

ELECTROCHEMICAL AND CHEMICAL REDUCTION OF
THE TRIFERROCENYL CYCLOPROPENIUM ION

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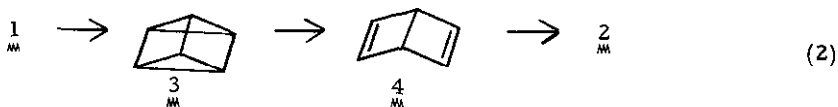
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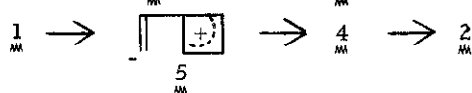
The mechanism of the thermal aromatization of bis-cyclopropenyls (1) to benzenes (2) (eq. 1), a reaction originally discovered by Breslow,¹ is unclear. The mechanism suggested by



Breslow, involving conversion of 1 successively to a prismane (3) and Dewar benzene (4) (eq. 2),

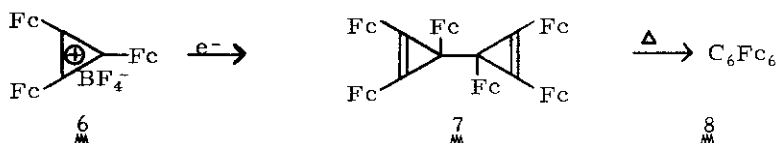


now appears unlikely on orbital symmetry grounds.² Weiss and co-workers^{3,4} have favored a mechanism involving conversion of 1 to zwitterion 5, which would then close to the Dewar

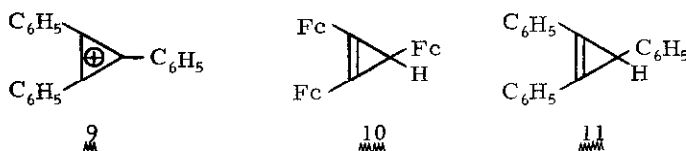


benzene. This mechanism seems to be well-supported for the reactions of bis-cyclopropenyls catalyzed by silver (I) salts to afford Dewar benzenes,³⁻⁵ but it is not so obvious that the thermal reaction also proceeds via 5, and there is even some question whether Dewar benzenes are involved in the thermal process.⁶ Since (a) the triferrocenylcyclopropenium ion (6) recently has become available,⁹ (b) the electrochemical reduction of cyclopropenium ions constitutes a convenient route to bis-cyclopropenyls 1,⁷ and (c) the ferrocenyl group strongly stabilizes a positive charge on a carbon to which it is attached,¹⁰ we felt that the electrochemical reduction of 6 might constitute a test of the Weiss mechanism. If the latter is operating, rearrangement of the dimer (7) ought to occur more readily than that of hexaphenyl-bis-cyclopropenyl, which rearranges at elevated temperatures (3 days at 135°C). We now wish

to report the results of electrochemical and chemical reduction of **6**.



Voltammetry of **6.** Triferrocenylcyclopropenium tetrafluoroborate (**6**) exhibits two polarographic waves at -1.33 and -2.05V,¹¹ respectively, in acetonitrile containing 0.1M tetrabutylammonium hexafluorophosphate. When examined by cyclic voltammetry at a platinum disc, (20V/sec), the two waves move to more negative potentials (-1.49 and -2.10V) and appear irreversible, behavior similar to that reported for the triphenylcyclopropenium ion (**9**).⁷ **6** is considerably harder to reduce than **9** (E_1 and $E_2 = -0.85$ and -1.73 V, respectively), presumably because of the powerful electron-supplying character of the ferrocenyl group¹⁰ and the collective effect of the three ferrocenyl groups in stabilizing the aromatic C_3^+ ring of **6**. Using an estimated pK_{R^+} of 10 for **6** (this is a lower limit),^{9,12} we calculate a pK_a of 61 for 1,2,3-triferrocenylcyclopropene (**10**). This compares with a pK_a of 50 for triphenylcyclopropene (**11**),⁷



the difference here again presumably associated with the electron-supplying effect of the ferrocenyl substituent.

Controlled-potential reduction of **6** under argon in acetonitrile at 0° at a mercury pool cathode, followed by low-temperature solvent evaporation and dry-column chromatography of the crude product over deactivated alumina at 0°, using carbon tetrachloride as eluant, afforded hexaferrocenylbicyclopropenyl (**7**) as a dark orange solid, soluble in common organic solvents and stable in the absence of air at low temperatures. The 1H -decoupled ^{13}C nmr spectrum (-40°C) exhibited a characteristic multi-line spectrum in the region of 69 ppm (ferrocene = 68) similar to that of **10** (*vide infra*).¹³ Dimer **7** is readily converted under argon at room-temperature ($t_{1/2}$, 25°C \leq 1 hr) to an orange isomeric solid, mp > 400°, insoluble in all organic solvents. The insolubility of this substance precludes spectral characterization, though by analogy with the thermal rearrangement of all other known *bis*-cyclopropenyls, this substance is probably hexaferrocenylbenzene (**8**).¹⁴ We are continuing our efforts to characterize **8** or a more tractable derivative thereof.²¹

Reaction of **6** with sodium borohydride in methylene chloride affords triferrocenylcyclopropene (**10**) (80% yield after purification by dry-column chromatography). The ^{13}C spectrum

consists of an eight-line multiplet from 66.6 to 69.8 ppm, consistent with the presence of two distinct types of ferrocene nucleus, along with anolefinic resonance at 109.37 ppm and a resonance for the saturated ring carbon at 20.22 ppm. The latter two resonances, as expected, appear upfield of the corresponding resonances of $\underline{11}$ (112.97 and 25.04, respectively).¹⁶ Cyclopropene absorption in the infrared is observed for $\underline{10}$ at 5.44 μ (very weak). We find that Mossbauer spectroscopy is not sufficiently sensitive to distinguish the two kinds of iron in $\underline{7}$ and $\underline{10}$, though the Mossbauer spectra of these substances are very similar, and somewhat different from that of the putative $\underline{8}$.¹⁷

During attempts to reduce $\underline{6}$ by sodium in ammonia, we have made the remarkable discovery that $\underline{6}$ reacts reversibly with ammonia: addition of a methylene chloride solution of $\underline{6}$ to liquid ammonia instantly quenches the deep red color of $\underline{6}$, but the color (and $\underline{6}$) reappears when the solvent is removed by rotary evaporation. This experiment provides dramatic proof of the high degree of stabilization of the positive charge in $\underline{6}$.

The low thermal stability of $\underline{7}$ could be viewed as evidence for the Weiss mechanism. In general, bis-cyclopropenyls bearing six electron-supplying groups do aromatize with great ease,¹⁸ and, conversely, one such substance bearing six electron-withdrawing groups has been shown to exhibit remarkably high thermal stability.¹⁹ Bergman and coworkers have however, recently proposed a biradical intermediate (rather than a zwitterion) for such isomerizations.²⁰ Furthermore, we cannot rule out catalysis of the aromatization by traces of electrophilic impurities; indeed we strongly suspect the latter.

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5. I. J. Landheer, W. H. deWolf, and F. Bickelhaupt, Tetrahedron Letters, 2813 (1974).
6. (a) For example, Breslow, et al., isolated hexamethylbenzene⁷ from the electrochemical reduction of trimethylcyclopropenium ion under conditions where the Dewar benzene⁸ is thermally stable; (b) See also R. Weiss and H. Kolbl, J. Amer. Chem. Soc., **97**, 3222, 3224 (1975).

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10. E. g., S. Lupon, M. Kapon, M. Cais, and F. H. Herbstein, Angew. Chem. Internat. Ed., **11**, 1025 (1972).
11. Potentials were measured relative to Ag/AgNO₃, 0.1M in CH₃CN, and corrected by using the relationship $E_{\text{rel to SCE}} = E_{\text{rel to Ag/Ag}^+} + 0.38\text{V}$.
12. If the pK_{R+} of **6** is actually 11, the pK_a of **10** is 60; if the pK_{R+} of **6** is 12, the pK_a of **10** is 59, etc.
13. The ¹³C spectrum of **7** consists of seven lines at 66.59, 66.89, 68.227, 68.50, 68.91, 69.02, and 69.32 ppm. The strongest line, at 69.02 ppm, apparently includes the unsubstituted rings of the ferrocene groups, so that the expected eight lines are not observed, though in **10** and some other derivatives of this system (to be described later) all eight lines can be discerned. The lines at 66.59 and 66.89 are quite small; they are due to the cyclopentadienyl carbons bound to the cyclopropene carbons. In substances such as **6** or diferrocenylcyclopropenone, with only one type of ferrocene, only one line appears at higher field. The quaternary carbons of **7** relax too slowly to be seen, even after several thousand transients in the presence of a relaxation reagent, Cr(AA)₃. Spectra were measured at 67.88 MHz in CCl₄ or CH₂Cl₂ (at -40° for **7**) and are reported relative to tetramethylsilane.
14. The infrared spectrum of this substance resembles that of 1,3,5-triferrocenylbenzene.¹⁵
15. N. Brawn, Ph.D. thesis, Brandeis University, 1968.
16. The ¹H nmr spectra exhibit the same effect: **10** exhibits a methine singlet (1H) at τ7.27, together with a multiplet (27H) centered at τ5.8, while the methine proton of **11** appears at τ6.79 (together with a 15-proton multiplet about τ2.6).
17. Professor R. Herber of Rutgers University has measured the Mossbauer spectra of **6**, **7**, **8**, and **10**, respectively; details of the experiments will be reported separately.
18. Methyl: ref. 7; methoxyl and dimethylamino: R. W. Johnson, Tetrahedron Letters, 589 (1976).
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21. It is possible that the compound which we suspect to be **8** is actually a polymer, although the high symmetry of **8** would confer high melting point and low solubility. We expect that methyl-substituted derivatives will prove more soluble and hence amenable to spectral methods.