

a sufficiently long excited-state lifetime permits a chain mechanism<sup>3a</sup> to operate. We are currently examining isomerization behavior of other 1-4 aryl-substituted butadienes and trienes both to determine the extent of this selectivity and the mechanism of the rapid-selective deactivation.

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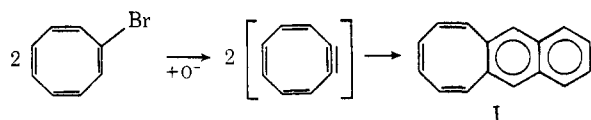
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## The Cyclooctatrienyl Anion Radical

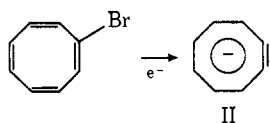
Sir:

Benzene has stirred considerable chemical interest but has just very recently been observed under conditions conducive to general spectrometric observation.<sup>1</sup> Here we wish to report the preparation and observation of a new anion radical, which from all indications is the anion radical of cyclooctatrienyl (II). This anion radical is the eight-member nine-electron analog of benzene.

Monobromocyclooctatetraene will react with strong base (potassium *tert*-butoxide) in etheral solvents to form naphthocyclooctatetraene.<sup>2</sup> This product is believed to be formed from the dimerization of cyclooctatrienyl as shown below.



We have attempted to trap the reactive cyclooctatrienyl as its anion radical. This was accomplished by allowing a solution of bromocyclooctatetraene to react in a mixture of 98% tetrahydrofuran and 2% HMPA<sup>3</sup> with a potassium mirror at  $-100^\circ$  under high vacuum. The esr pattern of this solution (Figure 1) consists of three triplets each due to two equivalent protons with coupling constants of 2.92, 3.55, and 4.06 G. There is also a splitting of 0.28 G due to the potassium cation. This esr pattern was observed at  $-100^\circ$  and disappears irreversibly at about  $-80^\circ$ .



This set of coupling constants is perfectly consistent with that expected for II. The coupling constant for the eight equivalent protons of cyclooctatetraene is 3.21 G,<sup>4</sup> and the average proton splitting for the new radical

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(3) HMPA (hexamethylphosphoramide) was purified as previously described: G. R. Stevenson, L. Echegoyen, and L. R. Lizardi, *J. Phys. Chem.*, **76**, 1439 (1972).

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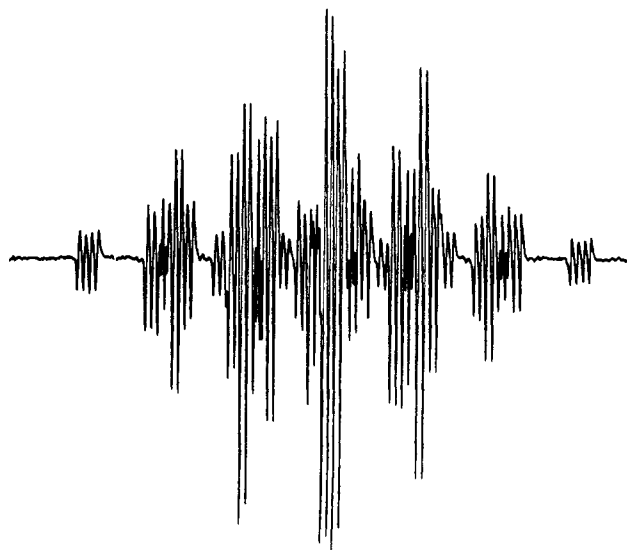


Figure 1. ESR spectrum of II at  $-100^\circ$  in tetrahydrofuran with added HMPA.

is 3.5 G. The fact that this average splitting is close to that for cyclooctatetraene indicates that the new radical is a perturbed cyclooctatetraene type anion with two protons missing.

The possibility existed that the new radical was simply the anion radical of the known cyclooctatetraene dimer (I). However, the reduction of I under the same conditions gave a radical yielding an entirely different esr spectrum consisting of more than 100 hyperfine lines.

It is also conceivable that the esr pattern for the new radical was due to the monobromocyclooctatetraene anion radical or the anion radical of some other monosubstituted cyclooctatetraene. This possibility was ruled out by the fact that all other monosubstituted cyclooctatetraene anion radicals, including those of *tert*-butoxycyclooctatetraene, ethylcyclooctatetraene, and phenylcyclooctatetraene, exhibit a pentet of quartets for the ring protons.<sup>5</sup> The esr coupling constants for the three sets of triplets observed for II are assigned and compared to those obtained from an INDO open shell calculation in Table I.

Table I. Calculated and Experimental Coupling Constants

The diagram shows a cyclooctatetraene ring with protons numbered 1 through 8. Protons 1 and 2 are on the right side, 3 and 4 are at the top, 5 and 6 are on the left side, and 7 and 8 are at the bottom.

| Position | $a_H(\text{exptl})$ , G | $a_H(\text{calcd})^a$ , G | $a_H(\text{calcd})^b$ , G |
|----------|-------------------------|---------------------------|---------------------------|
| 1, 2     |                         |                           |                           |
| 3, 8     | 4.06                    | 4.87                      | 4.71                      |
| 4, 7     | 2.92                    | 0.78                      | 1.38                      |
| 5, 6     | 3.55                    | 3.26                      | 3.06                      |

<sup>a</sup> The following bond distances were used for this INDO calculation: the C-C triple bond is 1.258 Å, all other C-C bonds are 1.415 Å, and C-H bonds are 1.08 Å. <sup>b</sup> This calculation was carried out using the same bond distances except that the C-C triple bond was considered to be 1.355 Å.

(5) (a) G. R. Stevenson and J. G. Concepcion, *J. Phys. Chem.*, **78**, 90 (1974). (b) The reduction of (phenyl-*ds*)cyclooctatetraene results in an anion radical that yields a pentet of 3.68 G due to four equivalent protons and a quartet of 2.38 G due to three equivalent protons in HMPA.

All of the above mentioned data indicate that the anion radical of the eight-member analog of benzyne has formed. The relative stability of II in comparison with benzyne is explained in part by the reduced ring strain caused by the triple bond in the eight-member system.

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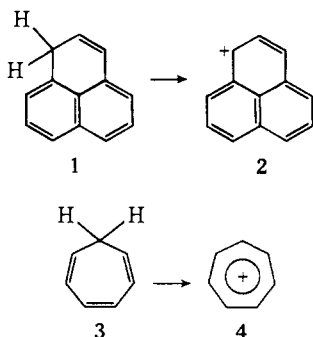
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### Carbonium Ion Formation by Oxidation of Hydrocarbons by Fluorosulfonic Acid Solutions

Sir:

The formation of carbonium ions from hydrocarbons in strong acids by a process which is formally a hydride abstraction is well known.<sup>1-3</sup> SbF<sub>5</sub> is known to be quite active<sup>4,5</sup> and both Olah and Hogeveen have presented evidence for hydride abstraction by a proton.<sup>6-9</sup> We wish to report that some hydrocarbons are oxidized to carbonium ions in fluorosulfonic acid with the concomitant production of sulfur dioxide. We also report the formation of carbonium ions by SO<sub>3</sub> oxidation in aprotic media. The formation of sulfur dioxide during the generation of carbonium ions from hydrocarbons in fluorosulfonic acid does not arise by reduction of SO<sub>3</sub> or fluorosulfonic acid by hydrogen. These observations, together with the report of facile hydride abstraction by SbF<sub>5</sub>,<sup>5</sup> indicate the existence of several mecha-



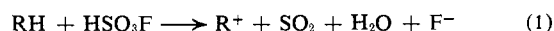
nisms for cation formation from hydrocarbons in superacids. Much work remains to be done in this area

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to unequivocally establish the mechanisms by which hydrocarbons form carbonium ions in superacids.

The compounds shown above give rise rapidly to the indicated carbonium ions when the hydrocarbons are dissolved in neat fluorosulfonic acid at 25°. In both cases the hydrocarbon was added slowly to a stirred solution of the acid. Carbonium ion structures were verified by nmr spectroscopy, the ions having been reported previously.<sup>10,11</sup> Gas samples were withdrawn into an evacuated bulb and analyzed by mass spectroscopy. Large peaks at *m/e* 64 and 48 were observed indicating the presence of SO<sub>2</sub> or SO<sub>3</sub>. No increase in the small background peak at *m/e* 2 was observed. To demonstrate that we would have detected hydrogen if it was present, we repeated the procedure using a small amount of zinc and sulfuric acid and observed a very large peak at *m/e* 2. Fluorosulfonic acid also was run in the mass spectrometer, and no peaks at *m/e* 64 and 48 were observed. To verify that these peaks were indeed due to SO<sub>2</sub>, classical qualitative analysis techniques were used since it proved impossible to distinguish between SO<sub>2</sub> and SO<sub>3</sub> using mass spectrometry.<sup>12</sup> Blank runs confirmed our ability to distinguish between SO<sub>2</sub> and SO<sub>3</sub>. No SO<sub>2</sub> could be detected in the vapors above pure fluorosulfonic acid, but a positive test for SO<sub>2</sub> was obtained following the generation of ions 2 and 4, confirming that the gas analyzed mass spectrometrically was SO<sub>2</sub>. Stirring fluorosulfonic acid with hydrogen gas produced no SO<sub>2</sub>, in agreement with earlier observations.<sup>13,14</sup>

The yields of carbonium ions vary with the precursor, the acid strength, and the mode of addition of the precursor to the acid. Using weighed amounts of tetramethylammonium bromide as an internal standard, the yield of ion from a precursor could be measured. Conversions ranging from 30% (cycloheptatriene in FSO<sub>3</sub>H at 25°) to 100% (cycloheptatriene oxidized with SO<sub>3</sub> in SO<sub>2</sub> at -28°) were observed. The other products were polymeric. The amount of SO<sub>2</sub> produced was determined by sweeping it out of the reaction mixture with a stream of dry N<sub>2</sub> into a standardized I<sub>2</sub> solution. The loss of I<sub>2</sub> was measured by titration with thiosulfate.<sup>15</sup> In all cases examined, SO<sub>2</sub> yields were within experimental error ( $\pm 1\%$ ) of the cation yields determined by nmr. We cannot distinguish between oxidation by FSO<sub>3</sub>H or by SO<sub>3</sub> formed by the equilibrium dissociation of FSO<sub>3</sub>H. The overall stoichiometry is the same and is shown in eq 1.



In another experiment cycloheptatriene was treated with SO<sub>3</sub> in SO<sub>2</sub> solution at -78°. The tropylium ion was formed quantitatively and cleanly. In sulfuric acid, cycloheptatriene and phenalene also give the tropylium ion and phenalenium ion (2), respectively. Deno has observed that xanthene forms the xanthyl cation in aqueous sulfuric acid concentrations greater

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