# Photoinduced Electron-Transfer Reactions: Rearrangement of a Bicyclopropenyl Radical Cation

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Abstract: The reaction of 3,3'-dimethylbicyclopropenyl (1) with photoexcited electron acceptors (chloranil, fluoranil) results in conversion to a 4:1 mixture of o- and m-xylene. Nuclear spin polarization effects observed during irradiation provide direct evidence for the intermediacy of 3,4-dimethylbenzvalene (2).

Whereas all benzene isomers and/or their simple derivatives are readily available and their chemistry is thoroughly explored, much less is known about the corresponding radical cations. The elucidation of the benzene isomers played an important role in the development of organic chemistry. Before the structure of benzene was generally accepted as the hexagonal aromatic entity formulated by Kekulé,<sup>1</sup> several alternative formulations for the (CH)<sub>6</sub> hydrocarbon had been proposed. Several of these, specifically the bicyclic structure proposed by Dewar<sup>2</sup> and the tetracyclic structure (prismane) proposed by Ladenburg,<sup>3</sup> have since "materialized" as valence isomers of benzene.<sup>4,5</sup> A tricyclic isomer, benzvalene, was identified<sup>6</sup> in 1962, and the last of the possible (CH)<sub>6</sub> isomers, bicyclopropenyl, began to attract attention in the early 1970's, possibly stimulated by the Kekulé centennial.



We are interested in the radical cations of strained-ring hydrocarbons.<sup>7</sup> In the course of these studies we have established the existence of discrete radical cations for derivatives of Dewar benzene,<sup>8</sup> Ladenburg's benzene,<sup>9</sup> and benzvalene<sup>10</sup> as well as the

Scheme H



0-XYLENE p-XYLENE

ready rearrangement of these species to benzene. In this publication we report the generation of the radical cation of 3,3'-dimethylbicyclopropenyl (1) by reaction with photoexcited electron acceptors and its subsequent rearrangements. The nature of the intermediates is probed by using the CIDNP technique, which has proved useful with other strained ring systems.<sup>7-10</sup>

For the following discussion it is useful to consider the mechanism for the thermal rearrangement of bicyclopropenyl derivatives. The elucidation of this mechanism was not without controversy.<sup>11-15</sup> Intermediates such as the benzene valence isomers, Dewar benzene,<sup>11</sup> benzvalene,<sup>12</sup> and prismane<sup>13</sup> were proposed as well as biradical or zwitterionic species.<sup>11,14</sup> The photochemical<sup>14</sup> and Ag(I)-catalyzed<sup>15</sup> rearrangements of these hydrocarbons are thought to proceed along similar mechanistic pathways. The former reaction gives mainly benzenes, whereas in the latter Dewar benzenes are the major products. The generally accepted mechanism of the thermal isomerization is outlined in Scheme L

#### **Experimental Section**

The electron acceptors, chloranil (Eastman Organics) and fluoranil (Aldrich), and the deuterated solvent, acetonitrile (99%, Merck Sharp and Dohme), were used without further purification. 3,3'-Dimethylbicyclopropenyl was prepared from the bis-dibromocarbene adduct of 2,3-dimethylbutadiene (Aldrich) according to the method of deWolf, Stol, Landheer, and Bickelhaupt.<sup>16</sup> It was purified by preparative gas

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Figure 1. <sup>1</sup>H NMR spectra (90 MHz) of an acetonitrile- $d_3$  solution containing 0.02 M chloranil and 0.02 M 1 in the dark (bottom) and during UV irradiation (top).

chromatography on a 6 ft  $\times$  <sup>3</sup>/<sub>8</sub> in. aluminum column packed with 10% SE-30 on 60/80 Chromosorb W.

The CIDNP studies were carried out with samples containing 0.02 M each of electron acceptor and 1, which were deaerated by purging with Ar for 3 min. They were irradiated in the probe of a Bruker WH 90 Fourier transform NMR spectrometer with the collimated beam of an Osram 200W high-pressure mercury lamp. Pyrex NMR tubes were employed to ensure that only the electron acceptors absorbed the incident light. A pulse angle of 90° was used, and only the data from a single sweep were accumulated because of the high reactivity of the system.

The photoreaction of 1 with chloranil and the conversion to o- and m-xylene were followed by NMR spectroscopy and by gas chromatography. The latter was performed on a Hewlett-Packard Model 5880 analytical gas chromatograph equipped with a 60 m OV-101 glass capillary column. The temperature was raised from 35 to 70 °C at a rate of 1 deg/min. Under these conditions, the retention times were the following: 1 (12.53 min), m-xylene (27.64 min), p-xylene (27.78 min), and o-xylene (30.50 min). The reaction is efficient at first but is progressively retarded with increasing conversion due to the formation of (a) highly absorbing side product(s). Accordingly, the reaction was not carried to complete conversion. The steady-state concentration of dimethylbenzvalene was not sufficient for NMR detection. Throughout the reaction the ratio of o- and m-xylene remained constant at 4:1. p-Xylene was observed only after substantial conversion and did not exceed 5% of the xylene mixture under any circumstances. The yield of xylenes based on starting material depletion was 30-40%.

#### **Results and Discussion**

The reaction of 1 with photoexcited chloranil in deaerated acetonitrile, when carried out in an NMR spectrometer, gives rise to strong CIDNP effects (Figure 1). The spectrum displays polarization from at least three rearrangement products. The olefinic protons of 1 show weak net emission whereas the ring protons of o-xylene show weakly enhanced absorption. The predominant features of the spectrum, a triplet at 3.6 ppm and a singlet at 1.6 ppm, both in emission, are assigned to the bicyclobutane bridgehead and the methyl protons, respectively, of 3,4-dimethylbenzvalene (2). This assignment is based on the following considerations: the chemical shifts of the polarized species are very close to the corresponding ones of 3-methylbenzvalene;<sup>17</sup> the coupling constant of the triplet is similar to the

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Scheme II

$$A \xrightarrow{hv} {}^{1}A^{*} \qquad (1)$$

$${}^{1}A^{*} \xrightarrow{isc} {}^{3}A^{*} \qquad (2)$$

$${}^{3}A + D \longrightarrow {}^{3}A^{-}D^{+} \qquad (3)$$

$${}^{3}\frac{}{A^{-}D^{+}} \xrightarrow{} {}^{1}\frac{}{A^{-}D^{+}} \qquad (4)$$

$${}^{1}\frac{}{A^{-}D^{+}} \xrightarrow{} A + D^{\dagger} \qquad (5)$$

$${}^{3}\frac{}{A^{-}D^{+}} \longrightarrow {}^{1}\frac{}{A^{-}D^{+}} \qquad (6)$$

$${}^{1}\frac{}{A^{-}D^{+}} \longrightarrow {}^{2}A^{-} + {}^{2}D^{+} \qquad (7)$$

$${}^{2}D^{+} \longrightarrow {}^{2}D_{r}^{+} \qquad (8)$$

$$D + {}^{2}D_{r}^{+} \longrightarrow {}^{2}D_{r} + \qquad (9)$$

analogous coupling in benzvalene;<sup>6</sup> and the polarization pattern is consistent with the pattern observed for benzvalene and naphthvalene (vide infra).<sup>10</sup>



As in other systems<sup>7-10</sup> this polarization is ascribed to a radical ion pair, which is generated by electron transfer from the hydrocarbon to the triplet state of the photoexcited quinone (eq 3). These pairs undergo hyperfine induced intersystem crossing (eq 4), leading to an overrepresentation of some nuclear spin states (and to an underrepresentation of others) in the resulting singlet pairs. The subsequent decay of singlet radical ion pairs (eq 5) transfers the unbalanced spin populations to the products. Triplet pairs, which carry the complementary polarization, tend to diffuse apart (eq 7) in highly dielectric solvents (acetonitrile), allowing the non-Boltzmann populations to return to equilibrium. The system discussed here is further complicated by the rearrangements of the donor-derived radical cations, either rapidly within a geminate radical ion pair (eq 6) or more slowly, in individual radical cations (eq 8) which have separated by diffusion from their counterions (eq 7). Rearranged products are formed by recombination of geminate pairs or by electron exchange between a rearranged radical cation and a donor molecule (eq 9).

The observed products as well as the direct evidence for a benzvalene intermediate indicate an isomerization mechanism quite different from that established for the thermal isomerization.<sup>11c</sup> Both the product distribution and the CIDNP results offer clues as to the prevailing mechanism. The polarization of the bicyclopropenyl indicates the existence of a radical cation which can regenerate 1 (albeit in low efficiency). The polarization of the benzvalene reveals a rapid rearrangement, since the signal directions identify it as a geminate recombination product (vide infra). Finally, the polarization of the o-xylene is different from that observed in the analogous reaction of chloranil with o-xylene. The latter reaction results in particularly strong polarization for the methyl groups, with an enhancement five times that of the

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Table I. Hyperfine Coupling Patterns of Various  $C_6H_4(CH_3)_2$ Radical Cations and CIDNP Results

radical	proton	hyperfine coupling	potential "product"	CIDNP	
cation				expected <sup>a</sup>	obsd
3 (planar)	H <sub>1</sub> -H <sub>4</sub> CH <sub>3</sub>	- negl	1	A -	E -
3 (pyramidal)	H <sub>1</sub> -H <sub>4</sub> CH <sub>3</sub>	+ negl	1	E 	E 
4	$\begin{array}{c} H_1, H_4 \\ H_2, H_3 \\ CH_3 \end{array}$	- + negl	1	E <sup>b</sup>	E ~
6	H <sub>1</sub> , H <sub>2</sub> H <sub>3</sub> H <sub>4</sub> CH <sub>3</sub> CH <sub>3</sub>	negl + negl negl		A - - -	c
8	$H_1, H_4 \\ H_2, H_3 \\ CH_3$	negl + +	2	– E E	E E
10	H <sub>1</sub> -H <sub>4</sub> CH <sub>3</sub>	- +	o-xylene	A E	A negl

<sup>a</sup>According to the sign rule of Kaptein.<sup>23</sup> <sup>b</sup>Assuming  $|a_{1,4}| < |a_{2,3}|$ . <sup>c</sup>The benzvalene corresponding to **6** is not observed.

aromatic protons. Obviously, the o-xylene polarization must arise from a species other than the o-xylene radical cation.

A comparison of the observed polarization patterns with the hyperfine coupling patterns of the potential intermediates elucidates several facets of the rearrangement mechanism. The first radical cation is likely to be the localized structure 3. The fact that only weak polarization is observed for 1 and the conclusion that the benzvalene 2 is a geminate recombination product suggest a short lifetime for this intermediate. The polarization of 1 is not compatible with a planar  $\pi$ -system, since the negative hyperfine coupling constant (hfc) expected for this structure would result in enhanced absorption (cf. Table I). A pyramidal radical cation, on the other hand, is compatible with the observed polarization since for any resonance structure the hfc of the  $\beta$ -proton (a > 0) should outweigh the hfc of the  $\alpha$ -proton (a < 0), as a comparison with the cyclopropyl radical suggests.<sup>18</sup> The presence of two hfc's of similar magnitude but opposite sign would explain the low CIDNP intensities. Olefin radical cations with pyramidal structures have been discussed recently, <sup>19,20</sup> but the sign of the relevant hfc's could not be determined.

Cyclization of the primary structure produces the tricyclic species 4 in which spin and charge are localized on two cyclopropane carbons in different rings. The hyperfine coupling pattern expected for this species is consistent with the polarization observed for 1. However, energy considerations eliminate 4 as a likely precursor for 1. The cycloreversion of 4 is more likely to generate the radical cation 5 and give rise to 1,1'-dimethyl-3,3'-bicyclopropenyl (9) than to regenerate the starting material via 3. Since 9 is not observed, the cycloreversion to 1 can be eliminated.

Cleavage of one internal cyclopropane bond concurrent with bicyclobutane formation places the radical cation onto the benzvalene surface. Initially, two benzvalene radical cations, **6** and **7**, can be formed, but once on this surface all nine dimethylbenzvalene radical cations are, in principle, accessible. For 2,3-dideuteriobenzvalene this type of tautomerization has been achieved photochemically.<sup>21</sup> The fact that **2** is the only benzvalene observed indicates a pronounced preference for this structure, no doubt due to the stabilization imparted by the methyl groups. The observed polarization identifies the radical cation as an interScheme III<sup>a</sup>



<sup>a</sup> The numbering system was chosen to illustrate the fate of the individual centers in the interconversions.

Scheme  $IV^a$ 

$$\overrightarrow{\mathbf{A}^{-} \mathbf{BV^{+}}} \longrightarrow \overrightarrow{\mathbf{A}^{-} \mathbf{11}} (10)^{\mathbf{b}}$$

$$\overrightarrow{\mathbf{A}^{-} \mathbf{11}} \longrightarrow \mathbf{A} + o \cdot \mathbf{xylene^{\dagger}} (11)$$

$$\overrightarrow{\mathbf{A}^{-} \mathbf{8}} \longrightarrow \overrightarrow{\mathbf{2}A^{-} + \mathbf{2}\mathbf{8}^{\ddagger}} (12)$$

$$\overrightarrow{\mathbf{28^{\ddagger}}} \longrightarrow \overrightarrow{\mathbf{211^{\ddagger}}} (13)$$

$$\overrightarrow{\mathbf{211^{\ddagger}}} + \mathbf{D} \longrightarrow o \cdot \mathbf{xylene^{\ddagger} + \mathbf{2D^{+}}} (14)$$

<sup>a</sup>  $\dagger$  and  $\pm$  represent different types of polarization. <sup>b</sup> BV<sup>+</sup> = 6, 7, or 8.

mediate with spin density in the  $\pi$ -orbital. In such a structure positive hfc's are expected for both the methyl and the bicyclobutane bridgehead protons (H-2, H-3). The protons adjacent to the double bond (H-1, H-4), on the other hand, are orthogonal to the  $\pi$ -orbital and therefore have negligible hfc's. Similar spin density patterns are reflected in the polarization patterns of benzvalene and naphthylene.<sup>10</sup>

In contrast to dimethylbenzvalene (2) and by analogy with the starting material, the polarization of the xylenes is less than straightforward.<sup>22</sup> The following discussion will be concerned only with the major product, o-xylene. Several of the logical precursors, e.g., 8 or 11, are known to generate strong polarization for the methyl groups as well as for the aromatic protons. Neither of these radical cations can be involved exclusively in the spin-sorting process which underlies the observed polarization. However, this polarization can be explained by the consecutive involvement of benzvalene and o-xylene radical cations and by two

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<sup>(22)</sup> The experiments show the persistent presence of *p*-xylene. In contrast to *o*- and *m*-xylene, the observed polarization is that of the methyl groups and not the aromatic protons. This polarization is ascribed to a small amount of *p*-xylene in the sample, a conclusion supported by the fact that *p*-xylene generates comparable CIDNP effects even in very dilute samples ( $10^{-5}$  M).

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different contributions to the o-xylene polarization. Some o-xylene would be formed as a geminate recombination product from 11 (eq 11), which is generated by rearrangement of benzvalene radical cations such as 6, 7, or 8 in the presence of the semiquinone anion (eq 10). This pathway can be expected to result in strong emission for the methyl protons and weaker emission for the aromatic protons. Another fraction of the o-xylene would be formed from free 3,4-dimethylbenzvalene radical cations which have been separated by diffusion from their semiguinone counterions (eq 12). This fraction would carry mainly the polarization complementary to that observed 2, i.e., enhanced absorption both for the aromatic and methyl protons. The sum of these two contributions may well be the weak absorption observed for the aromatic protons and a fortuitous cancellation of the methyl polarization. Additional support for this scheme is found in the reaction of 1 with photoexcited fluoranil. In this system, the methyl groups of o-xylene appear in emission, since the balance of these contributions is now perturbed. The xylene polarization is further complicated by the fact that 2 and o-xylene, formed by the mechanism discussed above, may reenter the photochemical reaction cycle and generate different contributions to the o-xylene polarization. Experimentally, the methyl groups appear in increasing emission after several seconds of irradiation time.

#### Conclusion

The radical-cation rearrangement of 1 stands in marked contrast to its thermal rearrangement. These results illustrate several interesting differences between the (CH)<sub>6</sub> energy surface and that of the corresponding radical cations. It is generally recognized that the barriers to radical-cation rearrangements are lower than the corresponding barriers in the parent system. It is also known that the stabilities of isomeric radical cations may be reversed relative to the neutral diamagnetic parents. Our results indicate, furthermore, that the relative barrier heights for the reorganization of a given radical cation to several different isomers may show an ordering different from those on the parent energy surface.

Registry No. 1, 31707-64-9; 1 radical cation, 96443-79-7; 2, 55711-03-0; chloranil, 118-75-2; o-xylene, 95-47-6; m-xylene, 108-38-3.

# Synthesis and Structures of $(C_5H_5)_2Mo_2Fe_xTe_2(CO)_7$ (x = 1, 2). Cluster Assembly Mechanisms and the Role of the Tellurium

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Abstract: The compound  $Cp_2Mo_2FeTe_2(CO)_7$  ( $Cp = \eta^5 - C_3H_3$ ), 2, is formed in high yield from the reaction of  $Fe_3Te_2(CO)_9$ and Cp2Mo2(CO)6 in hexane under CO. The product was characterized by spectroscopic methods and its structure determined and Cp<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub> in hexate under CO. The product was characterized by spectroscopic methods and its structure determined by X-ray crystallography. Compound 2 crystallizes in the PI space group with a = 13.216 (2) Å, b = 15.962 (3) Å, c = 21.710(5) Å,  $\alpha = 100.31$  (2)°,  $\beta = 104.74$  (2)°,  $\gamma = 94.20$  (1)°, Z = 8, and  $\rho_{calcd} = 2.547$  g cm<sup>-3</sup>. The structure was solved by direct methods. Blocked cascade refinement on 9947 reflections ( $F_o \ge 3\sigma F_o$ ) produced the final residuals  $R_F = 0.0354$  and  $R_{W_F} = 0.0394$ . The four molecules per asymmetric unit are quite similar, each consisting of a CpMo(CO)<sub>2</sub> fragment bridging the Te wing tips of a Cp(CO)<sub>5</sub>MoFeTe<sub>2</sub> butterfly. The 3.13-Å Te--Te distance is well within bonding distance and is proposed to be chemically significant. This interaction is discussed in the context of other nonmetal-containing cluster compounds. On the basis of these data, it is proposed that such interaction step nonmetal-interactions can have a significant influence the basis of these data, it is proposed that such intracluster nonmetal-nonmetal interactions can have a significant influence on the structures and reactivity of compounds in this class of clusters. The mechanism of formation of 2 is discussed in light of the sciencific structures and reactivity of compounds in this class of clusters. The mechanism of formation of 2 is discussed in fight of the recently reported compound  $Co_2Fe_2S_2(CO)_{11}$ . Thermolysis of 2 affords metallatetrahedrane  $Cp_2Mo_2FeTe(CO)_7$ ,  $Cp_2Mo_2Fe_2Te_3(CO)_6$ , and  $Cp_2Mo_2Fe_2Te_2(CO)_7$ , 3. Compound 3 crystallizes in the orthorhombic space group  $Pn_{2,1}a$  with a = 13.617 Å, b = 12.939 Å, c = 12.199 Å,  $Z = 4^\circ$ , (10)°, and  $\rho_{calcd} = 2.73$  g cm<sup>-3</sup>. The structure was solved by direct methods. Blocked cascade refinement on 1837 reflections ( $F_0 > 3\sigma F_0$ ) produced  $R_F = 0.0256$  and  $R_{W_F} = 0.0249$ . The molecule of approximately  $C_{2v}$  symmetry consists of a tetrahedral  $Mo_2Fe_2$  core with each  $Mo_2Fe$  face capped by a  $\mu_3$ -Te atom. The Fe-Fe distance of 2.433 Å is one of the shortest known single Fe-Fe bonds. The mechanism of formation of 3 from 2 was shown to involve an exampling of Mo metric (Cn labeling experiments) and receared actimally (60%) in the preserve of 10 convir to involve no scrambling of Mo moieties (Cp-labeling experiments) and proceeds optimally (60%) in the presence of 10 equiv of  $Fe(CO)_5$ . Compound 2 also reacts with  $CpCo(CO)_2$  to give two isomers of  $Cp_3Mo_2CoFeTe_2(CO)_5$ . These results imply that the recently reported isomers of  $Cp_2Mo_2Fe_2S_2(CO)_8$  are formed via a five-vertex  $Mo_2FeS_2$  intermediate.

Tellurium-bridged transition metal carbonyl clusters are notably stable in less highly condensed geometries than clusters derived from lighter nonmetals. However, the way that main group atoms influence the connectivity within transition metal-main group carbonyl clusters (TMMGCCs) is poorly understood. Schmid<sup>1</sup> has noted that for clusters of the core stoichiometry (MG)Co<sub>3</sub>, only those nonmetals whose covalent radius is less than 1.30 Å exist in the fully condensed, nonacarbonyl form.  $Co_2FeTe(CO)_9$ extends this series as this tetrahedral cluster features a large  $(r_{cov})$ 

= 1.37 Å) Te atom capping a closed  $Co_2Fe$  triangle with M-M distances of 2.60 Å.<sup>2</sup> The compound  $Fe_3(\mu_3-SnFe(C_5H_5) (CO)_2_2(CO)_9$  is a more spectacular example of a potentially strained cluster, as the large ( $r_{cov} = 1.41$  Å) Sn atoms cap a Fe<sub>3</sub> triangle with an average Fe-Fe bond length of 2.79 Å in this closo-trigonal bipyramid.<sup>3</sup> The effect of MG size on M-M bond

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