon distance is so comparatively short. The entire matter is under further investigation.



1,2-Bismethylenecyclobutane. - Once more, the methylene hfs were deceptively large and in addition, all eight protons were magnetically equivalent. The observed splittings are given over structure 5 and those for the 2,3-dimethylbutadiene anion radical for comparison, over 6. Note the gross dissimilarity. The hfs of anion radicals 7, 8, and 9 demonstrate that, contrary to our earlier



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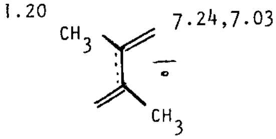

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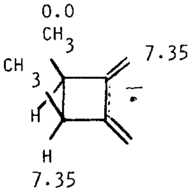
belief, the cyclobutane ring is intact in every case. In 7 and 8 the criterion is, again, the small a_{CH_3} expected for a gamma methyl splitting as opposed to the large a_{CH_3} expected for a beta methyl hfs in the ring-opened isomer. In the case of 9, ring opening is highly unlikely, but a nonet (8 equivalent protons) is still obtained, though the hfs is smaller than for 6.



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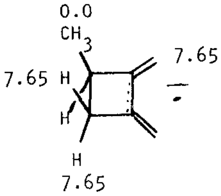

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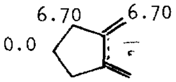

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A more detailed discussion of various aspects of electrocyclic reactions of anion radicals is contemplated in the near future.

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