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A Forbidden Rearrangement

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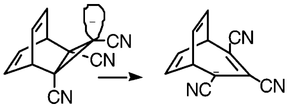
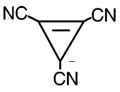
ABSTRACT



A barrelene derivative fragments to afford benzene and trappable 1,2,3-tricyanocyclopropene. The barrelene anion fragments more easily to liberate benzene and the 1,2,3-tricyanocyclopropenyl anion, which is not trappable or stable in solution. However, the major thermal product from the barrelene anion is a rearranged allyl anion that is formed by disrotatory cleavage of the cyclopropyl ring, a formally Woodward–Hoffmann-forbidden process. Several proposals are offered to rationalize this forbidden rearrangement.

For quite a while, we have been trying to synthesize the tricyanocyclopropenyl anion **1**, which should be strongly stabilized and a ground-state triplet. Our earliest approaches[1] involved the treatment of 1,2,3-tricyanochlorocyclopropane with base to first eliminate HCl and then deprotonate the resulting cyclopropene **2**, but in all cases we obtained only polymeric materials. Apparently, cyclopropene **2** undergoes anionic polymerization, initiated either by the base used or by the anion **1** if indeed that is formed. An attempt to generate **1** by reduction of 1,2,3-tricyanotrichlorocyclopropane was also unsuccessful.[1] Thus, we conceived a plan in which the double bond of **1** would be introduced *after* the negative charge was in place.



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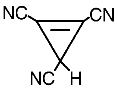

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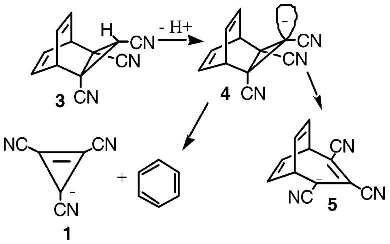
We synthesized compound **3**, a formal Diels−Alder adduct of benzene and tricyanocyclopropene, using the procedure described below. We hoped that its anion **4** would fragment to form benzene and **1** and that the alternative ring opening to form anion **5** would not occur since it is forbidden by the Woodward−Hoffmann general treatment,[2] which requires that the interconversion of a cyclopropyl anion with an allyl anion involve conrotation in the breaking or making of the cyclopropyl single bond. Such conrotation is not possible with anion **4**, since the product would not be **5** but instead a hopelessly strained stereoisomer. Even so, this forbidden rearrangement of **4** into **5** was the principal process.



Fumaronitrile was converted into **6**[3] by addition of methanethiol. Chlorination with *N*-chlorosuccinimide led to **7**,[3] and with base this afforded **8**.[3,4] Then reaction with (cyanomethyl)dimethylsulfonium triflate and NaH afforded **9**,[3,4] converted into **10**[3,4] with MeI and $AgBF_4$. (With base, compound **10** affords cyclopropene **2**, but under all conditions tried this again was converted into polymer, not to a stable solution of anion **1**.) The $Fe(CO)_3$ adduct **11**[3] of 1,3-cyclohexadiene was converted into cation **12**[3] by hydride abstraction with triphenylmethyl fluoborate, and capture of

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(1) Breslow, R.; Cortes, D.; Jaun, B.; Mitchell, R. *Tetrahedron Lett.* **1982**, *23*, 795.

(2) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970.

(3) Experimental details and characterization are found in the Supporting Information.

(4) A major and minor stereoisomer were formed and characterized.

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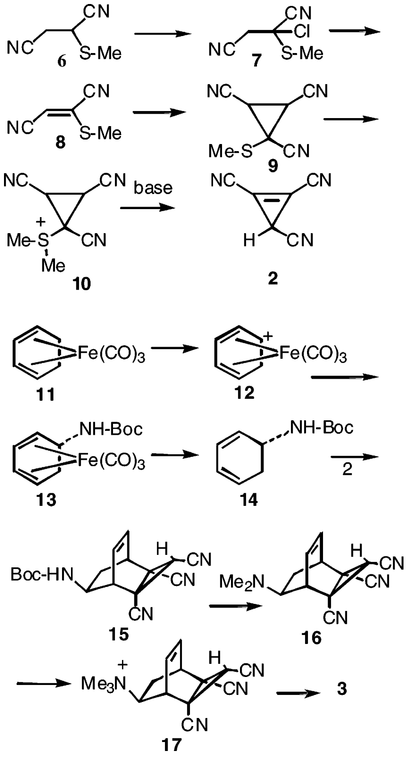
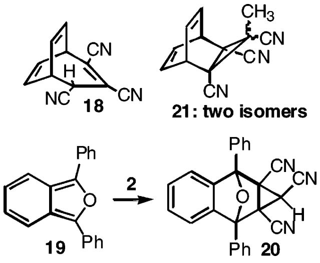
the cation with NH_2Boc afforded **13**.[3] Ceric ammonium nitrate converted this into diene **14**.[3] Reaction of **10** with **14** in the presence of *N*,*N*-diisopropylethylamine (generating **2**) afforded adduct **15**.[3,4] After removal of the Boc group, the amino group was dimethylated with formaldehyde and sodium triacetoxyborohydride to form **16**,[3] and quaternization with MeI afforded salt **17**.[3]



Treatment of **17** with KOtBu afforded **3**. However, during this process the allyl anion **5** was also formed by rearrangement of the cyclopropyl anion **4**. Thus, we have examined both the use of **3** to form cyclopropene derivatives by reverse Diels−Alder reactions and also the rearrangement of anion **4** into allyl anion **5**, a process involving the forbidden disrotatory cleavage of the cyclopropyl ring bond.

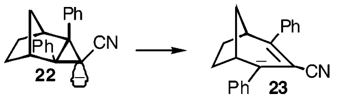
Compound **3** has the stereochemistry shown (NOE between the cyclopropyl proton and the upfield vinyl hydrogens of **3**) and allyl anion **5** was characterized by NMR (only two proton signals at δ 5.79 and 2.82, in a 2:1 ratio). Acid quenching of anion **5** afforded triene **18**.[3]



On heating above 170 °C in DMSO-d_6 in a sealed tube under argon, compound **3** undergoes a reverse Diels−Alder reaction to form benzene and 1,2,3-tricyanocyclopropene **2**. The latter can be trapped to furnish the known adduct **20**[1] (in equal amount to the benzene) if diphenylisobenzofuran **19** is present in solution during the thermolysis, but not if it is added later. Thus, even under these thermal nonbasic conditions cyclopropene **2** is not stable in solution, apparently again forming a polymer. When KOtBu is added to a solution of **3** in DMSO-d_6 under argon at 165 °C there is the immediate formation of some benzene, suggesting that the anion **3** cracks to liberate the cyclopropenyl anion **1**, but this could not be trapped with **19**, either present in the solution or added later with mild acid. In addition, the rearranged allylic anion **5** is formed in this process, in about a 10:1 ratio to the benzene formed. Thus, the principal process for anion **4** is rearrangement, not fragmentation.

Anion **4** can actually be formed at room temperature by treating **3** with NaH in DMSO-d_6. The cyclopropyl H signal of **3** at δ 3.24 is lost in the NMR, and the vinyl proton signals of **3** at δ 6.95 and 6.21 and the bridgehead proton signals at δ 4.35 move upfield to δ 6.68, 5.95, and 3.74, respectively, in anion **4.** The anion is moderately stable and can be reprotonated to form **3** (but not its epimer) or alkylated with methyl iodide to form the two isomers of **21**[3,4] (one with NOE of the methyl to vinyl hydrogens). However, on gentle warming or even on standing for 3−4 h at room temperature, anion **4** undergoes rearrangement into allylic anion **5** (15% also fragments to form benzene).

This rearrangement is a formally "forbidden" reaction: the disrotatory cleavage of the cyclopropane sigma bond is forbidden for the anion,[5] allowed for the cation. Since it occurs fairly readily, an explanation is needed. It should be mentioned that a related reaction has been seen previously (such violations of the Woodward−Hoffmann rules are apparently not widely known), the rearrangement of anion **22** into allylic anion **23**.[5] Thus the extra π electrons in our anion **4** are not part of the explanation.



We propose that several factors may be overcoming the electronic problem in the disrotatory ring opening of anion **4**. One is that the unshared carbon electrons in cyanocyclopropyl anions are in hybrid orbitals, not in p orbitals. This is revealed in stereochemical studies of such anions previously, in which deuterium exchanges involving such anions are faster than are inversion processes.[6,7] As a result, the disrotatory opening of the cyclopropane initially pushes the σ-bond electrons *away* from the carbanion electrons (Figure 1), and indeed the σ-bond electrons begin to overlap with the *empty* hybrid orbital of the carbanion, not the filled orbital. That is, the system begins to resemble an allylic *cation*, not just an anion, although later rehybridization of the three carbons to sp^2 indeed leads to the product allylic anion. In

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(5) Boche, G. *Top. Curr. Chem.* **1988**, *146*, 1−156, see p 22.

(6) Walborsky, H. M.; Youssef, A. A.; Motes, J. M. *J. Am. Chem. Soc.* **1962**, *84*, 2465.

(7) Breslow, R.; Douek, M. *J. Am. Chem. Soc.* **1968**, *90*, 2698.

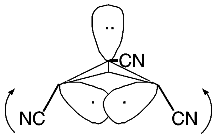

Figure 1. As the cyclopropyl single bond breaks by a disrotatory motion, the electrons are pushed away from the carbanion electrons and overlap with the empty hybrid orbital pointing down, not the filled orbital pointing up.

a sense, the factors involved are a little like those that lead to backside displacement reactions in which electron pairs interact with σ^*, avoiding the σ electrons of the leaving group.

A second factor might be special for our system, with its three cyano groups. They are expected to strongly stabilize the antiaromatic cyclopropenyl anion system by withdrawing π electrons, and the antiaromaticity of the forbidden transition state in disrotatory rearrangement of a cyclopropyl anion into an allylic anion might also be diminished by such electron withdrawal. Finally, it is possible that the rearrangements might be in a sense stepwise, with stretching of the single bond preceding the other geometric changes.

Whichever factors are involved, and we favor the first possibility mentioned above, it is clear that a formally forbidden reaction is actually occurring in this case. It competes with the observed fragmentation of **4** to form benzene and the tricyanocyclopropenyl anion **1** in solution, a fragmentation that is much faster with anion **4** than with the neutral **3**. Thus, the fragmentation is indeed being driven by the delocalization of charge in product **1**. However, we have no evidence for the formation of a *stable* solution of **1**, which remains a challenging target.

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Supporting Information Available: Experimental details and spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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