of syringes. The resulting solution was mixed thoroughly and put into the spectrometer. Determination of the extinction coefficients of Py and PyO permitted one to evaluate rates. The precision of rate determinations was usually ±2–4%.

Product yields were determined by running the reaction in vials ($[\text{pyridine}]_0 \simeq [\text{Caro's acid}]_0$) and allowing enough time to elapse such that all the Caro's acid reacted. The reaction mixture was then scanned (after dilution) in the UV. Absorbance readings were taken at 250 and 270 nm, and two simultaneous equations were solved to find the concentration of PyO.

The percent remaining of cyclohexanone (used to determine the percent of Baeyer–Villiger reaction) was evaluated by running the reaction in vials ($[\text{cyclohexanone}]_0 \simeq [\text{Caro's acid}]_0$, no pyridine) and allowing enough time to elapse such that all the Caro's acid reacted. An absorbance reading at 280 nm as compared with the initial absorbance due to cyclohexanone alone allows one to calculate the percent remaining. Similar procedures were followed for acetone and *p*-nitroacetophenone.

Acknowledgment. We are pleased to thank Montclair State College (for a sabbatical for A.R.G.) and the Army Research Office (Grant No. DAAG29-76-G-0277) for financial support. We have benefitted by discussions with our colleagues Drs. R. Curci, F. DiFuria, K. M. Ibne-Rasa, and R. Pater.

Registry No. HSO_5^-, 12188-01-1; Py, 110-86-1; PyO, 694-59-7; c-HxO, 108-94-1; acetone, 67-64-1.

Electrocyclic Ring Opening of the 6b,7a-Dihydro-7*H*-cycloprop[*a*]acenaphthylene Radical Anion

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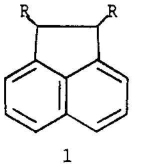
The Na–K alloy and electrochemical reduction of the naphthocyclopropane **6** were investigated. The radical anion of **6** was found to be very labile and could not be observed spectroscopically. In the Na–K reduction of **6**, the phenalenyl radical (**9**) was detected as an intermediate in the reduction, and the phenalenyl anion (**10**) and perinaphthane (**8**) were found to be the products of the reduction. Evidence was obtained from polarographic and cyclic voltammetric studies that **8**–**10** are also formed in the electrochemical reduction of **6**. A mechanism is proposed for this reduction which involves an initial electrocyclic ring opening of the cyclopropane ring in the radical anion of **6** which is followed by a 1,2-shift of hydrogen to yield the radical anion of phenalene (**11**). The radical anion of **11** is then further transformed into **8** and **10**; the latter transformation has previously been reported.

There has been increasing interest in recent years in the pericyclic reactions of radical anions[2] and, to a lesser extent, radical cations.[3] These reactions make interesting comparisons with the thermal and photochemical reactions of the corresponding neutral molecules, where the predictions of the Woodward–Hoffmann rules are easily made and usually verified experimentally. Ambiguities abound when one attempts to apply these simple rules to species which possess an odd number of electrons. In the electrocyclic ring opening of the benzocyclobutene radical anion, for example, the use of correlation diagrams yields a different prediction than the frontier orbital approach. Other examples of these ambiguities for the electrocyclic reactions of radicals and radical anions have recently been cited by Bauld and Cessac.[4] The electrocyclic reactions of radical cations, on the other hand, are almost always predicted to be forbidden by both orbital correlation diagrams and state symmetry, although the barriers to reactions are predicted to be low and the mode of ring opening is predicted to be identical with the thermal reaction of the neutral molecule.[4,5]

Acenaphthene (**1a**) is a particularly interesting molecule in this regard. Ring opening of the CH_2–CH_2 σ bond yields the 1,8-naphthoquinodimethane biradical (**2a**). The biradical **2a** possesses a degenerate set of nonbonding π molecular orbitals (MO's), one of which is symmetric and one of which is antisymmetric to a plane bisecting the molecule through the middle of the naphthalene ring.[6] In the neutral species these degenerate MO's will contain two electrons, which gives rise to not only singlet states but



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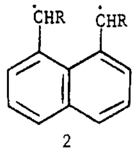

2

a)R=H, b)R=Ph, c)R=p-Ph-Ph-

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[1] (a) Emory University. (b) Present address: Conoco, Inc., Room 346, Research Building, Chemicals Research Division, Ponca City, OK 74601. (c) University of Tennessee. (d) Address correspondence to this author.

[2] (a) Nelsen, S. F.; Gillespie, J. P. *J. Org. Chem.* **1973**, *38*, 3592. (b) Rieke, R.; Ogliaruso, M.; McClung, R.; Winstein, S. *J. Am. Chem. Soc.* **1966**, *88*, 4729. (c) Katz, T. J.; Talcott, C. *Ibid.* **1966**, *88*, 4732. (d) Russell, G. R.; Ku, T.; Lokensgard, J. *Ibid.* **1970**, *92*, 3833. (e) Dodd, J. R., Winton, R. F., Pagni, R. M., Watson, C. R., Jr.; Bloor, J. *Ibid.* **1974**, *96*, 7846. (f) Gerson, F.; Huber, W.; Müller, K. *Helv. Chim. Acta* **1979**, *62*, 2109. (g) Müller, K.; Huber, W. *Ibid.* **1978**, *61*, 1310. (h) Bauld, N. L.; Young, J. D. *Tetrahedron Lett.* **1974**, 3143. (i) Bauld, N. L.; Hudson, C. E. *Ibid.* **1974**, 3147. (j) Bauld, N. L.; Chung, C.-S.; Farr, F. R. *J. Am. Chem. Soc.* **1972**, *94*, 7164. (k) Allendoerfer, R. D.; Miller, L. L.; Larscheid, M. E.; Chang, P. *J. Org. Chem.* **1975**, *40*, 97. (l) Elschenbroich, C.; Gerson, F.; Boekelheide, V. *Helv. Chim. Acta* **1975**, *58*, 1245. (m) Blankespoor, R. L.; Snavely, C. M. *J. Org. Chem.* **1976**, *41*, 2071. (n) Bauld, N. L.; Cessac, J. *J. Am. Chem. Soc.* **1975**, *97*, 2284.

[3] Haselbach, E.; Bally, T.; Gschwind, R.; Klemm, U.; Lanyiova, Z. *Chimia* **1979**, *33*, 405 and references cited therein.

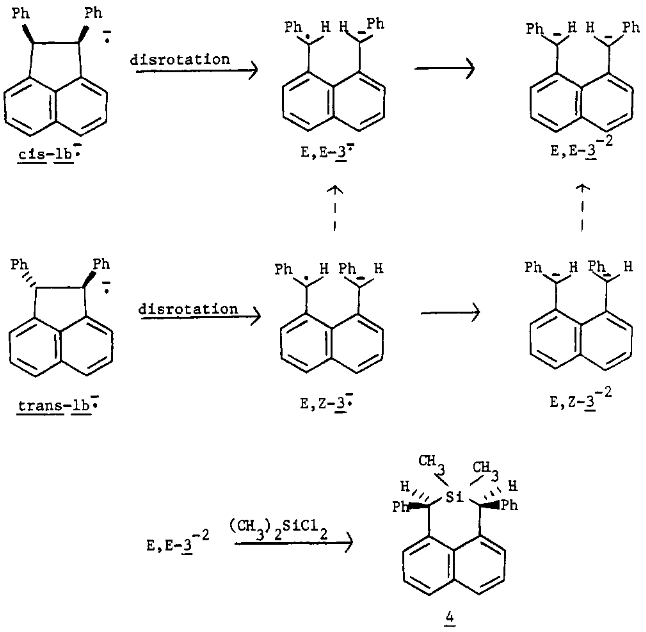
[4] Bauld, N. L.; Cessac, J. *J. Am. Chem. Soc.* **1977**, *99*, 23.

[5] Haselbach, E.; Bally, T.; Lanyiova, Z. *Helv. Chim. Acta* **1979**, *62*, 577.

[6] Coulson, C. A.; Streitwieser, A., Jr. "Dictionary of π Electron Calculations"; W. H. Freeman and Co., San Francisco, 1965; p 112.

0022-3263/81/1946-1688$01.25/0

Scheme I



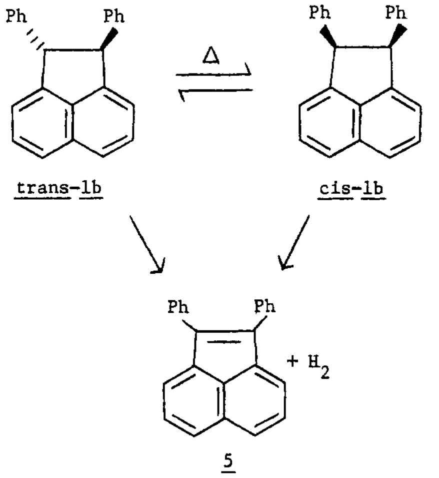
also a triplet state which, in fact, has been demonstrated to be the ground state for **2a** and related species.[7]

Ring opening of **1a**$^-$· will yield **2a**$^-$· in which the odd electron in this latter species occupies one of these degenerate MO's. As already noted by Bauld,[2i] orbital correlation shows that ring opening in this case will be disrotatory allowed; conrotation will be forbidden. Identical predictions are made by considering state symmetries. For the ring opening of the radical cation **1a**$^+$, on the other hand, conrotation is predicted to be allowed by orbital correlation and state symmetry, while disrotation is forbidden by both analyses. This represents one of the few cases in which the ring opening of a radical cation is predicted to be allowed.[5]

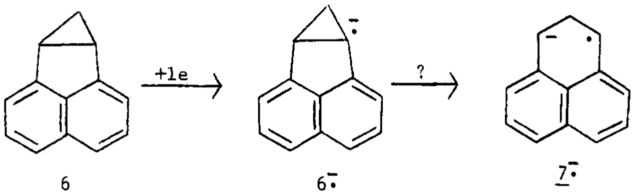
Ring opening of the radical anions of *cis*- and *trans*-**1b** and -**1c** (Scheme I) has already been examined.[2i] Bauld observed that cleavage of both *cis*- and *trans*-**1b**$^-$· did not ensue until 0 °C. Quenching with $(CH_3)_2SiCl_2$ yielded the same adduct in both cases. If these ring openings had proceeded in a disrotatory manner, as predicted, *trans*-**1b**$^-$· would yield a highly strained 1,8-naphthoquinodimethane radical anion, which might isomerize at an appreciable rate to the more stable 1,8-naphthoquinodimethane radical anion formed by ring opening of *cis*-**1b**$^-$·. Because these radicals anions should be easily reduced, the isomerization could also have occurred at the dianion stage. Similar results were obtained for *cis*- and *trans*-**1c**$^-$·, only the ring openings occurred at the much lower temperature of −95 °C. Because of the extreme congestion about the 1- and 8-positions of the naphthalene ring in these cases, other mechanisms are possible here.

One striking feature of these reactions is the ease with which they occur when compared to the thermal reactions of the neutral species. Thermolysis of *cis*-**1b** at 270 °C in diethyl phthalate for 10 h results in no epimerization,[2i] while heating neat samples of either *cis*- or *trans*-**1b** with a Bunsen burner (~500 °C) in the absence of air results in the epimerization to the other isomer and also to the dehydrogenated hydrocarbon **5**[8] (Scheme II). It is not clear, it should be noted, if the isomerization occurs through an electrocyclic ring opening and reclosure.

Scheme II

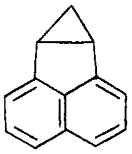


We report at this time our results on the behavior of the radical anion of the hydrocarbon 6b,7a-dihydro-7*H*-cycloprop[*a*]acenaphthylene (**6**). Because of the appreciable ring strain in this molecule, disrotatory ring opening of the corresponding radical anion should be very facile; external cleavage of the cyclopropane C–C bond is also possible here. In this regard, it should be mentioned that thermally induced epimerization and isomerization of **6** occur around 150 °C,[8,9] a temperature appreciably lower than for epimerization of **1b**.[10]



Results and Discussion

Contact of dilute solutions (~10^{-3} M) of **6** in tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) with Na–K at either 25 °C or at lower temperatures (−60 to −90 °C) afforded reddish brown paramagnetic solutions whose ESR spectra indicated the presence of the radical anion of perinaphthane (**8**). Reduction of **6** in THF-d_8 afforded **8**$^-$· in which no detectable deuterium was incorporated, demonstrating that solvent is not the source of hydrogen in the reductive transformation of **6** into **8**.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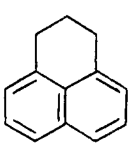
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All attempts to observe the labile **6**$^-$· at lower temperatures by ESR were unsuccessful. For instance, reduction

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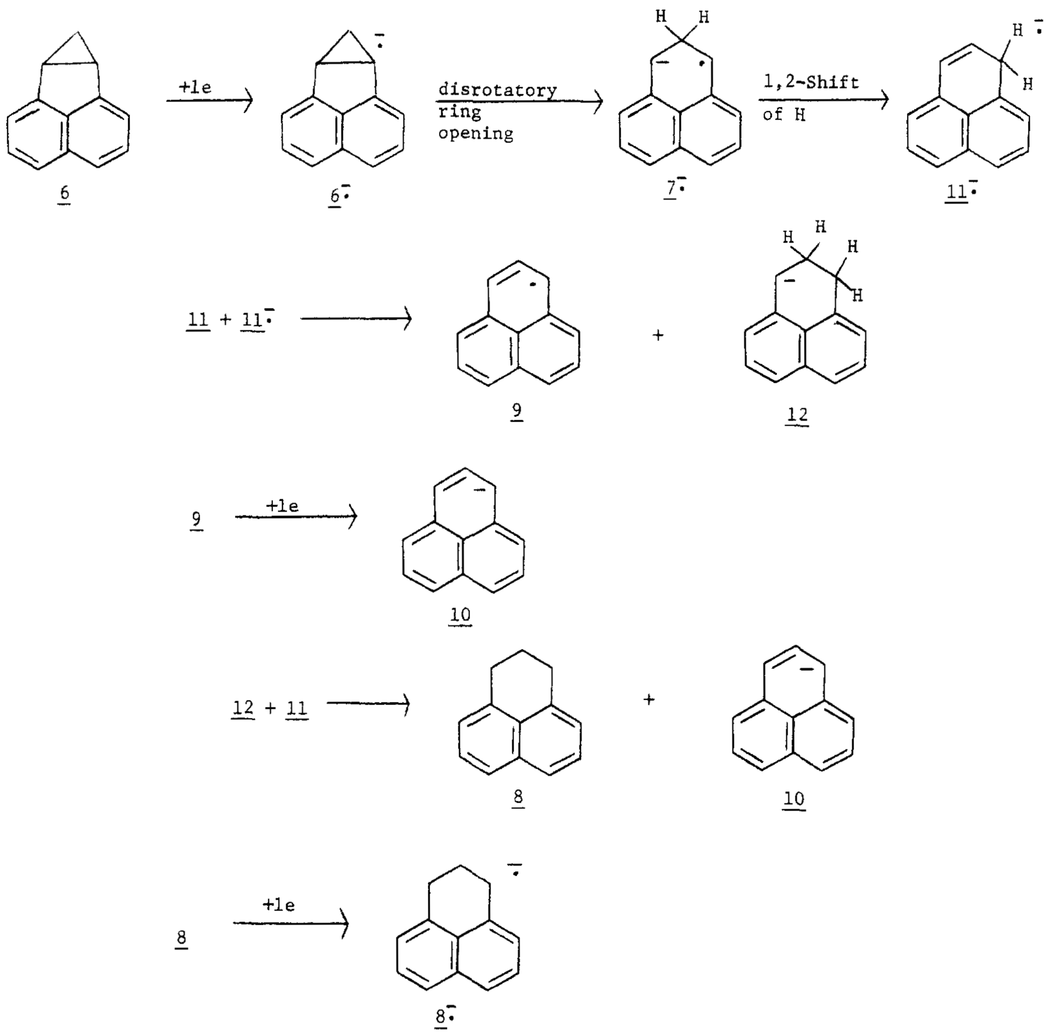
[7] (a) Gisin, M.; Rommel, E.; Wirz, J.; Burnett, M. N.; Pagni, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 2216. (b) Pagni, R. M.; Burnett, M. N.; Dodd, J. R. *Ibid.* **1977**, *99*, 1972. (c) Muller, J.-F.; Muller, D.; Dewey, H.; Michl, J. *Ibid.* **1978**, *100*, 1692. (d) Platz, M.; *Ibid.* **1979**, *101*, 3398.

[8] (a) Burnett, M. N. Ph.D. Dissertation, University of Tennessee at Knoxville, August 1979. (b) These results will be reported in detail elsewhere.

[9] Roth, W. R.; Enderer, K. *Justus Liebigs Ann. Chem.* **1969**, *730*, 82.

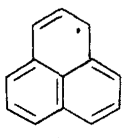
[10] Hydrocarbon 6 is also an excellent candidate to look for the disrotatory ring opening of the corresponding radical cation. Although formally forbidden, this reaction could be facile because appreciable ring strain would be removed in the reaction. External C–C bond cleavage is, of course, also possible here. The chemistry of the radical cation will be reported elsewhere.

Scheme III



of **6** as a dilute solution in 2:1 2-methyltetrahydrofuran–1,2-dimethoxyethane with Na–K at −110 °C (EtOH slush) yielded only **8**$^{-}\cdot$ as the first detectable paramagnetic species. Similarly, electrolytic reduction inside the ESR cavity of a dilute solution of **6** in 2:1 THF–DME at −100 °C afforded only a weak spectrum of **8**$^{-}\cdot$.

A considerable amount of additional information was provided by carrying out the reduction of **6** in an incremental fashion and observing the progress by both NMR and ESR. Brief contact of a solution of **6** with Na–K afforded a yellow solution whose ESR spectrum indicated[11] the presence of the phenalenyl radical (**9**); further brief contacts with Na–K resulted in an increase in the ESR signal intensity of **9** followed by the decrease and disappearance of the signal of **9**. During this period only **6** was detected by NMR. More extensive contact of the solution with Na–K afforded, successively, orange and then reddish brown solutions for which the NMR signals of **6** decreased in intensity and, concurrently, the NMR signals of two reduction products appeared and increased in intensity. The appearance of a doublet at δ 5.20 and a triplet at δ 5.98 in a 2:1 ratio indicated[12] the formation of the phenalenyl anion (**10**), while the appearance of a pentet at δ 2.01 and a triplet at δ 3.06 indicated the formation of **8** as the second product. During these stages, the aromatic multiplet gradually changed from the multiplet characteristic of **6** to a multiplet that is identical with that of authentic **8**, the latter being observed at the stage of reduction where **6** had just disappeared. The sample did not exhibit ESR absorption at these times. Analysis of the integrated NMR spectrum indicated that **8** and **10** were present in a ratio of 1:2 when two-thirds of **6** had been consumed; at the stage where the NMR resonances of **6** had just disappeared, however, this ratio was somewhat higher (1:2.7). Further reduction afforded a paramagnetic solution whose ESR spectrum was sufficiently well-resolved at −50 °C to indicate formation of **8**$^{-}\cdot$. The NMR resonances of **8** had disappeared at this time, as would be expected due to extreme broadening as a result of a rapid electron exchange. After the ESR signal had become very intense and broadened into a single line, no further changes were observed by ESR or NMR upon further contacts with Na–K.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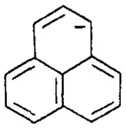
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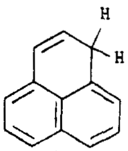

11

The above observations are strikingly similar to those previously reported[12] for the alkali metal reduction of phenalene (**11**) in which **9** was detected as an intermediate in the reduction and **8** and **10** in a 1:2 ratio were found as products. This close similarity[13] suggests that **11**$^{-}\cdot$ (and/or

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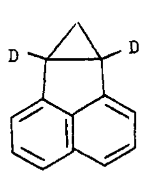
[11] Gerson, F. *Helv. Chim. Acta* **1966**, *49*, 1463.

[12] Shannon, R. L.; Cox, R. H. *Tetrahedron Lett.* **1973**, 1603.

11) upon formation is then further transformed into **8** and **10**. In Scheme III is illustrated what is perhaps the simplest mechanism consistent with the above observations that one can propose for the reduction of **6** involving the intermediacy of $\mathbf{11}^{-\cdot}$. The one-electron reduction of **6** affords its radical anion $\mathbf{6}^{-\cdot}$ which then undergoes a disrotatory electrocyclic ring opening to intermediate $\mathbf{7}^{-\cdot}$. A process which can formally be considered as a 1,2-shift of hydrogen in $\mathbf{7}^{-\cdot}$ affords $\mathbf{11}^{-\cdot}$ which is then reductively transformed, as shown in the bottom part of Scheme III, into **8** and **10**.

Several aspects concerning the above mechanism require further comment. The disrotatory opening of $\mathbf{6}^{-\cdot}$ to $\mathbf{7}^{-\cdot}$, as already noted, is predicted on the basis of both MO and state correlation diagrams to be a symmetry-allowed process. The transformation of $\mathbf{7}^{-\cdot}$ to $\mathbf{11}^{-\cdot}$ can only formally be regarded as a 1,2-shift to hydrogen, since our present results do not distinguish whether an intramolecular or intermolecular process is involved. Since the intramolecular 1,2-shift of hydrogen is apparently not a facile process in either radicals[14a] or carbanions,[14b] one might a priori expect this process also to be unfavorable in radical anions. Thus the above hydrogen transfer may well involve an intermolecular process. A base-catalyzed tautomerization, as has been proposed[2a] for related hydrogen transfers in other radical anions, would appear to be a possible intermolecular mechanism for this process.[15] The transformation of $\mathbf{11}^{-\cdot}$ into **8** and **10** may proceed via the disproportionation mechanism previously suggested,[12] although another mechanism involving only the processes of one-electron reduction, proton transfer, and hydrogen atom abstraction can be written that is consistent with the experimental findings[12] and is an attractive alternative. On the assumption that the basic mechanism outlined in Scheme III is correct, our results indicate that $\mathbf{6}^{-\cdot}$, $\mathbf{7}^{-\cdot}$, and $\mathbf{11}^{-\cdot}$ are all relatively short-lived species, since none of them was detected in our experiments. The finding that **9** could be detected only during the very initial stage of reduction suggests that **9** is reduced at a less negative potential than **6** and hence remains in very low concentration throughout the reduction.

Attempts were made to prove this mechanism further by alkali metal reduction of **13**. Unfortunately, the ESR spectra were too complex to analyze unambiguously. Because of this, no attempts were made to reduce **14** and **15**. These results are not surprising in that each ESR-active species may or may not contain deuterium, which, of course, is a magnetically active nucleon in the ESR. Each species, in turn, may be a jumble of partially deuterated entities. Several reasons for this are apparent: (1) **13** may contain small amounts of d_0 and d_1 contributions that are not apparent in the NMR spectrum; (2) the conversion of $\mathbf{7}^{-\cdot}$ to $\mathbf{11}^{-\cdot}$ may be intermolecular which could scramble H and D; (3) phenalene is known to scramble H under basic conditions;[16] (4) the reduction of **11** is an intermolecular reaction which also will move H and D around; (5) other minor reaction pathways may occur that will yield the observed product(s) with different distributions of H and D than the major one.[13] Even if we could unambiguously analyze the ESR spectra and even if one isolated the products and analyzed the products by NMR and mass spectrometry, it is doubtful if one could unambiguously find a "unique" scheme to account for the results. Isotope effects would further complicate the analysis.



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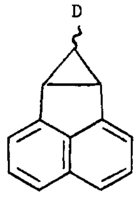
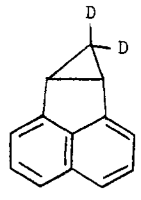


14 a) exo D
b) endo D



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Polarographic and cyclic voltammetric studies of the reduction of **6**, nonetheless, provided additional evidence in support of the above mechanism. The polarogram of **6** exhibited two reduction waves (see Table I). The first wave ($E_{1/2} = -2.42$ V) was nearly diffusion controlled, although the finding that the function $i_d/h^{1/2}$ (i_d = diffusion current, h = height of the Hg column of the DME) increased slightly[17] with increasing h indicates that (to a small extent in this case) the height of this wave is also governed by the rate of some process other than just diffusion to the electrode. A standard logarithmic plot ($-E$ vs. $\log i/i_d - i$) for this wave was initially linear with a slope of 60 mV but deviated slightly from linearity at higher values of $-E$. The diffusion current constant I_d measured for this wave was essentially one-third greater in magnitude than those measured under identical conditions for the well-known one-electron reduction waves of naphthalene and anthracene. On the basis of the above findings, we believe that the first polarographic wave corresponds not only to reduction of **6** to $\mathbf{6}^{-\cdot}$ (which is then rapidly transformed as shown in Scheme III) but also to reduction of the intermediate **9**, which is rapidly formed from $\mathbf{6}^{-\cdot}$, to **10**. The observation that this wave has an I_d that is essentially one-third greater than those observed for typical one-electron reduction waves of related hydrocarbons is in agreement with the prediction that one-third of **6** is transformed into **9** via $\mathbf{11}^{-\cdot}$. Furthermore, the finding that the initial portion[18] of the logarithmic plot for this wave is linear with a slope of 60 mV indicates that the initial reduction process involves the addition of one electron to **6** and is electrochemically reversible.

The second wave in the polarogram of **6** corresponds to reduction of **8** to $\mathbf{8}^{-\cdot}$; this finding demonstrates that **8** is

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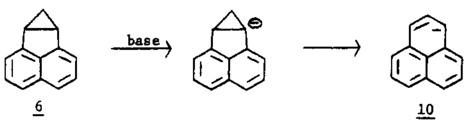
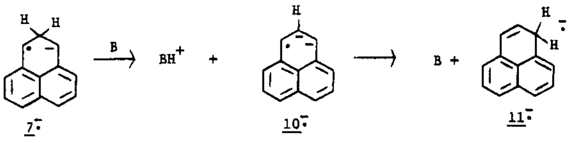
[13] The finding that the **8**/**10** ratio changes (from an earlier value of 1:2 to a later value of 1:2.7) suggests that **10** is also formed by a second process which competes with the above-described process more favorably at later stages of the reduction. A possible competing process for formation of **10** from **6** is the formation of the anion of **6** (at the naphthalylic position) and the opening of this anion to **10**. The latter process is known to occur. See ref 21.



6 10

[14] (a) Wilt, J. W. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, p 378. (b) March, J. "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure"; McGraw-Hill: New York, 1968; p 793.

[15] In the above case this process would involve the phenalenyl dianion radical as an intermediate; although this species has not yet been successfully prepared, it may nevertheless be generated as a reactive intermediate in this case.



[16] Reid, D. H. *Q. Rev., Chem. Soc.* **1965**, *19*, 274.

[17] This ratio increased by 5.4% with a 30-cm increase in h. For discussion of this function, see: Meites, L. "Polarographic Techniques"; Wiley: New York, 1965; pp 133–134.

[18] At times corresponding to the initial portion of this plot (low values of $-E$), little of **9** has formed, and hence this portion of the wave and plot reflects only the initial addition of an electron to **6**.

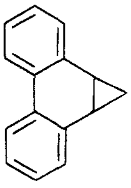
Table I. Polarographic Data

compd[a]	$E_{1/2}$[b]	I_d[c]
naphthocyclopropane 6	−2.42	2.54
	−2.67	1.06
naphthalene	−2.54	1.89
anthracene (1st wave)	−1.98	1.86
perinaphthane (8)	−2.67	1.58

[a] All measurements in Me_2SO containing 0.1 M Bu_4NClO_4. [b] Half-wave potential in volts vs. SCE. [c] Diffusion current constant in $\mu A\ mmol^{-1}\ L\ mg^{-2/3}\ s^{1/2}$.

rapidly formed upon reduction of **6**. Cyclic voltammetric studies also indicate that $\mathbf{6}^{-}\cdot$ is rapidly transformed irreversibly. The cyclic voltammogram of **6** in acetonitrile exhibited a totally irreversible[19] wave at −2.44 V; at scan rates up to 104 mV/s, no reoxidation wave was observed in the cyclic scan of **6**.

Admittedly, the reduction of **6** is complex; the evidence is, nonetheless, convincing that $\mathbf{6}^{-}\cdot$ undergoes an electrocyclic ring opening to $\mathbf{7}^{-}\cdot$. This is made even more convincing when one compares the alkali metal reduction of **6**, which, as has been repeatedly noted, has an allowed ring opening, with that of **16** which is forbidden to undergo the geometrically feasible disrotatory ring opening.[2k] The radical anion of **6** cleaves easily at −110 °C, while the radical anion of **16** is stable and observable up to 25 °C.[2k] The radical anion of **6** undergoes exclusive cleavage of the internal carbon carbon bond, while $\mathbf{16}^{-}\cdot$ cleaves both internal and external bonds.[2k,20]



16

Experimental Section

6b,7a-Dihydro-7*H*-cycloprop[*a*]acenaphthylene (6). This hydrocarbon was prepared from acenaphthylene according to the procedure of Wittig,[21] modified by replacing the bis(chloromethyl)zinc with methylene iodide and a zinc–copper couple.[22]

6b,7a-Dideuterio-7*H*-cycloprop[*a*]acenaphthylene (13). (a) 1,2,2-Trideuterio-1-acenaphthenol. The alcohol was prepared by the reduction of acenaphth-1-one-d_2 with lithium aluminum deuteride in ether according to the procedure of Hunter.[23]

(b) Acenaphthylene-d_2. The xanthate ester (23.0 g), prepared in the standard way from 13.6 g of 1,2,2-trideuterioacenaphth-1-ol, was heated at 170 °C under nitrogen until gas evolution ceased. The oily residue was chromatographed carefully on an alumina column. Elution with ligroine afforded 4.0 g of acenaphthylene-d_2 which was slightly contaminated with a sulfur compound. The impurity was easily removed by chromatography on a 5% silver nitrate alumina column.

(c) Hydrocarbon 13. This was prepared as previously described by starting with acenaphthylene-d_2. Mass spectral analysis revealed a very large M − 1 peak even at very low ionization voltage which precluded determining the deuterium distribution on **13** itself. Mass spectral analysis of acenaphthylene-d_2 did reveal 5% d_0, 9.0% d_1, and 86% d_2 compounds. These values certainly apply to the cyclopropane itself.

Perinaphthane (8).[12] This hydrocarbon was prepared by catalytic hydrogenation of phenalene (**11**).[24]

ESR and NMR Samples. All samples for ESR and NMR studies of the reduction of **6** were prepared on a high vacuum line using techniques that have been previously described in detail.[25] A weighed amount of **6** was placed at the bottom of either an ESR or NMR sample preparation tube containing a side arm in which Na–K alloy was placed. The sample tube was evacuated on the high-vacuum line. Dry solvent (THF, MeTHF, or DME) was then vacuum transferred to the sample tube from a solvent bulb containing solvent stored over anthracene radical anion. The solvent in the sample tube was degassed by means of several freeze–thaw cycles. The Na–K alloy was then distilled from the side arm into the sample tube to afford a Na–K mirror above the solvent. The tube was then sealed in vacuo at <0.1 μm.

The samples were developed in the standard manner by inverting the tube and contacting the solution of **6** with the Na–K mirror. Samples were developed either at ambient temperature or at subambient temperatures in a suitable low-temperature bath (hexane slush, ethanol slush, or dry ice–acetone bath). For the subambient runs, each sample was quickly transferred from the low-temperature bath to the precooled ESR cavity.

^1H NMR spectra were recorded on a JEOL 100-MHz spectrometer. ESR spectra were recorded on a Varian V-4500 ESR spectrometer equipped with a Varian variable-temperature accessory for the low-temperature runs.

Polarography. The polarographic studies were conducted by using a Sargent Model XVI polarograph equipped with a Sargent Model A IR compensator and a dropping mercury electrode. The Me_2SO that was used for the polarographic samples had been distilled from calcium hydride under reduced pressure and was stored over molecular sieves. The $(n\text{-}Bu)_4NClO_4$ used was reagent grade and had been dried at 80 °C overnight on a high-vacuum line (<1 μm) prior to use. All of the polarographic samples were 0.1 M in the supporting electrolyte and $\sim 1 \times 10^{-3}$ M in the electroactive substrate. All polarographic measurements were conducted at ambient temperature in a three-electrode polarographic cell equipped with a saturated calomel electrode as the reference electrode. The m and t values characteristic of the capillary of the DME were measured with the capillary immersed in a 0.1 M solution of $(n\text{-}Bu)_4NClO_4$ in Me_2SO with the circuit closed and with the potential set at the $E_{1/2}$ of the polarographic wave being studied.

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Registry No. 6, 6840-31-9; **8**, 479-58-3; **9**, 3924-44-5; **10**, 42464-32-4; **13**, 76599-68-3; acenaphthylene-d_2, 72526-88-6; 1,2,2-trideuterioacenaphth-1-ol, 50442-48-3; 1,2,2-trideuterioacenaphth-1-ol xanthate ester, 76599-69-4.

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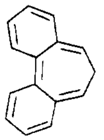
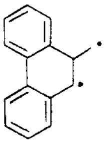
[19] The wave observed by cyclic voltammetry is "irreversible" since **6** is rapidly transformed further and does not exist at the electrode for a long enough period to be reoxidized. The process of addition of one electron to **6** is by itself, however, electrochemically reversible as the polarographic data indicate.

[20] (a) Strain and other effects may also be important in determining the reactivity of $\mathbf{6}^{-}\cdot$ and $\mathbf{16}^{-}\cdot$. Application of Benson's method for the calculation of ΔH_f's[20b] shows that the conversion of **6** into **7** is somewhat less exothermic than the conversion of **16** into i and ii. On the basis of these calculated ΔH_f's and the Hückel MO properties of these species, the conversion of $\mathbf{6}^{-}\cdot$ into $\mathbf{7}^{-}\cdot$ should be less exothermic than the conversion of $\mathbf{16}^{-}\cdot$ *into the radical anions of* i *and* ii. *Solvent effects could also be* important. (b) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.



i



ii

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