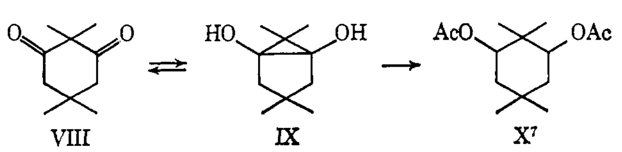
taining impurity mentioned earlier. The nmr spectrum of II in DMSO-d_6 exhibited singlets at δ 0.90 (6 H), 0.94 (6 H), 1.00 (3 H), 1.18 (3 H), and 4.48 (2 H) and doublets ($J \sim 5$ cps) at δ 3.38 (1 H) and 4.33 (1 H). The signals at δ 4.33 and 4.48 vanish on exchange with D_2O, while that at δ 3.38 becomes a singlet. A triacetate derivative, III, mp 159–160.5°, was prepared by treatment of II with acetyl chloride. The infrared and nmr spectra of III are in complete accord with the structure assigned here.

Reduction of I with 2 equiv of lithium gave 2,2,4,4,6,-6-hexamethyl-1,5-dihydroxybicyclo[3.1.0]hexan-3-one (VI) in 55% yield (70% based on recovered I). This crystalline substance melted with decomposition above 150° and exhibited infrared absorption at 1730 cm^{-1} and nmr absorption (in pyridine) characterized by singlets at δ 1.15 (3 H), 1.32 (6 H), 1.50 (6 H), and 1.56 (3 H). The corresponding diacetate derivative VII, prepared in 80% yield by treatment of VI with acetyl chloride, was crystallized from methanol (mp 128–130°) and displayed infrared absorption at 1750 and 1735 cm^{-1} and nmr singlets at δ 1.17 (3 H), 1.27 (9 H), 1.43 (6 H), and 2.14 (6 H).

We find that solutions of VI are readily oxidized by the oxygen in air. An ethyl acetate solution of VI was stable under a blanket of nitrogen for a 24-hr period at 25°. When air was admitted under the same conditions, only the triketone I was recovered. The crystalline state of VI is apparently unaffected by exposure to air for longer periods longer than a month.

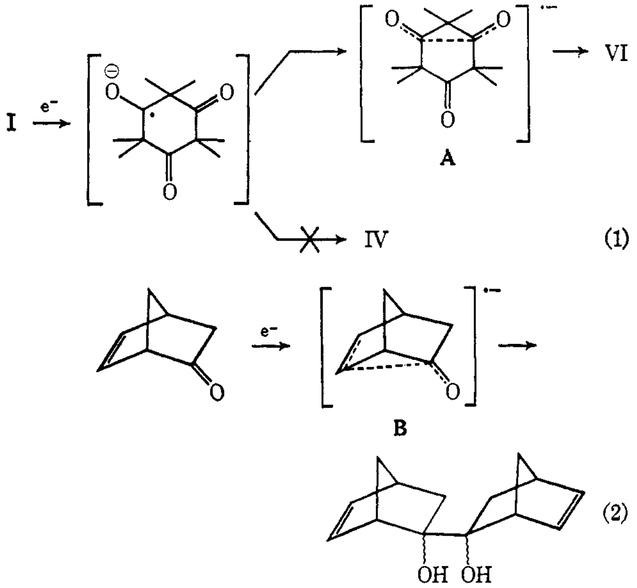
Since the three-membered ring of cyclopropanols is known to be cleaved by the action of acids or bases,[8] a corresponding reaction of the cyclopropanediols reported here would help to confirm our structural assignments. Treatment of VI (under nitrogen) with refluxing methanolic potassium hydroxide for 8 hr gave IV in 62% yield. No reaction of VI was apparent after 24 hr in methanolic hydrogen chloride, but more vigorous acid treatment (*e.g.*, concentrated H_2SO_4) gave rearrangement products that are currently being studied. A similar treatment of II with refluxing methanolic potassium hydroxide in the absence of oxygen gave a complex mixture of diastereoisomeric keto diols apparently contaminated with IV.

When 2,2,5,5-tetramethyl-1,3-cyclohexanedione (VIII) was reduced by lithium in ammonia solutions, an unstable colorless solid was obtained. This material was essentially transparent in the carbonyl stretching region of the infrared, but reverted to diketone VIII on standing overnight at room temperature. Acting on the assumption that this reduction product was the cyclopropanediol IX, we prepared a diacetate derivative (X), mp 87–89°, in the usual manner. The structure of X was confirmed by a strong carbonyl absorption at 1745 cm^{-1} in the infrared and an nmr spectrum (in $CDCl_3$) displaying singlets at δ 0.92 (3 H), 0.96 (3 H), 1.16 (6 H), and 2.10 (6 H) and an AB quartet (4 H) at δ 1.65 and 2.00 ($J \sim 14$ cps).



Some of the cyclopropanediol derivatives reported here have been examined by mass spectrometry, but the spectra have not been very informative. Since the molecular ions could not be detected and since complex fragmentation patterns were observed, we decided to confirm the molecular weights of III and VII by vapor pressure osmometry (the rapid oxidation of dilute solutions of VI prevented us from including this compound as well). The observed molecular weights agreed well with the expected values: III, 347 ± 10 (calcd 340); VII, 297 ± 6 (calcd 296).

The timing of the three-membered ring formation in these reactions is defined in the following manner. The ground-state conformation of I is a twist boat,[9] and the electronic spectrum of this compound shows no evidence of interaction between the carbonyl functions ($\lambda_{max}^{C_6H_{12}}$ 300 mμ (ϵ 80)). However, since reduction of I with a limited amount of lithium gave VI as the only reduction product, the radical anion A is apparently formed more rapidly than conventional reduction to IV (eq 1). A similar radical anion (B) was proposed in the Li-NH_3 reduction of norbornenone to diastereoisomeric pinacols (eq 2).[10]



Cyclopropanediols have been proposed as intermediates in the Clemmensen reduction of β diketones.[11,12]

Acknowledgment. We thank the National Institutes of Health for their support of this work (AM 10849).

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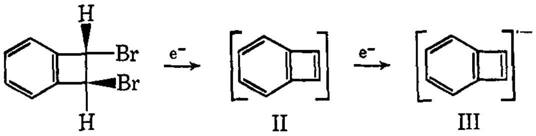
Received April 9, 1969

Benzocyclobutadiene Radical Anion

Sir:

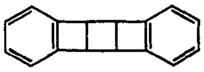
We wish to report the preparation of a new radical anion which from all indications is the benzocyclobutadiene radical anion. Neutral benzocyclobutadiene has been prepared previously by Cava[1] by refluxing *trans*-1,2-dibromobenzocyclobutene[2] with zinc in ethanol. The parent compound, being very reactive, was not isolated; instead, its dimer was isolated. In later experiments, Cava[3] was able to trap the parent compound by treating it with dienes.

We have attempted to trap the reactive benzocyclobutadiene as its radical anion. The method involves the addition of *trans*-1,2-dibromobenzocyclobutene (I) to an excess of solvated electrons[4] in a mixture of glyme and diglyme at −60°. The two bromine atoms are reduced off, yielding II; compound II should be reduced in a diffusion-controlled process by the excess solvated electrons before it can dimerize. Following this procedure, we found that treatment of I with excess solvated electrons yielded a paramagnetic species which exhibited a 27-line spectrum.[7] The observed splitting constants were $a_H = 11.05$ G (two protons), $a_H = 7.60$ G (two protons), and $a_H = 1.48$ G (two protons).

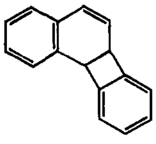


I II III

The possibility existed that the paramagnetic species was merely the radical anion of one of the two known dimerization products of benzocyclobutadiene, namely the head-to-head dimer[8] (IV) or the Diels–Alder dimer[1] (V). These compounds were prepared and reduced under the identical conditions used for the dibromide. They both yielded paramagnetic species, but neither species was similar to that obtained from the dibromide.[9]



IV



V

A second possibility was that we were observing the radical anion of the bromide itself. This is seemingly ruled out by the fact that the diiodo compound upon reduction yielded the same paramagnetic species as the dibromide.[10]

Additional support for the benzocyclobutadiene radical anion comes from the over-all width of the spectrum, 40.3 G, and the hyperfine coupling constants. The observed coupling constants of $a_H = 1.48$ G and $a_H = 7.60$ G are comparable with the aromatic proton splitting constants of benzocyclobutene,[12] $a_H = 1.40$ G and $a_H = 7.60$ G, and other *o*-dialkylbenzene radical anions. However, the $a_H = 11.05$ G splitting constant is much larger than the methylene splitting constant of benzocyclobutene,[12] $a_H = 5.50$ G, or the methyl splitting constants of *o*-xylene,[13] $a_H = 2.00$ G. Therefore, this large value would seem unlikely for a methylene proton but would be possible for a proton attached to an sp^2 carbon which has a bond angle[14] much smaller than 120°. Nelson and Trost[17] have observed that the Q value necessary to explain the unusually large hyperfine splitting constants of the 1,2,5,6 protons of paracyclene must be 30 G. In the benzocyclobutadiene radical anion, the bond angles of the four-membered ring are much smaller than in the five-membered ring of paracyclene, and we might expect a Q value for these positions to be even larger. Thus the large splitting constants would be expected even though the spin density in the four-membered ring may be small. In addition, the over-all width of the spectrum would be expected to be much larger than the usual 22–28 G.

All the data we have collected to date indicate that the paramagnetic species is the benzocyclobutadiene radical anion. We are presently carrying out additional experiments which will shed further light on the exact nature of this species.

Acknowledgment. Financial support of this investigation by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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(4) The solution of solvated electrons was prepared by allowing a mixture of diglyme and glyme to stand in contact with a potassium mirror at Dry Ice–acetone temperatures for 1–2 hr. A study of the concentration of solvated electrons *vs.* solvent and temperature has been reported.[5,6]

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Received April 2, 1969

Origin of the Rotational Strength of Heme Transitions in Myoglobin

Sir:

Recently, Cotton effects associated with the heme electronic transitions have been studied in a number of heme proteins.[1] Several proposals have been made for the origin of these Cotton effects. In principle, the

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