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# Cathodic Reduction of (*Z*,*E*)-4,8-Cyclododecadien-1-one. Studies on the Regiochemistry and Mechanism of Ketyl Radical Anion Intramolecular Cyclizations

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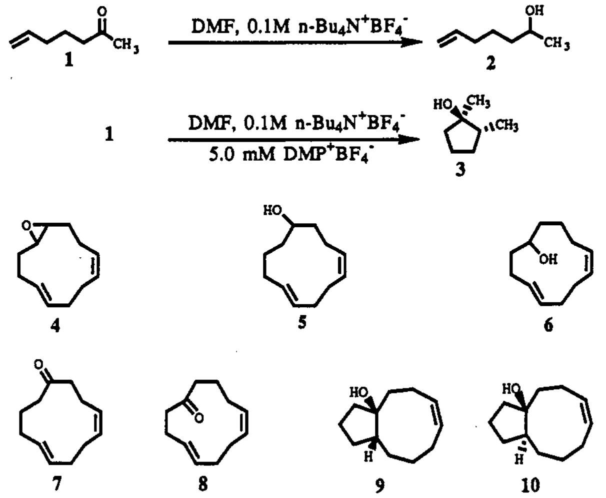
The electroreductive transannular cyclization of the title compound was studied. It was found that two bicyclic alcohols are formed and their structure was determined by using 2D-NMR techniques and a lanthanide shift reagent (LSR). MM2 calculations were also performed to confirm the proposed structures. The evidence presented here supports a reversible cyclization of the initially formed ketyl radical to yield bicyclic alcohol products.

Ketones are known to undergo electrochemical reduction to ketyl radicals and, if the molecule also bears a suitable alkenyl moiety, the radical may undergo intramolecular cyclization. This electroreductive cyclization process constitutes a powerful method of ring formation.[1] However, the yield of cyclized products can be sensitive to the reaction conditions. For instance, reduction of 6-hepten-2-one (1) in DMF containing 0.1 M $n\text{-Bu}_4\text{N}^+\text{BF}_4^-$ as supporting electrolyte yields only the simple reduction product 6-hepten-2-ol (2) (Scheme I). When a low concentration ($5 \times 10^{-3}$ M) of *N*,*N*-dimethylpyrrolidinium tetrafluoroborate ($\text{DMPBF}_4$) was added, two catalytic effects were observed. First, the reduction potential was shifted to a more positive value −2.70 V (SCE). Second, the reaction mechanism changed to yield a cyclization product, 1,2-dimethylcyclopentanol (Scheme I). It is important to point out that the 1,2-dimethylcyclopentanol is almost exclusively the cis 3 (ratio cis:trans > 48:1). Other ketones such as 7-octen-2-one, 6-heptyn-2-one, and 5-phenyl-2-pentanone behave similarly. At −2.70 V, $\text{DMP}^+$ combines with a mercury cathode[2] to form $\text{DMP(Hg}_5)$. It is thought that this composite acts as a mediator during the course of the reaction. A study of the reduction of 1 using homogeneous redox catalysts has recently been published.[3]

Transannular cyclizations giving bicyclic and tricyclic compounds have been reported by Takahashi[4] and White.[5] In the first case a transannular Diels–Alder reaction was used to form a steroidal derivative, and in this particular case three rings were formed in one step from a monocyclic precursor. In the second case the cyclization of a decenone via its allylsilane derivative was exploited and applied to form a hydroazulenol with a cis ring fusion.

Since we wanted to investigate the behavior of a diolefin with respect to the regio- and stereochemistry of the radical ring closure, we became interested in the two isomeric ketones (*Z*,*E*)-4,8-cyclododecadien-1-one (7) and (*E*,*Z*)-4,8-cyclododecadien-1-one (8). These compounds possess several interesting features. Ketyls formed from such compounds could cyclize in a transannular fashion, yielding bicyclic and/or tricyclic products by a mono or a tandem cyclization. The former case, however, appeared more feasible, given the strain associated with a second, transannular, radical cyclization. In the case of a single ketyl radical cyclization, there is the possibility, in principle, of eight products per each ketone (two double bonds are present in each isomer and the ring fusion could be cis or trans). We were also interested in the stereochemistry of such a cyclization reaction as a valuable synthetic aspect.

**Scheme I**



Finally, since the possibility of a reversible cyclization step had been adumbrated,[3] it was of interest to investigate such a possibility in these rather more complex cyclic molecules.

## Results

The compounds 7 and 8 are readily prepared from the commercially available (*Z*,*E*)-5,9-cyclododecadiene (*E*)-1,2-epoxide (4) by either a $\text{MgI}_2$-catalyzed rearrangement[6] or a $\text{MgBr}_2\cdot\text{OEt}_2$ rearrangement.[7] The rearrangement gave a mixture of ketones 7 and 8 that were not separable by using conventional chromatography or chromatography on $\text{Ag}^+$-doped silica, thus the mixture of the two compounds was studied. The ratio of the two isomeric ketones was found to be 79:21 in favor of isomer 7. An identical mixture of ketones was also prepared in two steps by LAH ring opening followed by oxidation of the resulting monocyclic

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alcohols (*Z*,*E*)-4,8-cyclododecadien-1-ol (**5**) and (*E*,*Z*)-4,8-cyclododecadien-1-ol (**6**) with $P_2O_5$/DMSO.[8] The ratio of the two alcohols **5** and **6** is in agreement with the reported[9] ratio and so is the chemical shift of the carbinolic proton in each isomer (see Experimental Section). The products of rearrangement, **7** and **8**, are the same products that are obtained by oxidation of **5** and **6**, and their ratio reproduces the reported value.[9]

A cyclic voltammetric (CV) study was performed on the mixture to investigate the electrochemical behavior of the system. A reduction wave appeared at −2.9 V (vs SCE) in a 0.1 M solution of *n*-tetrabutylammonium tetrafluoroborate in DMF and the current increased as the substrate concentration was increased. At the low concentration of $5 \times 10^{-3}$ M, the wave due to the reduction of the ketones overlapped with the supporting electrolyte discharge wave. The absence of any oxidation wave is indicative of an irreversible process, i.e., the reduction product(s) undergoes a fast follow-up reaction, not allowing their reoxidation. CVs in the presence of a concentration of $2 \times 10^{-3}$ M of $DMPBF_4$ were also performed, but no increase of the reduction wave or decrease of the oxidation wave of $DMP^+$ was detected, thus indicating the absence of catalysis by $DMP^+$ on the time scale of the experiment (100 mV/s).

A series of constant current preparative reductions of the mixture of ketones were performed. The amount of charge transferred was 2.3 F/mol. The results were reproducible and, invariably, a mixture of two bicyclic alcohols, (*Z*)-(3a$\alpha$,10a$\alpha$)-1,2,3,3a,4,5,8,9,10,10a-decahydrocyclopentacyclononen-3a-ol (**9**) and (*Z*)-(3a$\alpha$,10a$\beta$)-1,2,3,3a,4,5,8,9,10,10a-decahydrocyclopentacyclononen-3a-ol (**10**) was formed, with a ratio of **9**/**10** of 1.5. Traces (3%) of monocyclic alcohol **5** were also detected. The reactant was completely consumed and the GC (isolated) yields were 42% (30%) for **9** and 28% (20%) for **10**. When $5 \times 10^{-3}$ M $DMPBF_4$ was added as a catalyst, the **9**/**10** ratio was unaffected, but there was no **5** detectable and 9% (close to half of the starting amount) of **8** remained unreacted after a charge equivalent to 2.3 F/mol was passed. Electrolysis with $DMPBF_4$ took place at a more positive potential (−2.60 to −2.74 V vs SCE) than electrolyses without it (−2.76 to −2.94 V vs SCE).

Samples obtained after partial charge transfer were analyzed to learn about the reaction progress. An internal standard was added to the solution prior to electrolysis and each sample, including the initial one (0 F/mol), was subjected to the same workup. The reacted amount of each ketone was calculated as a percent of the initial amount (at 0 F/mol). The results are listed in Table I. The rate of reaction of ketones **7** and **8** was significantly different. While **7** was almost depleted after transfer of 1 F/mol, only a small amount of **8** was absent. The products **9** and **10** started forming from the beginning, the amount of **9** prevailing. In the initial stages (up to 0.75 F/mol) the ratio **9**/**10** was slightly higher (2.0) than at completion (1.5).

The results above indicated that the bicyclic **9** and **10** originate from **7**, but **8** follows some different pathway. This is not surprising since formation of **9** or **10** from minor reactant **8** would entail complex rearrangements to accommodate generation of its cis double bond via the 4,10 bicyclic radical anion intermediate. To probe this observation and to confirm it, we utilized the higher reactivity of **7** and a ketone mixture enriched with **8**. The synthetic ketone mixture (**7**/**8** = 79/21) was electrolyzed (60 mA) in DMF (0.1 M *n*-$Bu_4NBF_4$) to partial conversion, transferring 1.3 F/mol. As expected, much of **7** was consumed and after the separation by flash chromatography,[10] **8** was the main component of the unreacted ketone fraction. The **8** enriched mixture contained **7** and **8** in the ratio of 14:86 and was used for the following series of experiments.

**Table I. Rate of Consumption of Ketones 7 and 8 in Preparative Electrolyses**[a]

| F/mol | E (V vs SCE) | amount of 7 reacted,[b] % | amount of 8 reacted,[b] % | 9/10 |
|---|---|---|---|---|
| 0 | −2.74[c] | 0 | 0 | – |
| 0.5 | −2.79 | 44 | 0 | 2.0 |
| 0.75 | −2.81 | 69 | 0 | 1.6 |
| 1.0 | −2.85 | 87 | 10 | 1.6 |
| 1.25 | −2.91 | 97 | 36 | 1.6 |
| 1.5 | −2.91 | 100 | 53 | 1.5 |
| 1.75 | −2.94 | 100 | 71 | 1.5 |
| 2.0 | −2.94 | 100 | 90 | 1.5 |
| 2.25 | −2.94 | 100 | 100 | 1.5 |

[a] 0.1 M $(C_4H_9)_4NBF_4$ in DMF; constant current 35 mA; calibrated GC amounts (±2%). Cyclooctanol as internal standard. [b] The percentage of reacted ketones is calculated on the basis of the initial amount of each ketone taken as 100%. [c] This was the initial electrolysis potential.

Constant current electrolysis in DMF (0.1 M *n*-$Bu_4NBF_4$) was performed under the same conditions of the experiment described in Table I. After transfer of a charge equivalent to 0.25 F/mol, the ketone **7** was completely consumed, the ketone **8** was unreacted, and the only products formed were small amounts of the bicyclic **9** and **10**. The ratio of total bicyclic products to **8** was 13:87, very close to the initial ratio of **7**/**8**, confirming that **9** and **10** originate from **7**. After transferring 2.1 F/mol, some of ketone **8** had reacted but the amount of bicyclic product was the same. The ratio of bicyclic alcohols to **8** was 31:69 and a new product (less polar, by TLC, than either the reactants or the previously observed products) was formed. Thus, **9** and **10** are not products of **8** and it is noteworthy that their respective yields here were **9**/**10** = 1.5, identical with the experiments in Table I. The structure of the cathodic product of **8** was not pursued.

Constant current electrolysis of the **8**-enriched ketone mixture, with $5 \times 10^{-3}$ M $DMPBF_4$, proceeded at a less negative potential than that without it. After transfer of charge equivalent to 0.25 F/mol, most of **7** had reacted, **8** was intact, and the cyclic **9** and **10** were the only products [**7**/(**9** + **10**)/**8** = 4/9/87]. After transfer of 2.1 F/mol, all **7** was consumed, yielding bicyclic **9** and **10**, 93% of **8** was still unreacted and traces of the new product of **8** were present. Thus $DMP^+$-mediated reduction increases the selectivity and can be used for selective reduction of **7**.

1D- and 2D-NMR techniques, together with the use of lanthanide shift reagents (LSR), were necessary in order to determine the structure of the bicyclic products **9** and **10**. MM2 calculations were performed to provide stability data for the cis and trans configurations of the ring fusion and the bond angles and distances that were used in the calculations for the lanthanide-induced shift (LIS) experiments. The results of MM2 calculations showed the total steric energy of **9** to be 36.6 kcal/mol while a value of 32.8 kcal/mol was found for **10**, thus indicating a significant difference in the stability of the two isomers, in favor of the trans-fused isomer **10**.

The cis stereochemistry across the double bond was determined from the $^3J$(HH) of the olefinic protons. In **10**, both olefinic protons appear as poorly resolved quartets

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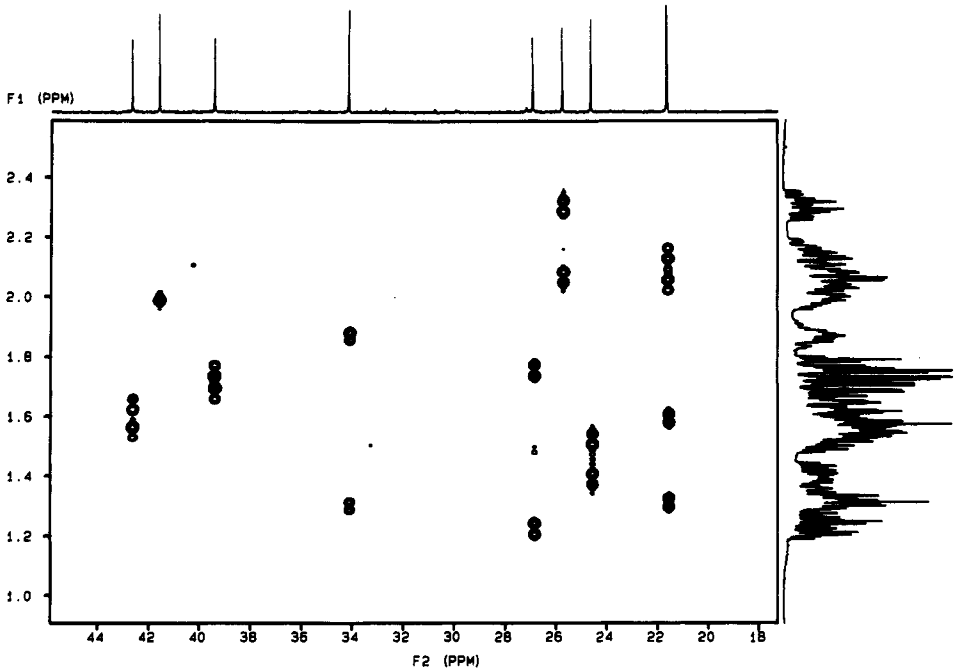

**Figure 1.** 2D $^1H$, $^{13}C$ heteronuclear correlation of trans-fused isomer **10**. One-dimensional spectra ($^{13}C$, top, and $^1H$, side) are included.

**Table II. Chemical Shifts and Lanthanide-Induced Shifts for 9 and 10**[a]

| | | | | | europium-induced shifts[c] | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | chemical shifts | | | dilute Eu soln | | | concd Eu soln | |
| assignment | | $^{13}C$ | $^1H$ | | $^{13}C$ | $^1H$ | | $^{13}C$ | $^1H$ | |
| **9**[b] | | | | | | | | | |
| 31 | CH= | 132.97 | 5.75 | | 0.32 | 0.21 | | 1.35 | 0.82 | |
| 32 | CH= | 127.07 | 5.31 | | 0.23 | 0.17 | | 1.16 | 0.70 | |
| | C | 87.98 | | | 2.99 | | | 12.69 | | |
| 33 | CH | 44.53 | 1.94 | | 0.55 | 1.0 | | 2.52 | 4.15 | |
| 10, 11 | $CH_2$ | 39.17 | 1.56 | 1.56 | 1.15 | 0.92 | 0.58 | 5.31 | 4.26 | 2.49 |
| 16, 17 | $CH_2$ | 37.06 | 1.64 | 1.93 | 1.19 | 0.58 | 0.98 | 4.93 | 2.42 | 4.14 |
| 5, 6 | $CH_2$ | 32.61 | 2.08 | 1.38 | 0.81 | 0.79 | 0.45 | 3.38 | 3.24 | 1.78 |
| 19, 20 | $CH_2$ | 28.61 | 1.43 | 0.98 | 0.26 | 0.50 | 0.37 | 1.17 | 2.05 | 1.52 |
| 22, 24 | $CH_2$ | 25.53 | 1.29 | 1.43 | 0.28 | 0.22 | 0.27 | 1.13 | 0.87 | 1.05 |
| 29, 30 | $CH_2$ | 23.36 | 1.96 | 2.55 | 0.24 | 0.19 | 0.33 | 0.95 | 0.72 | 1.29 |
| 7, 9 | $CH_2$ | 21.01 | 1.68 | 1.75 | 0.71 | 0.38 | 0.49 | 2.96 | 1.60 | 2.07 |
| 25, 26 | $CH_2$ | 20.47 | 1.94 | 2.39 | 0.71 | 0.37 | 0.81 | 2.93 | 1.34 | 3.29 |
| **10**[b] | | | | | | | | | |
| 32 | CH= | 132.21 | 5.62 | | 0.32 | 0.17 | | 1.20 | 0.66 | |
| 33 | CH= | 128.04 | 5.40 | | 0.16 | 0.13 | | 0.89 | 0.52 | |
| | C | 82.59 | | | 2.79 | | | 10.31 | | |
| 17, 18 | $CH_2$ | 42.77 | 1.71 | 1.61 | 1.15 | 0.87 | 0.63 | 4.80 | 3.75 | 2.24 |
| 3 | CH | 41.68 | 2.06 | | 0.26 | 0.39 | | 1.46 | 1.63 | |
| 11, 12 | $CH_2$ | 39.55 | 1.82 | 1.74 | 1.02 | 0.82 | 0.68 | 4.03 | 3.31 | 2.42 |
| 6, 7 | $CH_2$ | 34.26 | 1.37 | 1.93 | 0.51 | 0.58 | 0.34 | 2.18 | 1.86 | 1.63 |
| 20, 21 | $CH_2$ | 26.96 | 1.29 | 1.82 | 0.51 | 0.43 | 0.68 | 2.10 | 1.64 | 2.65 |
| 30, 31 | $CH_2$ | 25.81 | 2.14 | 2.37 | 0.17 | 0.14 | 0.21 | 0.75 | 0.61 | 0.85 |
| 23, 25 | $CH_2$ | 24.70 | 1.59 | 1.46 | 0.23 | 0.17 | 0.20 | 1.04 | 0.71 | 0.84 |
| 26, 27 | $CH_2$ | 21.75 | 2.21 | 2.10 | 0.41 | 0.33 | 0.33 | 1.73 | 1.27 | 1.30 |
| 8, 10 | $CH_2$ | 21.69 | 1.38 | 1.66 | 0.55 | 0.33 | 0.40 | 2.18 | 1.33 | 1.57 |

[a] Atoms are numbered according to MM2 calculations. [b] The spectra of **9** and **10** were recorded at a concentration of 1.1 M and 3.3 M of alcohol, respectively. [c] Values in $\Delta\delta$, ppm.

with $J$(HH) ranging between 8 and 10 Hz. In **9** the olefinic protons appear as a double triplet with one $J(HH) = 7$ Hz and the other two = 10 Hz. Thus, the maximum possible olefin coupling constant is 10 Hz and the olefin configuration must be cis.

The ring structure was next determined from a combination of 2D $^1H$–$^1H$ COSY and $^{13}C$ INADEQUATE experiments.[11] The COSY spectrum established the proton–proton connectivities to the allylic protons, but the remainder of the proton spectrum was too complex, even at high field, to analyze. The INADEQUATE correlations depend on $^1J(CC)$ and, since $J({=}CH, CH_2)$ is typically 50% greater than $J(CH_2, CH_2)$, it is difficult to simultaneously observe aliphatic–aliphatic and aliphatic–olefinic connectivities. Consequently, the experiment was set up to give only the carbon–carbon connectivities between all the aliphatic carbons. A 2D $^1H$–$^{13}C$ COSY then identified the allylic carbons (Figure 1), which had been assigned from the $^1H$–$^1H$ COSY experiment. The 2D $^1H$–$^{13}C$ COSY

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[11] Sanders, J. K. M.; Hunter, B. K. In *Modern NMR Spectroscopy*; Oxford, 1987.

spectrum shows a pair of doublets for each geminal methylene in the molecule, which permitted the assignment of the chemical shifts of all the aliphatic protons in the molecule.[11] These spectra unambiguously identified the ring structure for **9**. The $^{13}$C and $^{1}$H chemical shifts are given in Table II.

The assignment of the cis/trans structure across the fused ring requires determination of the orientation of the hydroxyl group relative to the methine proton. Large shifts were observed with the addition of a shift reagent, Eu(fod)$_3$, to the sample.[12] The Eu binds to the oxygen and induces shifts that are proportional to $(3\cos^2\theta - 1)/r^3$, where $r$ is the internuclear distance from Eu to the nucleus being observed and $\theta$ is the angle between the Eu-nucleus axis and the magnetic axis of the molecule. Numerous examples indicate that the magnetic axis is approximately colinear with the C-O bond.[12] $^{1}$H and $^{13}$C spectra were obtained as a function of added shift reagent in order to follow Eu-induced shifts vs Eu concentration. Heteronuclear correlated spectra were obtained at two different Eu concentrations in order to also correlate the proton chemical shifts with Eu concentration. The $^{13}$C- and $^{1}$H-induced chemical shifts for two different Eu concentrations are also given in Table II. Within experimental error, the ratios for all the protons and carbons between concentrated and dilute solutions of Eu(fod)$_3$ are 4.0. The concentrations vs chemical shift analysis enabled the assignment of all the protons and carbons in the solutions containing Eu relative to the pure sample.

Comparison of the methine-induced shift with that of the adjacent methylenes determines the stereochemistry. A very large induced shift was observed for the methine in **9** but a very small induced shift in **10**. Thus **10** is trans fused and **9** is cis fused.

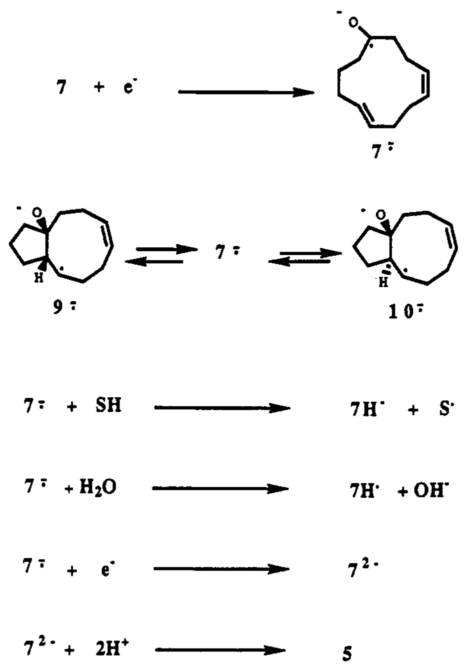
Molecular modeling calculations were also performed to assign the stereochemistry. The Eu-induced shifts were calculated for the cis- and trans-fused isomers and show excellent agreement with the observed shifts, confirming the stereochemistry. The minor differences are in part due to conformational changes in the structure that must occur to allow for the presence of the large Eu on a tertiary alcohol. Large differences are also observed for carbons close to the Eu, which experience contact as well as dipolar shifts. These calculations also enable a complete assignment of all the protons since different relative Eu-induced shifts are predicted for each pair of geminal protons.

## Discussion

Cathodic reduction at a constant current of a mixture of **7** and **8** shows that **7** is more reactive and the products of **7** are formed faster. Monitoring the reaction progress (Table I) shows that during electrolysis the potential becomes 300 mV more negative. A negative shift, during an organic reduction, is not unusual. It is significant, however, that no products of **8** were formed before the potential changed from −2.74 to −2.85 V. This suggests that the reduction potential of **8** is more negative than that of **7**.

The difference in reactivity between **8** and **9** is more pronounced when DMPBF$_4$ is present in solution. Although catalysis is not detectable on the time scale of cyclic voltammetry, it occurs in preparative experiments. The catalytic reduction takes place at a less negative potential and allows selective reduction of **7**. It seems to slow electron transfer to both **7** and **8** but not to the same extent as shown by the improved selectivity. The participation of the catalyst is most likely, as previously shown for other ketones, via DMP(Hg$_5$), which forms around −2.7 V.

**Scheme II**



In the direct reduction, or the one mediated by DMP$^+$, **7** is initially reduced to the radical anion $\mathbf{7}^{\bullet-}$, which can in turn cyclize to give $\mathbf{9}^{\bullet-}$ or $\mathbf{10}^{\bullet-}$. This is not, however, the only follow-up process that $\mathbf{7}^{\bullet-}$ may undergo (Scheme II). It may abstract H$^\bullet$ from the solvent (DMF), or be protonated by adventitious water (or another available proton source), or further reduce to $\mathbf{7}^{2-}$. All possible follow-up reactions of $\mathbf{7}^{\bullet-}$, except for cyclization, would ultimately yield the simple alcohol **5**. Yet, **5** is a minor product, not even always present in the reaction mixture. The predominance of cyclic products at all reduction stages and the minute amount of **5** formed provide evidence for a rapid cyclization of $\mathbf{7}^{\bullet-}$. The preferred 5-exo-trig mode of cyclization[13] leads to the formation of $\mathbf{9}^{\bullet-}$ and eventually to the cis isomer **9**. On the other hand the trans isomer **10** is more stable. The experiments show that a mixture of **9** and **10** is formed, under all conditions, with some preference for **9**. Thus the reaction seems to exhibit a mixed kinetic and thermodynamic control with some preference to the former.

In the case of the cyclization of **1**, several explanations were offered to account for the almost exclusive formation of the *cis*-1,2-dimethylcyclopentanol.[1b] A feasible hypothesis involves ion pairing between the oxygen of the cyclic radical anion and the tetraalkylammonium cation of the electrolyte. Such ion pairing can reinforce the stereochemical preference for the cis configuration that exists even for simple carbon 6-heptenyl radicals.[14] In the case at hand, this factor should be even more important, considering the bulkiness of the methine radical and the large steric interactions that have to be accommodated in the transition states leading to the bicyclic $\mathbf{9}^{\bullet-}$ and $\mathbf{10}^{\bullet-}$.

In any event the predominance of the kinetic product **9** is indicative of a fast follow-up reaction after the cyclization of $\mathbf{7}^{\bullet-}$. The radical anions $\mathbf{9}^{\bullet-}$ and $\mathbf{10}^{\bullet-}$, en route to the bicyclic products, may be protonated or may be reduced further, or may abstract a hydrogen atom (as

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[12] Paasivirta, J. In *Lanthanide Shift Reagents in Stereochemical Analysis*; Morrill, T. C., Ed.; VCH: New York, 1986; p 107.

[13] (a) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734. (b) Baldwin, J. E. *Ibid.* 1976, 738.

[14] Beckwith, A. L. J.; Blair, I.; Phillipou, G. *J. Am. Chem. Soc.* **1974**, *96*, 1613. Garst, J. F.; Hines, J. B. *J. Am. Chem. Soc.* **1984**, *106*, 6443.

shown for $7^{\bullet-}$ in Scheme II). There is no experimental evidence but it is reasonable that, like in the cathodic cyclization of 1, protonation follows the initial formation of the cyclic radical anions.

The difference in the **9**/**10** yields ratio, at different stages of conversion, indicates that the cyclizations of $7^{\bullet-}$ to $9^{\bullet-}$ and $10^{\bullet-}$ are reversible. At the beginning of electrolysis the yield ratio **9**/**10** is 2.0. It reflects the rate of protonation in the initial solution. As the reaction proceeds, the proton content of the solution is depleted (generation of base is inherent to cathodic reductions). Slower protonation allows equilibration and results in more **10** and lower **9**/**10** yield ratio (1.5). Reversible cyclization has been reported for the radical ion of **1**.

To summarize, the main cathodic process of **7** is reductive cyclization, which can be catalyzed by DMP$^+$. The products are **9** and **10** and the stereochemistry of their ring fusion was proven by combining old (LIS) and new 2D-NMR techniques. There are indications for a reversible radical cyclization and an equilibrium between the initial radical ion $7^{\bullet-}$ and the two bicyclic radical ions $9^{\bullet-}$ and $10^{\bullet-}$. The final product distribution reflects combined kinetic and thermodynamic controls.

## Experimental Section

**Materials and Solvents.** The supporting electrolyte $n$-$Bu_4N^+BF_4^-$ was prepared by reaction of $n$-$Bu_4N^+Br^-$ with $HBF_4$[15] and recrystallized twice from AcOEt. $DMPBF_4$ was prepared according to a reported procedure.[16] These salts were dried under vacuum and stored in a dessicator. DMF was purchased from Burdick & Jackson and vacuum distilled. The middle 60% was retained and stored over activated 4-Å Davison molecular sieves under $N_2$. The DMF used for the experiment was withdrawn via cannula under a dried $N_2$ flow and filtered through activated alumina immediately prior to electrolyses. THF was distilled from sodium–benzophenone immediately before its use. Anhydrous diethyl ether (Mallinckrodt) was used without further purification except for the $MgI_2$-catalyzed reaction, for which freshly distilled (from sodium) $Et_2O$ was used. All other reactants were commercially available products and were used without further purification.

**Apparatus.** The cyclic voltammetry (CV) cell was a four-necked 25-mL flask equipped with an argon inlet, a sessile hanging mercury drop electrode (HMDE),[17] a saturated calomel electrode, and a platinum wire electrode. Preparative-scale electrolyses were performed in a divided cell (sintered glass frit), using a platinum flag (4 cm$^2$) anode. All experiments were run under a positive pressure of $N_2$.

Princeton Applied Research (PAR) Models 173 and 175 instruments were used for the CV measurements. Preparative electrolyses were performed, using an ESC potentiostatic controller and an EM DC power source equipped with two Keithley Model 169 digital multimeter instruments. MM2 calculations were performed on a VAX 11-780 computer, using the Chem-X program for structure drawing. IR spectra were recorded on a Perkin-Elmer 1710 FT-IR spectrometer. HR mass spectra were obtained with a VG 7070E-HF spectrometer operating at an ionizing voltage of 30 eV. GC analyses were performed on a Hewlett-Packard 5890 gas chromatograph equipped with a bonded Superox column (30 m × 0.32 mm) or a Varian 3700 gas chromatograph equipped with a Megabore DB-17 column (30 m). NMR spectra were recorded on an IBM AC-200, an IBM AC-300, and a Varian XL-400 instruments. The proton–carbon correlations were determined by a heteronuclear correlation experiment including a BIRD sequence to fully decouple all the protons except the nonequivalent geminal methylene protons.[11] Typical spectra were obtained in 12 h with a 1.6-s recycle time, 3 kHz $^{13}C$ spectral width, 1300 Hz $^1H$ spectral width, and 256 increments. The olefinic carbons were distinguished by single frequency decoupling of the proton resonances, as were the two nearly degenerate carbons at 21.75 and 21.69 ppm in **10**. This was necessary since the olefinic carbons were not included in the 2D experiment to minimize the number of data points and the resolution was insufficient to distinguish the latter two carbons. 2D INADEQUATE spectra were obtained on 300 (**10**) or 100 (**9**) mg samples in 0.5 mL to which sufficient $Cr(acac)_3$ was added to reduce all the carbon relaxation times to less than 0.4 s. The spectra were acquired overnight (15 h) with a 1.0-s repetition time, 7550-Hz spectral width, and 32 or 64 increments. The delays were optimized for $J(CC) = 35$ Hz.

**Preparation of (*Z*,*E*)-4,8-Cyclododecadien-1-one (7) and (*E*,*Z*)-4,8-Cyclododecadien-1-one (8). A.** A suspension of 1 g of $MgI_2$ (3.60 mmol, 5 mol %) and 12.82 g of **4** (71.9 mmol) in 6 mL of anhydrous diethyl ether were heated at 70 °C in a stainless steel hydrogenation vessel for 94 h. After being cooled to room temperature, the sealed vessel was opened and the brownish suspension transferred to a flask and refluxed for 20 min with charcoal in diethyl ether to afford a colorless oil. Distillation under reduced pressure (bp 123 °C/7 mm) afforded 5.64 g (43%) of ketones **7** and **8** in a 71:29 ratio, respectively, as determined by GC.

**B.** Five grams of **4** (28 mmol) dissolved in 160 mL of anhydrous diethyl ether was added to a solution of 14.48 g of $MgBr_2{\cdot}OEt_2$ (56 mmol) in 60 mL of $Et_2O$ and 30 mL of anhydrous benzene, and the resulting mixture was refluxed for 72 h, monitoring the disappearance of the epoxide by GC (DB-17 Megabore column; 90 °C initial temperature; 5 °C/min temperature gradient; 12 psi initial pressure). The mixture was poured into a flask containing 100 mL of a saturated $NH_4Cl$ solution and the layers were separated after 10 minutes of stirring. The aqueous layer was extracted with $Et_2O$ (2 × 100 mL), and the $Et_2O$ layers were dried and decolorated with charcoal. Evaporation of the solvent left a residue of 4.2 g (84%), which was distilled to yield **7** and **8** in the same ratio of method A. This preparation was repeated twice to afford a 65% yield of ketones after distillation, in both cases. IR (mixture): 3001, 2981, 2851, 1710, 1670, 1442, 1400, 1371, 1100, 975, 707 cm$^{-1}$. $^1H$ NMR (mixture, $CDCl_3$) $\delta$: 1.56–1.69 (m, 2H), 1.97–2.13 (dist. septet, 7 H), 2.32–2.49 (m, 5 H), 5.01–5.48 (m, 4 H). $^{13}C$ NMR ($CDCl_3$) $\delta$ **7**: 19.65, 23.91, 27.55, 31.07, 31.65, 40.50, 43.07, 129.87, 129.94, 130.03, 131.28, 211.13. **8**: 21.42, 24.76, 27.40, 28.66, 31.52, 32.01, 40.69, 127.79, 129.71, 131.02, 131.89, 211.66. (Assignments based on relative intensities of the signals in the spectrum of the mixture.)

**Preparation of Alcohols 5 and 6.** To a suspension of 1.664 g of LAH (44 mmol) in freshly distilled THF (30 mL) was added 6.02 g of **4** (38 mmol) dropwise in 15 mL of THF. After refluxing the suspension for 2 h the GC trace showed complete disappearance of the epoxide. Usual workup (saturated $NH_4Cl$) afforded 4.80 g (81%) of a mixture of **5** and **6** as a white crystalline solid in the reported ratio of 9:1 (**5**/**6**). Several attempts to separate the alcohols via either chromatography or fractional crystallization were unsuccessful. The $^1H$ NMR values ($\delta$, $CCl_4$) for the carbinolic ($CH$–OH) protons are in good agreement with reported values:[9] lit. **5**, 3.55; **6**, 3.69; found **5**, 3.52; **6**, 3.64.

**Oxidation of Alcohols 5 and 6.** A sample of the mixture of the alcohols was oxidized with $P_2O_5$/DMSO,[8] and the resulting ketones were found to have the same GC behavior as the compounds obtained by direct opening of the epoxide via either method A or B. Boiling point and position of the carbonyl $^{13}C$ signal (**7**, 211.13 ppm; **8**, 211.66 ppm) are also in agreement with the data obtained by the direct opening procedures A or B.

**Preparative-Scale Electrolysis of 7 and 8. Typical Procedure.** Three hundred milligrams (1.68 mmol) of the 71:29 mixture of **7** and **8** was added to 20 mL of a 0.1 M solution (cathode compartment) of $TBA^+BF_4^-$ in DMF, previously deaerated, via syringe. A constant current of 30 mA was passed until the amount of the electricity was 2.3 F/mol. The solution was quenched with 2 mL of brine added through a septum and then extracted with $Et_2O$ (4 × 25 mL). The ethereal layers were washed (2 × 10 mL) with brine and dried ($MgSO_4$), and the solvent was removed. Flash chromatography (10% AcOEt/Hexane, $SiO_2$) afforded **9** (85.8 mg, 28.6%) and **10** (59.4 mg, 19.8%) as a crys-

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talline solid (mp 66–67 °C, hexane) and a clear oil, respectively. HRMS calcd for $C_{12}H_{20}O$: 180.1509. Found: **9**, 180.1509. **10**, 180.1513. IR **9** ($CDCl_3$): 3392, 3004, 2929, 2868, 1652, 1449, 1070, 969, 733 $cm^{-1}$. IR **10** (neat): 3450, 3002, 2927, 2863, 1652, 1447, 1070, 958, 728 $cm^{-1}$. NMR data: see text.

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**Supplementary Material Available:** MM2-derived conformations, calculated and experimental lanthanide-induced shifts for **9** and **10**, partial INADEQUATE spectrum, and slices from the HETCOR experiment for **10** (6 pages). Ordering information is given on any current masthead page.

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# Photochemistry of 1-Phenyl-1,2-dihydronaphthalene in Methanol

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The photochemistry of 1-phenyl-1,2-dihydronaphthalene (**1**) in methanol and hexane has been investigated. The lack of influence of solvent polarity and of the presence of sulfuric acid on the rate of formation of *exo*-4-phenylbenzobicyclo[3.1.0]hex-2-ene (*exo*-**2**) from the primary, ring-opened photoproduct *cZt*-**3a** of **1** precludes a sudden-polarized, zwitterionic excited state from being involved in the intramolecular [4 + 2] photocycloaddition reaction leading to *exo*-**2**. The experimental results can be rationalized by assuming that this photoprocess involves a concerted $\pi_4a + \pi_2a$-type electrocyclic reaction. *cis*-Dibenzobicyclo[3.3.0]octa-2,7-diene (**8**) is proposed to arise by photocyclization of *cZc*-**3b**, followed by a thermal rearrangement. On irradiation of **1** with a broad-spectrum lamp, the ratio of the photoproducts *exo*-**2** and **8** is correlated with the ratio of the pe and pa conformers of **1**. The novel compound 1-(*o*-benzylphenyl)allene (**6**) is also formed under these conditions. Irradiation of **1** at 254 nm yields **8** as the only photoproduct. Photochemical addition of methanol was observed to compete with the photoprocess, leading to *exo*-**2**, though at a comparatively low level. A photodecomposition mode of *exo*-**2**, presumably involving heterolytic cleavage of the cyclopropane ring, presents the chief source of methoxylated photoproducts at low temperatures in methanol.

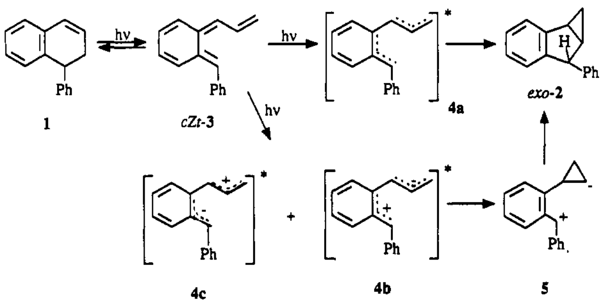
## Introduction

Previously, it was reported[1,2] that irradiation of 1-phenyl-1,2-dihydronaphthalene (**1**) with a broad-spectrum lamp in hexane affords exclusively the exo isomer of 4-phenylbenzobicyclo[3.1.0]hex-2-ene (*exo*-**2**). On the basis of these data, *exo*-**2** was supposed to arise from excitation of the pe conformer (**1**-pe, with the phenyl group occupying the pseudo-equatorial position) of **1**. Within this assumption two possible reaction pathways leading to *exo*-**2** were postulated,[1,2] i.e., a concerted, intramolecular [4 + 2] cycloaddition reaction involving an unpolarized excited singlet state of *cZt*-**3**, or a mechanism involving a sudden-polarized,[3] twisted, zwitterionic excited singlet state of *cZt*-**3** (Scheme I).

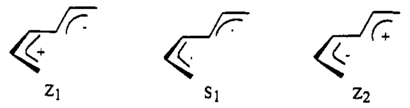
Considering the possibility of a concerted, intramolecular [4 + 2] photocycloaddition reaction of *cZt*-**3**, the structure of the end product *exo*-**2** requires the excited triene moiety in **4a** to cyclize in a $\pi_4a + \pi_2a$ fashion. Although this conclusion obviously violates the Woodward–Hoffman rules,[4] Tanaka et al.[5] emphasizes the possibility of photochemical, intramolecular $\pi_4a + \pi_2a$ cross-bicyclization in excited trienes of low symmetry.

A mechanism involving a sudden-polarized, zwitterionic state (**4b**) has been used to rationalize the observed stereochemistry of several bicyclo[3.1.0]hex-2-enes originating from apparently concerted, but symmetry-forbidden, intramolecular $\pi_4a + \pi_2a$ photocycloadditions of *cZt*-hexatrienes.[6–10] A two-step mechanism has been invoked[6] to explain the observation that the configuration of the asymmetric center resulting from the formation of the five-membered ring of the corresponding bicyclo[3.1.0]hex-2-ene is thermodynamically controlled. The photocycloaddition product of *exo*-**2** (Scheme I) can be rationalized as the thermodynamically favorable relaxation

### Scheme I



### Scheme II



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