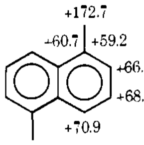
ences are even more remarkable because the relative spread of the chemical shifts in the case of ^{13}C is larger than for ^{1}H. The electron-deficient carbon 1 in ion 7a exhibits a chemical shift (δ −7.4 ppm from $^{13}CS_2$) which is deshielded by 64.5 ppm from its position in the neutral hydrocarbon (see Figure 10). A tentative assignment of the carbon absorptions is shown below and is compared with the cmr chemical shifts found for toluenium ion **19**, revealing that the unprotonated ring preserves much of its aromatic character.[4a]



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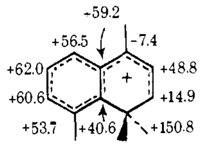
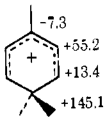


7a



19

The application of the Fourier-transform natural abundance carbon nmr spectroscopy to the investigation of carbocation intermediates thus proves very useful and promises to open up a new dimension in our ability to elucidate in detail structures of even quite complicated and large ions.

Experimental Section

Materials. All the organic compounds used in this study were commercially available in high purity. Antimony pentafluoride (Allied Chemical) was triply distilled; fluorosulfuric acid was doubly distilled.

Preparation of Ions. The solution of naphthalenium ion was prepared as reported previously in this series for protonations in superacid media and studied directly by nmr spectrometry. The quenching of solutions of naphthalenium ions and the analysis of recovered hydrocarbons (by glc and pmr) were also carried out as described.[4a]

Nuclear Magnetic Resonance Measurement. Spectra were obtained on Varian Associates Model A56/60A, HA100, and HR300 spectrometers. Fourier-transform spectra were recorded either with a Bruker HX-90 nmr spectrometer (22.63 MHz) or with a Varian HA-100 FT nmr spectrometer (25.16 MHz). With the Bruker instrument ^{19}F was used for locking the system (either $Cl_2C{=}CF_2$ for low-temperature or C_6F_6 for room-temperature measurements). With the Varian instrument, a ^{13}C lock (^{13}C-enriched CH_3I) was used for both low- and high-temperature measurements. In both cases a broad band (2 KHz) noise generator was used for proton noise decoupling.

Acknowledgment. Support of our work by the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We express our thanks to Dr. Toni Keller and Mr. Werner Schittenhelm (Bruker Scientific, Inc.) for the opportunity to record some of the early carbon-13 spectra with their instrument. The assistance of Dr. LeRoy F. Johnson and Mr. Lewis Cary (Varian Associates, Palo Alto, California) in recording the 300-MHz pmr spectra is acknowledged.

Radical Anions of 1,8-Bis-Unsaturated Naphthalene Derivatives

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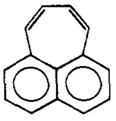
Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received July 13, 1972*

Abstract: The synthesis of 7,8-dimethylenenaphtho[1′,8′]bicyclo[3.2.0]hept-2-ene and its conversion into 2,3-dimethyl- and 2,3-cyclobutapleiadiene are described. The epoxide derived from naphtho[1′,8′]bicyclo[3.2.0]-hepta-2,5-diene and the related hydrocarbon give the peri-bridged 1,8-divinylnaphthalenes resulting from cyclobutane cleavage upon pyrolysis. The esr spectra of the radical anions from six pleidaiene derivatives, 1-oxo-4-naphtho[1′,8′]cycloocta-2,4,7-triene, and 1,8-divinylnaphthalene are reported and discussed.

We report here the synthesis of some 1,8-bis-unsaturated derivatives of naphthalene, some limitations on the use of thermal cleavages of acenaphthene derivatives to prepare such compounds, and the esr spectra of several such radical anions. Experimental comparisons of the spin distributions of pleiadiene (**1**), the related enol ether **2**, and 1,8-divinylnaphthalene radical anions were of particular interest, to see if simple MO calculations would be successful for predictive purposes and, if not, to see what spin distributions actually result.



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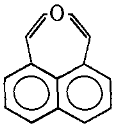

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Synthesis. Several derivatives of pleiadiene (**1**) were prepared using the method of Meinwald and coworkers,[1] who employed the heavy-atom solvent enhanced photocycloaddition of maleic anhydride to acenaphthylene to give **3a** after work-up, lead tetraacetate decarboxylation to **4a**, and pyrolytic cyclobutene ring opening to give **1a**. Starting the sequence with 3,6-di-*tert*-butylacenaphthene gave **1c**, and preparation of **3b** by base-catalyzed exchange (KOD–D_2O, 150°) on **3a** gave **1b** after completion of the sequence. We were unable to repeat the reported[1] 28% yields in the bis-decarboxylations and observed serious falling-off of the yield in runs at a larger scale than 4 g. Attempts to improve conditions showed that saturation of the reaction mixtures with oxygen[2] shortened the

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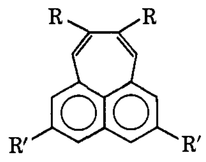
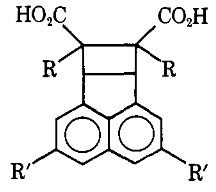
(1) J. Meinwald, G. E. Samuelson, and M. Ikeda, *J. Amer. Chem. Soc.*, 92, 7604 (1970).

(2) C. M. Cimarsturi and J. Wolinsky, *ibid.*, 90, 113 (1968).



1

a, R = R' = H
b, R = D; R' = H
c, R = H; R' = *tert*-butyl



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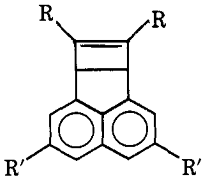
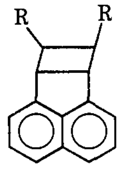
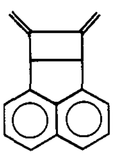


4

reaction time from 2 hr to 5 min, facilitating sequential runs of small scale reactions to build up material.



5, R = CO$_2$Me
6, R = CH$_2$OH
7, R = CH$_2$OMs
8, R = CH$_2$I



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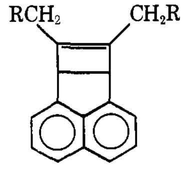
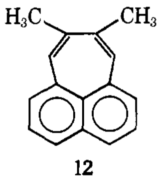


10, R = Br
11, R = H



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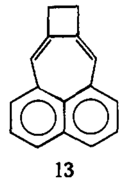
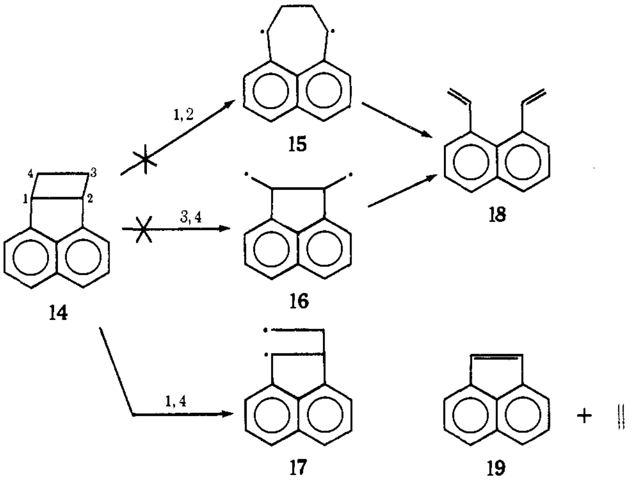


13

We also prepared two 2,3-dialkylpleiadienes starting from cyclobutanedicarboxylate **3a**. Diazomethane esterification (giving **5**), lithium aluminum hydride reduction (to **6**), mesylation (to **7**), and reaction with potassium iodide in HMPA gave the bis-iodide **8**, which was dehydrohalogenated to the dimethylenecyclobutane **9** in 91% yield using potassium *tert*-butoxide in THF. Reduction of **9** to **11** was accomplished by addition of bromine and cleavage of the dibromide **10** with lithium aluminum hydride. Thermal opening of **11** to **12** was accomplished by subliming and sweeping **11** through a heated column (hereafter referred to as "pyrolysis"). Although **4a** was completely converted to **1a** during one pass at a column temperature of 350°, three passes at 380° were required to give a 93:7 mixture of **12**:**11** (by nmr). **9** is a very labile compound, polymerizing rapidly at room temperature in concentrated solution. It is not sublimable but was successfully pyrolyzed by injection as a benzene solution into the heated flask normally used for sublimation. Pyrolysis of **9** gave 2,3-cyclobutapleiadiene (**13**). This rearrangement is formally analogous to the isomerization of 1,2-bis(methylene)cyclobutane, which is only detectable through the use of labels,[3] although in our case the extra ring should prohibit the preferred conrotatory ring opening[3c] and also not allow the intermediacy of a perpendicular bisallyl radical. At 515°, only a 60:40 mixture of **9**:**13** was observed after the first pass, and an 88:12 mixture after two passes; a third pass still gave the same product ratio. Unfortunately, we did not succeed in separating the residual **9** from **13**, and were unable to establish whether the observed mixture was really an equilibrium mixture, as seems likely.

We also investigated the possibility of generating 1,8-divinylnaphthalene derivatives by thermal cleavage of derivatives of cyclobutane **14**. Most cyclobutane cleavages appear to be nonconcerted reactions which proceed through diradical intermediates,[4] although Baldwin and Ford[5] have suggested that about 30% of the decomposition of 7,8-*cis*-*exo*-dideuteriobicyclo-[4.2.0]octane occurred *via* a concerted mechanism. Bicyclo[3.2.0]heptane itself thermally cleaves both to 1,6-heptadiene and to ethylene and cyclopentene, although the latter process has about a 3.3 kcal/mol lower activation energy.[6] Of the three types of cyclobutane bonds in **14**, cleavage of the 1–2 bond might be predicted to lead to the stablest diradical, since both radical centers formed would be benzylic. Cleavage of the 1–2 bond is, however, very poor stereoelectronically, since this bond is in the nodal plane of the aromatic rings in **14**, and overlap giving benzylic resonance would be very low until far along the reaction coordinate for bond cleavage. In contrast 1,4 cleavage leads to benzylic stabilization at one center, which is available at an early stage on the reaction coordinate. Pyrolysis of **14** gave no detectable amount of 1,8-divinylnaphthalene (**18**) or its pyrolysis products,[7] but acenaphthalene (**19**) was formed, demonstrating that 1,4 cleavage is in fact strongly preferred over 1,2 or 3,4 cleavage.



Fusion of a small ring on the 3,4 positions of **14** was expected to facilitate divinylnaphthalene derivative formation, both because of raising the activation energy for 1–4 bond cleavage, and because 3,4 cleavage would be enhanced by ring strain. Treatment of **4a** with *m*-chloroperbenzoic acid gave the epoxide **20**,

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(3) (a) W. von E. Doering and W. R. Dolbier, Jr., *ibid.*, **89**, 4534 (1967); (b) J. J. Gajewski and C. N. Shih, *ibid.*, **89**, 4532 (1967); (c) *ibid.*, **94**, 1675 (1972).

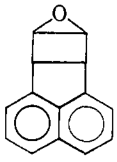
(4) (a) T. A. Bancock, *ibid.*, **91**, 1967 (1969); (b) A. T. Cocks and H. M. Frey, *J. Chem. Soc. A*, 1671 (1969); (c) A. T. Cocks, H. M. Frey, and I. D. R. Stevens, *J. Chem. Soc. D*, 458 (1969).

(5) J. E. Baldwin and P. W. Ford, *J. Amer. Chem. Soc.*, **91**, 7192 (1969).

(6) R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 4184 (1964).

(7) S. F. Nelsen and J. P. Gillespie, *J. Amer. Chem. Soc.*, **94**, 6237 (1972).

which pyrolyzed at 400° to give a 73% yield of the divinyl ether derivative **2**. No acenaphthalene was observed. The carbon analog **21** proved to be more difficult to prepare. Addition of diazomethane to the cyclobutene **3a** was remarkably sluggish, but stirring with ethereal diazomethane for over 2 weeks did give the 1,3-dipolar adduct **22**. Although photolysis in cyclohexane gave a reasonable yield of **21** on a 50-mg scale, the yield plunged upon attempted scale-up, and an alternate route to **21** was sought. We were unable to obtain any methylene addition under ordinary Simmons-Smith conditions[8] or using the diazomethane-zinc iodide modification,[9] but reaction with diethylzinc-methylene iodide[10] was more successful, although complete removal of side products involving addition of methylene to the naphthalene ring was not accomplished. Pyrolysis of bicyclo[2.1.0]pentane gives almost exclusively the hydrogen shift product derived from the diradical intermediate, although a 0.4% yield of 1,4-pentadiene has been observed.[11] In contrast, pyrolysis of the bicyclo[2.1.0]pentane derivative **21** gave an 80% yield of **23**. We have not established that the hydrogen shift product **24** is not an intermediate, although we doubt that **24** would completely rearrange to **23** under our reaction conditions, and suggest that cleavage of the 1,4 diradical initially formed might be expected to be substantially more rapid for **21** than for the unsubstituted case.



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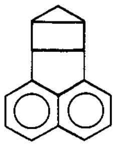

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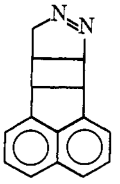
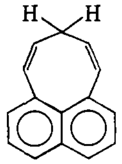
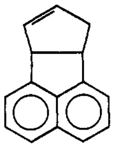


22

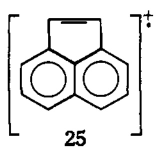


23



24

The mass spectral cracking patterns of **14**, **20**, and **21** show a parallel to the observed thermal chemistry.[12] Meinwald and Young[13] have shown that the base peak in the mass spectrum of **14** appears at *m/e* 152, which is assigned to acenaphthylene cation **25**. In contrast, epoxide **21** and its diene isomer **2** show nearly identical spectra, *m/e* 194 (P, 12%), 165 (27, 100%). The case is somewhat less clear-cut for **21**, for both types of cleavage are important: *m/e* 192 (P, 80%), 191 (P − 1, 100%), 165 (**27**, 85%), 152 (**26**, 30%).



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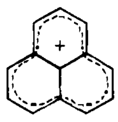


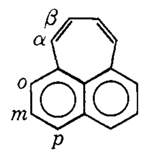
26

Radical Anions. We studied the esr spectra of the radical anions of **1a**, **1b**, and **1c** at room temperature in DMSO, using tetrabutylammonium perchlorate as the electrolyte and electrolytic generation. Low temperatures proved to be necessary for the other species studied, and were obtained by sodium-potassium alloy reduction in THF, at −50 to −80°. Since **1a** gave identical splittings to within ±0.02 G in DMSO at room temperature, in butyronitrile at −40°, and in DME at −80°, we believe solvent and temperature effects are negligible for these ions and will make direct comparisons of the splittings obtained. We usually were able to work at high enough temperatures to exchange out important variable line-width effects, such as have been seen with 1,8-dialkylnaphthalenes.[14] Our esr data are summarized in Table I, using the positional references shown on structure **27**. We were unable to obtain esr spectra of ($\mathbf{23}\cdot^-$), even in 2-methyltetrahydrofuran-dimethoxyethane and developing at −110°, possibly because the methylene hydrogens are too acidic and protonate the radical anion.

Table I. Esr Splitting Constants (G) for 1,8-Unsaturated Naphthalene Derivatives[a]

Compd	Line width[b]	*p*	*m*	*o*	*α*	*β*	Other
$\mathbf{1a}\cdot^-$	70	1.93	0.23	0.80	6.29	2.62	
$\mathbf{1b}\cdot^-$	70	1.93	0.17	0.77	6.27		0.40 (2 D)
$\mathbf{1c}\cdot^-$	70	1.89		0.87	6.48	2.62	
$\mathbf{12}\cdot^-$	110	1.83	0.18	0.66	5.92		2.23 (6 H)
$\mathbf{13}\cdot^-$	300[c]	1.68	unobsd	0.61	6.15		6.78 (4 H)
$\mathbf{2}\cdot^-$	50	5.66	0.09[d]	3.75	0.24[d]	2.48	
$\mathbf{2}\text{-}d_2\cdot^-$	40	5.64	0.09[d]	3.74	0.24[d]		0.39 (2 D)

[a] All 2 H triplets except where noted. [b] Line width (mG) used in simulations (Lorentzian shape). [c] Some viscosity broadening is probably observed at the −80° temperature necessary for enough stability to allow recording to spectra; this apparently obscured the tiny meta splitting. [d] Arbitrary assignment.



27

The esr spectrum of $\mathbf{1b}\cdot^-$ allows assignment of the second largest splitting of $\mathbf{1a}\cdot^-$ to the *β* position, as is expected from MO calculations. The spectrum of $\mathbf{1c}\cdot^-$ verified the expectation that the meta splitting was the smallest one. The only assumption required in assigning the splittings is that the para splitting is larger than the ortho one; a considerable body of analogies for this is available. The near equality of the *α* and methylene splittings of the dimethylenecyclobutane derivative $\mathbf{13}\cdot^-$ is expected, as it is also seen in other dimethylenecyclobutane anions.[15] The comparison between the spin density distributions of 2,3-dimethylpleiadiene ($\mathbf{12}\cdot^-$) and the cyclic modifica-

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(8) L. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1968, p 1019.

(9) G. Wittig and K. Schwantzenback, *Justus Liebigs Ann. Chem.*, 650, 1 (1961).

(10) S. Mizano and H. Hashimoto, *J. Chem. Soc. D*, 1418 (1971).

(11) C. Steel, R. Zand, P. Horwitz, and S. G. Cohen, *J. Amer. Chem. Soc.*, **86**, 679 (1964).

(12) For other examples, see T. W. Bentley and R. A. W. Johnstone, "Advances in Physical Organic Chemistry," Vol. 8, V. Gould, Ed., Academic Press, New York, N. Y., 1970, pp 236–241.

(13) J. Meinwald and J. W. Young, *J. Amer. Chem. Soc.*, **93**, 725 (1971).

(14) A. Hudson and G. R. Luckhurst, *Chem. Rev.*, **69**, 191 (1969).

(15) N. L. Bauld and G. R. Stevenson, *J. Amer. Chem. Soc.*, **91**, 3675 (1969).

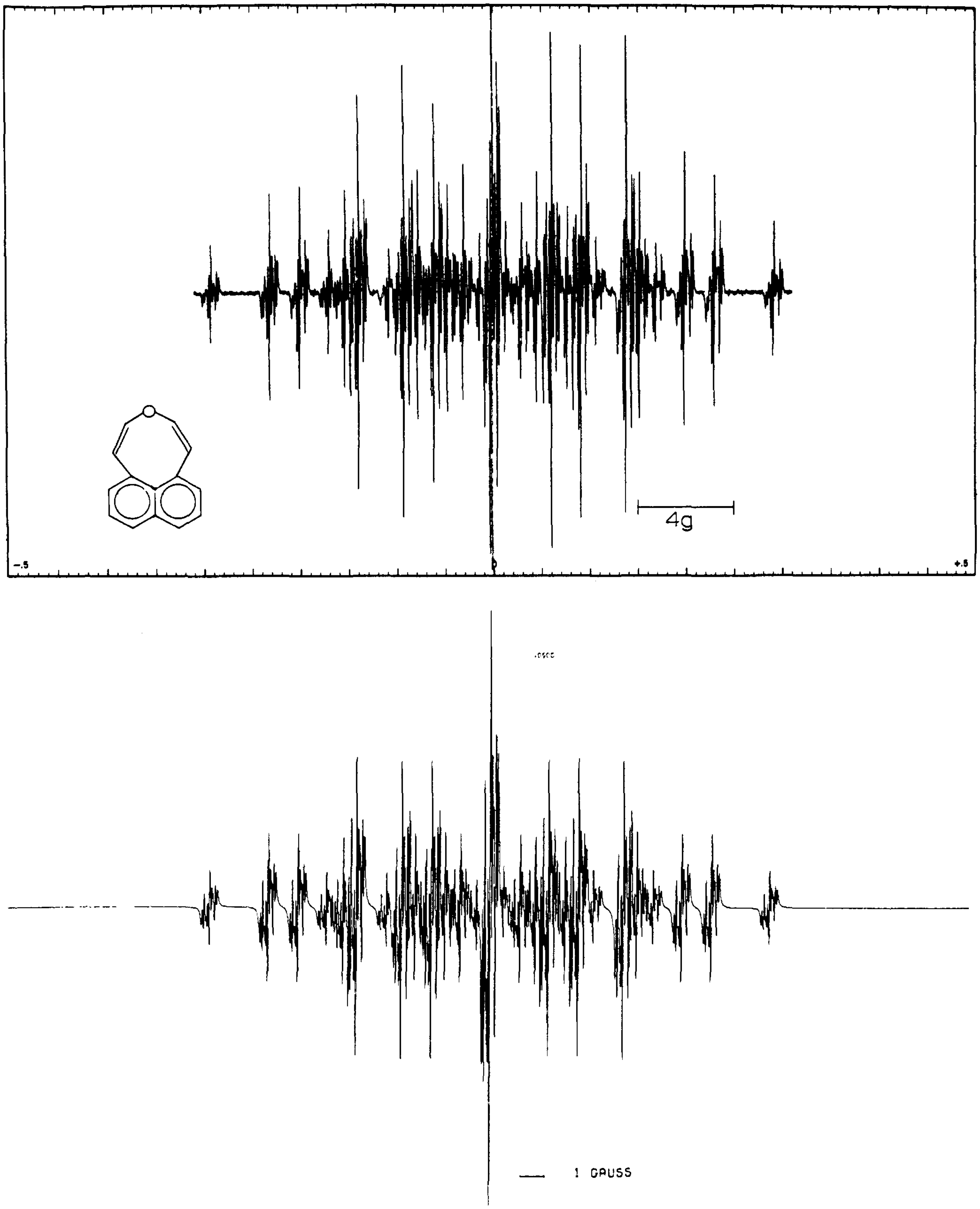

Figure 1. The esr spectrum of **2**·⁻ in THF at −50°.

tion **13**·⁻ is made in Table II. The effect of modifying the 2,3-methyl groups into a four-membered ring is clearly to place more spin density in the butadiene portion of the radical anion, although the choice of the exact Q parameters which should be used in estimating ρ_β, and hence the size of the effect, is arguable. The effect is exactly analogous to that described by Rieke and coworkers[16] for 2,3-disubstituted naphthalenes, and may be rationalized in terms of Streitwieser's

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(16) (a) R. D. Rieke, C. F. Meares, and C. J. Rieke, *Tetrahedron Lett.*, 5275 (1968); (b) R. D. Rieke and W. E. Rich, *J. Amer. Chem. Soc.*, **92**, 7349 (1970); (c) R. D. Rieke, W. E. Rich, and T. H. Ridgeway, *ibid.*, **93**, 1962 (1971).

Table II. Spin Densities for 2,3-Substituted Pleiadiene Anions ($Q = 24$)

	12$\cdot^-$	**13**$\cdot^-$
ρ_p	0.076	0.070
ρ_m	-0.008	≤ 0.005
ρ_o	0.028	0.025
ρ_α	0.247	0.256
ρ_β	0.076[a]	0.129[b]
$2(\rho_\alpha + \rho_\beta)$	0.65	0.77

[a] From $a(\mathrm{CH_3})$, using $Q_{\mathrm{CH_3}} = 29.2$ ($B_0/B_2 = 0.018$, $B_2 = 65.4$, $\langle \cos^2 \theta \rangle = 0.5$). [b] From $a(\mathrm{CH_2})$, using $\theta = 16°$, $B_0/B_2 = 0.018$, $B_2 = 56.4$.

rehybridization model,[16] which states that since the C_β–CH_2 bonds contain extra p hybridization because of ring strain, there is extra s hybridization in the C_α–C_β bonds, which increases the effective electronegativity of the β carbons.

The esr spectrum of **2**$\cdot^-$ was unusually well resolved (Figure 1) and that of **2**-β,β-d_2 demonstrates that the third largest splitting must be assigned to H_β. The meta and α splittings should both be small, and our assignment of these two small splittings is totally arbitrary. From the fact that we obtained the spectrum of tetrahydro-**2** anion, which is very different, and that cleavage products would certainly lack the observed symmetry, we are confident that the reported esr spectrum is caused by **2**$\cdot^-$.

The experimental and calculated spin distributions for pleiadiene are compared in Table III. The fit is unimpressive for either Hückel or McLachlan calculations, since both predict nearly equal ortho and para spin densities, whereas they actually differ substantially. Reasonable adjustments of h and k parameters do little to remedy this discrepancy. Pleiadiene is a nonalternate system, and the inability of simple MO theories for treating such systems is again brought out here.[17] The calculations do successfully predict that three-quarters of the odd electron density appears in the butadiene portion of the molecule. Although the fit found between the observed and calculated spin densities for pleiadiene anion was not very good, it is far worse for the divinyl ether derivative **2**$\cdot^-$ (Table IV). The two columns of McLachlan calculations are included to demonstrate that the calculated densities are insensitive to the oxygen parameters used; neither is usefully close to reality. Because a node in the odd electron MO lies along the C_2 axis of the molecule, the calculation is essentially on two noninteracting hexatriene units, with slight perturbations caused by induced negative spin densities at the nodal positions, and the inductive effect of the oxygen. The only way to polarize the spin into the naphthalene ring (over three-quarters of the spin density appears at the ortho, meta, and para positions) would be to substantially lower the electronegativities of the carbons near the oxygen.

Table III. Comparison of Experimental and Simple MO Calculations for Pleiadiene Anion

Position	Obsd ($Q = 24$)	Hückel	McLachlan (λ 1.2)
p	0.080	0.037	0.042
m	0.010	0.001	-0.022
o	0.033	0.032	0.032
α	0.105	0.112	0.085
β	0.262	0.238	0.299

Table IV. Observed and Calculated Spin Densities for **2**$\cdot^-$

Position	Exptl ($Q = 24$)	McLachlan $h_0 = 0.9$, $k_{\mathrm{CO}} = 1.5$	McLachlan $h_0 = 1.5$, $k_{\mathrm{CO}} = 0.9$
p	0.236	0.186	0.184
m	0.004	-0.011	-0.011
o	0.156	0.110	0.098
α	0.010	-0.005	-0.016
β	0.103	0.179	0.186

Cyclic voltammetry (cv) measurements on these compounds showed reversible waves, substantiating that electron transfer to give the radical anions occurs. Even **23**, which did not give observable concentrations of **23**$\cdot^-$ in our hands, appeared reversible. Since the cv experiment is complete in seconds, rather different time scales are involved. The observed reduction potentials appear in Table V.

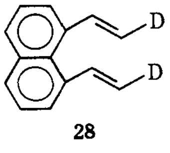
Table V. Reduction Potentials for 1,8-Bis-Unsaturated Naphthalene Derivatives

Compd	$-E_2{}^{1a}$	Compd	$-E_2{}^{1a}$
1a	1.85	**23**	2.26
12	1.99	**2**	2.05
13	1.91		

[a] In V *vs.* sce, DMSO containing 0.1 M TBAP.

The more negative $E_{1/2}$ for **12** than **1a**, and intermediate value for the cyclobutylated derivative **13**, once again parallel Rieke and coworker's observations for 2,3-disubstituted naphthalenes.[16b,c] We find the 21-mV anodic shift for **2** *vs.* **23** rather surprising in view of the fact that spin density in the product radical anion is repelled from the divinyl ether portion of the molecule. Rather smaller anodic shifts have been reported for methoxylation products of anthracene.[18]

Although the following result may yet be proven wrong, we wish to report our observations on the reduction of 1,8-divinylnaphthalene (**18**), because they are of great interest if our interpretation is correct. Sodium-potassium alloy reduction of **18** in THF gave a rather unstable radical, which had splittings for five pairs of hydrogens, $a(2\ \mathrm{H}) = 5.93$, 4.38, 2.99, 0.99, and 0.15 G. At the −75° temperature necessary for sufficient stability to record the spectrum, a line-width effect broadening the center lines of some of the splittings was apparent (Figure 2). Reduction of a sample containing 58% **28**, 34% d_1, and 8% d_0 (prepared for



28

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[17] McLachlan calculations similarly fail even for styrene anion, although by selection of enough parameters of unprecedented (and, we believe, unjustifiable) size, a good fit to the experimental data was claimed: A. R. Buick, T. J. Kemp, and T. J. Stone, *J. Phys. Chem.*, 74, 3439 (1970).

[18] A. Zweig, A. H. Mauer, and B. G. Roberts, *J. Org. Chem.*, 32, 1322 (1967).

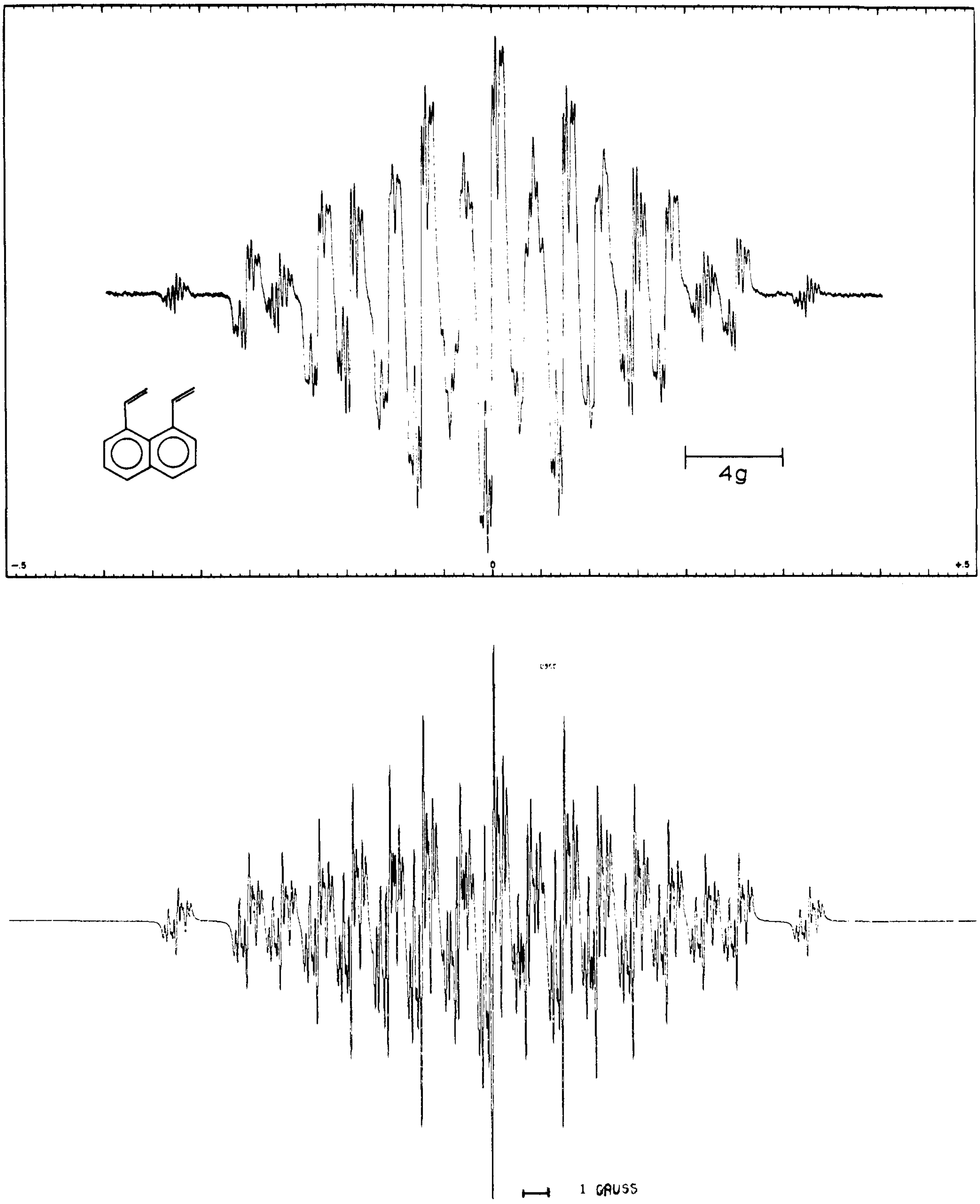

Figure 2. The esr spectrum of **18**·⁻ in THF at −75°. Broadening near the center of the spectrum, presumably caused by ion-pairing effects at the low temperature necessary for sufficient stability to record the spectrum, is apparent.

another study[7]) gave a complex spectrum because of the mixture but was clearly almost completely lacking the 5.93 G splitting, which we assign to H_β(trans). The only reasonable possibility for a_β(H(cis)) is then 4.38 G. Although the cis and trans β hydrogens are in different chemical environments, and might well show different splittings, the observed 1.35 splitting ratio for two hydrogens attached to the same unsaturated carbon is without precedent. For example, styrene anion shows equivalent β splittings.[17] Far smaller differences have been observed for isoprene anion[19] (but not butadiene) and allyl and allenyl radicals;[20] the largest splitting ratio reported has been about 1.04. Since unprecedented results, particularly in esr work, have so often turned out to be wrong, the first thing of which the reader must demand to be convinced is that we really observed **18**$\cdot^-$. Other reduction products of **18** besides the simple radical anion are obvious candidates for the observed spectrum, but the pairwise equivalence observed rules most of them out. Acenaphthene, perinaphthene, pleiadiene, and alkylnaphthalene structures are clearly ruled out by the magnitudes of the observed splittings. Although we have only negative arguments to support our contention, we do not have a structure other than **18**$\cdot^-$ to which the esr spectrum observed from **18** can be assigned.

A McLachlan calculation for **18**$\cdot^-$, assuming planarity, gives numbers similar to those given for **2**$\cdot^-$. **18** is, in fact, a fairly strained compound, as evidenced by its unusual thermal chemistry.[7] The vinyl groups cannot be planar because of steric interactions, and the π clouds of the vinyl groups interact seriously in twisted conformations because of the peri substitution. We suggest, then, that through space interaction of the π clouds of **18**$\cdot^-$ leads to the observed polarization of the spin density away from the napthalene ring, and onto the vinyl groups. We have shown above that a butadiene which is peri-fused to the naphthalene results in most of the spin density appearing in the butadiene portion of the molecule. To the extent that vinyl–vinyl π ovelap because of the unusual spacial proximity of the vinyl π systems is effective, a butadiene-like unit is in fact peri-fused to the naphthalene in **18**$\cdot^-$.

How to treat interacting π systems which are not planar is by no means yet clear, but large deviations in effective Q values seem to result,[21] which might account for the odd splittings observed. We suggest that the large difference in $a(\mathrm{H}_\beta(\mathrm{cis}))$ and $a(\mathrm{H}_\beta(\mathrm{trans}))$ is a result of such interactions. Work on the problems of how to interpret the esr spectra of nonplanar π systems more quantitatively is continuing.

Experimental Section

General Comments. Spectra were recorded on Beckman IR 8, Cary 15, Varian A-60A or HA 100, Varian E 15, and AEI MS-902 instruments. The pyrolysis apparatus used consisted of a vertical column with a 20-cm long hot zone packed with $^1/_8$-in. glass helices, and a heated side arm leading to a liquid nitrogen cooled U-trap. Most compounds were introduced by sublimation, with a stream of nitrogen flowing over the heated sample and up through the column. Pyrolyses were conducted at 2–3 mm pressure, and the residence time was estimated to be 1–5 sec. THF was purified by distillation from benzophenonedisodium.

Pleiadiene (1a), naphtho[1′,8′]bicyclo[3.2.0]hepta-2,5-diene (4a), naphtho[1′,8′]bicyclo[3.2.0]hept-2-ene (14) and *cis-anti*-naphtho[1′,8′]bicyclo[3.2.0]hept-2-ene-6,7-dicarboxylic acid (3a) were prepared by the methods of Meinwald and coworkers,[1] except for the following modification of the bis-decarboxylation of **3a**. In 50 ml of pyridine (distilled from BaO and stored over KOH) was suspended 4.0 g (15 mmol) of **3a**, and pure oxygen was bubbled through the stirred solution for about 5 min. Then 9.84 g (1.5 equiv) of lead tetraacetate (G. F. Smith) was added all at once, and the flask was immediately immersed in an oil bath heated to 68° for 5 min. After 1.5–2 min, vigorous bubbling commenced and rapidly subsided with a concurrent color change to dark brown. The solution was cooled, poured into 350 ml of 13% nitric acid, and filtered. The solids were extracted with boiling benzene (3 × 100 ml) and the filtrate was extracted with 4 × 100 ml portions of ether. The combined organic fractions were dried ($\mathrm{MgSO_4}$), and the solvent was removed to give 400 mg of crude **4a** which was sublimed to give 190 mg (7.1%) which, when recrystallized from pentane, yielded 100 mg, mp 118–119° (lit.[1] 118–119°).

Naphtho[1′,8′]bicyclo[3.20]hept-2-ene-6,7-dicarboxylic acid-*6,7-d*$_2$ (3b). In a solution of KOD in $\mathrm{D_2O}$ (from 3.9 g of K and 30 ml of $\mathrm{D_2O}$), 9.0 g of **3a** was dissolved and heated to 150–160° in a sealed tube overnight. The excess $\mathrm{D_2O}$ was pumped off, and the residue, combined with that from an identical run, was dissolved in 50 ml of $\mathrm{D_2O}$ and heated again in a sealed tube for 10 hr. The filtered solution was acidified to pH 3 with 30% $\mathrm{H_2SO_4}$ and the solid was collected by filtration, giving 14.53 g (81%): nmr ($\mathrm{D_2O}$, $\mathrm{K_2CO_3}$, TPSS) δ 2.45–2.8 (m, 0.2 H), 3.65–4.10 (m, 2 H), 6.70–7.10 (m, 6 H).

Naphtho[1′,8′]bicyclo[3.2.0]-2,6-diene-*6,7-d*$_2$ (4b) was prepared as in the undeuterated case. The yield was 260 mg (9.8%): mp 118–119° (pentane, Norit); nmr ($\mathrm{CDCl_3}$) δ 4.65 (2, 2 H), 6.33 (s, 0.097 H), 7.45 (m, 6 H); ir ($\mathrm{CHCl_3}$) 3.31, 4.41, 6.21 μ; mass spectrum (12 eV) *m/e* (%) 180 (100), 179 (25).

Pleiadiene-2,3-*d*$_2$ (1b) was prepared as in the undeuterated case. The yield was 140 mg (93%): mp 92–93° (pentane); nmr ($\mathrm{CDCl_3}$) δ 6.0 (s, 2 H), 6.5–7.3 (m, 6 H); ir ($\mathrm{CHCl_3}$) 3.31, 4.3, 6.25, 6.38, 6.40 μ.

3 6-Di-*tert*-butylacenaphthylene. A solution of 18.5 g (69.5 mmol of 2,5-di-*tert*-butylacenaphthene and 15.7 g (69.1 mmol) of DDQ (69.5 mmol) in 500 ml of benzene was refluxed for 33 hr and filtered, and the solid was washed with 250 ml of ether. The combined filtrates were extracted (3 × 150 ml) with 10% NaOH and then with 100 ml of saturated NaCl. After drying, the solvent was rotovaporated, leaving a reddish residue which was taken up in a minimum amount (about 20 ml) of benzene and passed through a plug of alumina ($\mathrm{HF_{254}}$, 75 g) by washing with an additional 200 ml of pentane, to yield 17.0 g (92%) of a yellow solid which was further purified by sublimation: mp 108–109°; nmr ($\mathrm{CDCl_3}$) δ 1.41 (s, 18 H), 7.0 (s, 2 H), 7.72 (s, 4 H); ir 3.38, 3.42, 3.48, 6.16, 6.78, 7.31 μ. *Anal.* Calcd for $\mathrm{C_{20}H_{24}}$: C, 90.85; H, 9.14. Found: C, 91.08; H, 9.09.

***cis-anti*-Naphtho[1′,8′]bicyclo[3.2.0]hept-2-ene-3′,6′-di-*tert*-butyl-6,7-dicarboxylic acid (2c).** A solution of 7.42 g of 3,6-di-*tert*-butylacenaphthylene and 30.0 g of maleic anhydride in 900 ml of propyl bromide was photolyzed as in the unsubstituted case, giving 6.1 g (57%) of **2c** and 3.2 g of dimer: nmr ($\mathrm{D_2O}$, $\mathrm{K_2CO_3}$) δ 0.89 (s, 18 H), 2.86 (m, 2 H), 4.15 (m, 2 H), 7.12 (m, 6 H).

3′,6′-Di-*tert*-butylnaphtho[1′,8′]hepta-2,6-diene (4c) was prepared as in the unsubstituted case giving 142 mg (13.1%): mp 142–143°; nmr δ 1.41 (s, 18 H), 4.59 (s, 2 H), 6.28 (s, 2 H), 7.27 (s, 2 H), 7.47 (d, J = 1 Hz, 2 H); ir ($\mathrm{CHCl_3}$) 3.38, 6.21, 6.81, 6.89, 7.37, 11.44 μ. *Anal.* Calcd for $\mathrm{C_{22}H_{26}}$: C, 90.97; H, 9.02. Found: C, 90.90; H, 9.11.

6,9-Di-*tert*-butylpleiadiene (1c), which was prepared as in the unsubstituted case, yielded 200 mg (95%) of red crystals: mp 118–120°; nmr δ 1.27 (s, 18 H), 5.29 (dd, J = 3.5, 9.5 Hz, 2 H), 6.05 (dd, J = 3.5, 9.5 Hz, 2 H), 6.64 (d, J = 2 Hz, 2 H), 7.14 (d, J = 2 Hz, 2 H); ir 3.38, 3.45, 3.49, 6.20, 11.40 μ; uv 232 (4.39), 246 (4.35), 253 (4.43), 294 (3.41), 308 (3.46), 332 (3.59), 348 (3.68), 367 (3.43), 420 (2.43), 444 (2.51), 473 (2.48), 507 (2.30); exact mass 290.2031 (calcd, 290.2034).

Dimethyl *cis-anti*-Naphtho[1′,8′]bicyclo[3.2.0]hept-2-ene-6,7-dicarboxylate (5). A suspension of 1.0 g of **3a** in 25 ml of THF was treated with ethereal diazomethane until the yellow color persisted. The insoluble residue was filtered and the solvent rotovaporated. Crystallization from $\mathrm{CHCl_3}$–pentane gave 0.78 g (71%) of white needles: mp 152–153°; nmr ($\mathrm{CDCl_3}$) δ 3.23 (m, 2 H), 3.80 (s, 6 H), 4.52 (m, 2 H), 7.51 (m, 6 H); ir 3.28, 3.38, 5.75 μ. *Anal.* Calcd for $\mathrm{C_{18}H_{16}O_4}$: C, 72.96; H, 5.44. Found: C, 72.87; H, 5.48.

***cis-anti*-6,7-Dihydroxymethylnaphtho[1′,8′]bicyclo[3.2.0]hept-2-ene (6).** To 5.1 g (134 mmol) of LiAlH in 400 ml of THF was added dropwise a solution of 20.62 g (69 mmol) of **5** in 150 ml of THF over a period of 1 hr. After the mixture was stirred at room temperature overnight, the excess $\mathrm{LiAlH_4}$ was destroyed by the addition of 6.1 ml of $\mathrm{H_2O}$, 5.1 ml of 15% NaOH, and 15.3 ml of $\mathrm{H_2O}$. Filtration through a plug of magnesium sulfate and rotovaporation of the solvent gave 15.40 g (88%) of the diol as a microcrystalline powder, mp 130–131°.

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[20] J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **92**, 4110 (1970).

[21] (a) F. Gerson, K. Müllen, and E. Vogel, *ibid.*, **94**, 2924 (1972); (b) J. Harbour and U. A. Guzzo, *Mol. Phys.*, **23**, 151 (1972).

***cis-anti*-6,7-Dimethanesulfanoxymethylnaphtho[1′,8′]bicyclo[3-2.0]hept-2-ene (5).** To a solution of 5.51 g (22.96 mmol) of **6** in 150 ml of pyridine was added 5.38 g (47.1 mmol) of methanesulfonyl chloride in 20 ml of pyridine over a period of 1 hr. The pyridine was rotovaporated and the residue, suspended in ether, was washed with 1 *M* HCl (3 × 100 ml) and with water (1 × 100 ml). Rotovaporation of the ether and crystallization from methanol afforded 7.76 g (85%) of the product as needles: mp 116–117°; nmr δ ($CDCl_3$) 2.40 (m, 2 H), 3.09 (s, 6 H), 3.99 (m, 2 H), 5.58 (m, 4 H), 7.17–7.75 (m, 6 H); ir ($CHCl_3$) 3.30, 3.38, 6.22, 7.40, 8.51, 10.30, 10.60 μ; exact mass 396.0695 (calcd for $C_{18}H_{20}O_6S_2$, 396.0701).

***cis-anti*-6,7-Diiodomethylnaphtho[1′,8′]bicyclo[3.2.0]hept-2-ene (8).** A solution of 0.5 g (1.75 mmol) of **7** and 0.0900 g (6.0 mmol) of anhydrous sodium iodide in 10 ml of HMPA was stirred overnight at room temperature. The golden solution was added to 300 ml of water and extracted with 3 × 100 ml portions of ether. Preparative tlc (PF$_{254}$, $CHCl_3$, 1 ×, R_f 0.65) gave 430 mg (54%) of product: mp 108–111°; nmr δ 3.4 (m, 2 H), 3.1–3.8 (m, 6 H), 7.1–7.7 (m, 6 H); ir ($CHCl_3$) 3.28, 3.32, 3.40, 6.24, 7.44, 8.40, 8.40, 8.61 μ.

7,8-Dimethylenenaphtho[1′,8′]bicyclo[3.2.0]hept-2-ene (9). A solution of 1.1 g of **8** (2.7 mmol) in 20 ml of dry THF was treated with 0.8 g (7.13 mmol) of potassium *tert*-butoxide (MSA Research Corp.) in 20 ml of THF. After the solution was stirred for 5 min, analytical tlc indicated complete conversion. The solvent was rotovaporated and the ether suspension was washed with water (3 × 100 ml). The dried ethereal extracts were rotovaporated (after addition of a single crystal of hydroquinone to act as a polymerization inhibitor) to yield 0.457 g (91%) of product: mp 90–91°; nmr δ ($CDCl_3$) 4.76 (s, 2 H), 4.98 (s, 2 H), 5.17 (s, 2 H), 7.12–7.75 (m, 6 H); ir 3.28, 3.39, 6.09, 6.25, 6.70, 11.37 (vs) μ; uv λ_{max} (log ϵ), 227 (4.88), 253 (3.83), 271 (sh) (3.39), 280 (3.78), 290 (3.83), 302 (3.66), 306 (3.48), 317 (2.83), 322 (2.80); exact mass 204.0934 (calcd for $C_{16}H_{12}$, 204.0939).

2,3-Cyclobutapleiadiene (13). A solution of 110 mg of 9 in 300 μl of benzene was injected 50 μl at a time through the septum cap of the pyrolysis apparatus (column temperature: 515°, oil bath; 130°). The red material collected in the trap was determined by nmr to be about 60% converted to product. The mixture was then sublimed through the column in the normal way and was determined to be 88% converted. Another pass gave the same ratio. The mixture was destroyed by vpc and silver nitrate tlc, and would not separate on alumina. Spectroscopic determinations are on mixtures of variable composition but are greater than 88% pure: mp 64–94°; nmr δ 2.45 (broad s, 4 H), 5.51 (broad s, 2 H), 6.2–7.1 (m, 6 H); uv λ_{max} (log ϵ) 232 (4.46), 242 (4.45), 249 (4.42), 279 (3.58), 284 (3.70), 297 (3.71), 312 (3.57), 334 (3.81), 343 (3.95), 356 (3.88), 367 (3.75), 379 (3.78), 387 (3.34), 430 (2.60), 457 (3.69), 489 (2.68), 524 (2.54), 570 (2.20); exact mass 204.0928 (calcd for $C_{16}H_{12}$, 204.0939).

6,7-Bis(bromomethyl)naphtho[1′,8′]hepta-2,6-diene (10). To 310 mg (1.52 mmol) of **9** in 120 ml of CCl_4 (cooled to 0°) was added 207 mg (1.52 mmol) of bromine in 10 ml of CCl_4 over a period of 10 min. The ice bath was removed, and the solution was allowed to stir at room temperature for 1 hr. The solution, which was light yellow, lost its color as the solvent was rotovaporated. The residue was chromatographed (tlc; PF$_{254}$, CCl_4) to give 360 mg (65%) of product; mp 127–130°; nmr δ 3.85 (s, 4 H), 4.65 (s, 2 H), 7.2–7.7 (s, 6 H).

6,7-Dimethylnaphtho[1′,8′]hepta-2,5-diene (11). To a suspension of 300 mg of $LiAlH_4$ (7,69 mmol) in 150 ml of THF was added 240 mg of **10** (0.659 mmol) in 20 ml of THF. After the mixture was refluxed for 2 hr, the usual work-up followed by tlc (PF$_{254}$, pentane) afforded 130 mg (95%) of product which was sublimed: mp 94.5–95.5°; nmr δ 1.60 (s, 6 H), 4.35 (s, 2 H), 7.0–7.68 (m, 6 H); ir 3.28, 3.38, 3.42, 3.51, 6.25, 6.71, 6.99, 7.30, 7.90, 9.04 μ. *Anal.* Calcd for $C_{16}H_{14}$: C, 93.15; H, 6.84. Found: C, 93.11; H, 6.91.

2,3-Dimethylpleiadiene (12). Pyrolysis of **11** (50 mg) under the usual conditions (380°) required three passes to attain a 93% conversion as determined by nmr. Separation of the isomers was accomplished on alumina (HF$_{254}$, pentane) to yield 30 mg (60%) of product: mp 97.5–99° (after sublimation)); nmr δ 1.78 (s, 6 H), 5.93 (s, 2 H), 6.35–7.2 (m, 6 H); ir 3.27, 3.38, 3.42, 3.47, 6.26, 6.41, 6.94, 7.30, 7.41, 11.59 μ; uv λ_{max} (log ϵ) 242 (4.21), 250 (4.91), 272 (3.44), 283 (3.46), 299 (sh) (3.39), 332 (3.55), 343 (3.71), 358 (3.67), 368 (3.59), 376 (3.55), 387 (3.25), 422 (2.66), 447 (2.63), 478 (2.52), 513 (1.25), 655 (0.82). *Anal.* Calcd for $C_{16}H_{14}$: C, 93.15; H, 6.84. Found: C, 93.06; H, 6.90.

***anti*-Naphtho[1′,8′]tricyclo[3.3.0.0^{6,8}]-7-oxooct-2-ene (20).** A solution of 210 mg (1.08 mmol) of **4a** and *m*-chloroperoxybenzoic acid (about 50% pure, 560 mg, 1.62 mmol, Aldrich Chemical Co.) in 100 ml of methylene chloride was stirred at room temperature overnight. The solvent was rotovaporated, replaced with ether, and extracted with 10% sodium sulfide (3 × 50 ml) and then with water (3 × 50 ml). The dried organic extracts were rotovaporated and the residue was sublimed to give 170 mg (64%) of product: mp 130–131°; nmr δ ($CDCl_3$) 3.88 (d, J = 2.3 Hz, 2 H), 4.08 (d, J = 2.3, 2 H), 7.1–7.75 (m, 6 H); ir 3.28, 3.31, 3.38, 6.23, 7.56, 8.89, 10.05, 10.62, 11.06 μ; mass spectrum *m/e* (%) 195 (P + 1, 2), 194 (P, 12), 165 (100). *Anal.* Calcd for $C_{14}H_{10}O$: C, 86.57; H, 5.20. Found: C, 86.45; H, 5.19.

***anti*-Naphtho[1′,8′]tricyclo[3.3.0.0^{6,8}]-7-oxooct-2-ene-*6,7-d*$_2$ (20-*6,8-d*$_2$).** In an analogous fashion to the undeuterated case 70 mg (54%) of product, mp 129–130°, was obtained: nmr δ ($CDCl_3$) 3.88 (d, J = 2.3 Hz, 0.97 H), 4.08 (s, 2 H), 7.1–7.75 (m, 6 H); ir 3.28, 3.38, 4.34, 6.22, 7.34, 7.78, 7.66, 8.88, 10.00, 10.78, 11.78 μ.

1-Oxo-4-naphtho[1′,8′]cycloocta-2,4,7-triene (2). Pyrolysis under the usual conditions at 400° gave 73 mg (73%) of product: mp 96–97° after sublimation; nmr δ 6.16 (d, J = 6.5 Hz, 2 H), 6.66 (d, J = 6.5 Hz, 2 H), 7.25–7.95 (m, 6 H); ir 3.30, 3.32, 6.02, 6.11, 7.37, 7.95, 8.67, 8.90, 9.47, 9.81, 11.92 μ; uv λ_{max} (log ϵ) 237 (sh (4.60), 241 (4.61), 307 (sh) (3.90), 319 (3.97), 338 (3.85); mass spectrum *m/e* (%) 195 (P + 1, 2), 194 (P, 12), 165 (100); exact mass 194.0739 (calcd, 194.0732).

1-Oxo-4-naphtho[1′,8′]cycloocta-2,4,7-triene-*2,8-d*$_2$ (2-*d*$_2$). In an analogous fashion to the undeuterated case, 20 mg (40%) of product, mp 95–96°, was obtained: nmr δ 5.99 (s, 2 H), 6.52 (d, J = 6.5 Hz, 0.097 H), 7.05–7.77 (m, 6 H); ir 3.26, 3.28, 4.43, 6 .02, 6.11, 7.48, 7.74, 8.60, 8.85, 9.28, 11.51 μ.

***anti*-3,4-Diazanaphtho[1′,8′]tricyclo[5.3.0.0^{2,6}]deca-3,8-diene (22).** In a 200-ml round-bottomed ring-necked flask were placed 800 mg of **3a** and an *ca.* 8.5-fold excess of diazomethane in ether. After stirring for 3 days, an nmr of an aliquot indicated about 33% conversion. The ether was rotovaporated and replaced with ethereal diazomethane as before. After a repetition of the above procedure four times, 78% conversion was indicated. Preparative thin layer chromatography (PF$_{254}$, $CHCl_3$) gave starting material, 240 mg, and **22**, 540 mg, which corresponds to a 78% yield based on recovered starting material. Recrystallization from benzene–cyclohexane gave a colorless microcrystalline powder: mp 172–172.5°; nmr ($CDCl_3$) δ 2.31 (m, 1 H), 3.45 (m, 1 H), 4.05 (m, 1 H), 4.5–4.8 (m, 2 H), 5.05 (m, 1 H); ir 3.31, 3.40, 6.21, 6.50, 6.68, 7.0, 7.31 μ; uv λ_{max} (log ϵ) 224 (4.90), 229 (5.19), 271 (sh) (3.77), 282 (3.98), 293 (4.04), 302 (3.87), 307 (3.78), 317 (3.38), 321 (3.41), 330 (sh) (2.82); exact mass 220.0992 (calcd for $C_{15}H_{15}N_2$, 220.1000).

***anti*-Naphtho[1′,8′]tricyclo[3.3.0.0^{6,8}]oct-2-ene (21). (a) By Photolysis of 22.** Preliminary experiments were performed on 50-mg samples of the pyrazole (Hanovia 450-W Lamp, Pyrex filter, 3 hr) in 125 ml of the solvent indicated. Isolated yields were determined after preparative tlc. Solvent (% yield): ether (47), cyclohexane (76), methylene chloride (0), tetrahydrofuran (0), cyclohexane with 50 mg of benzophenone added (0). Scale-up of the reaction resulted in much lower yields. Thus, 250 mg of the pyrazole, photolyzed for 36 hr (monitored by nmr) in 1 l. of cyclohexane, yielded 30 mg (12%) of the desired product: mp 123–124°; nmr δ 0.85–1.09 (m, 2 H), 1.65 (broad d, J = 5 Hz, 2 H), 3.67 (broad s, 2 H), 7.1–7.67 (m, 6 H); ir 3.23, 3.26, 3.30, 3.36, 6.15, 6.23, 7.33, 12.29 μ; mass spectrum *m/e* (%) 193 (P + 1, 10), 192 (P, 65), 191 (P − 1, 100), 165 (85), 152 (30). *Anal.* Calcd for $C_{15}H_{12}$: C, 93.76; H, 6.29. Found: C, 93.48; H, 6.47.

(b) By a Simmons–Smith Reaction[10] on 3a. To a solution of 1.0 g (5.62 mmol) of **3a** in 10 ml of dry benzene (degassed with Ar, Ar atmosphere) was added 10 ml of an *ca.* 1.0 *M* solution of diethylzinc (Alfa Inorganics) in benzene while the flask was maintained at 60° in an oil bath. Then 3.82 ml of CH_2I_2 (44 mmol) in 5 ml of benzene was added dropwise over a period of 20 min. The reaction was monitored by vpc (195°) which indicated no reaction at that time. Dry air was then passed over the surface of the solution, and after 40 min at 55° a starting material–product ratio of 4:1 was found; after 15 additional min, 3:1; after 7 additional min, 2:1. Because preliminary experiments indicated optimum yields at this point, the reaction was quenched by pouring it into 50 ml of 10% HCl and then extracting successively with saturated sodium carbonate and water. The organic layer was dried ($MgSO_4$) and rotovaporated. The crude material was purified by tlc (PF$_{254}$ impregnated with 12.5% by weight silver nitrate, benzene). Work-up gave 310 mg of product, which was contaminated by products of methylene addition to the naphthalene moiety. The other major band (R_f 0.4) contained 550 mg of starting material, similarly contaminated.

23 was prepared by pyrolysis, under the usual conditions, of impure **21** (110 mg, prepared by path b above) which yielded, after $AgNO_3$ tlc (benzene), 88 mg of product. Preparative vpc gave a sample: mp 76–76.5°; nmr δ ($CDCl_3$) 3.08 (t, J = 7.5 Hz, 2 H), 5.95–6.7 (m, 4 H), 6.95–7.80 (m, 6 H); ir 3.27, 3.29, 3.38, 3.42, 7.45, 9.12, 9.88 μ; uv λ_{max} (log ϵ) 243 (4.41), 325 (3.84); mass spectrum m/e (%) 194 (P + 2, 3), 193 (P + 1, 12), 192 (P, 80), 191 (P − 1, 100), 165 (90); exact mass (using the intense P − 1 peak) 191.0867 (calcd for $C_{15}H_{11}$, 191.0860).

1,8-Divinylnaphthalene (18) was prepared by the method of Mitchell and Sondheimer[22] in 79% yield, mp 43–45° (methanol), lit. 47–47.5°.

Cyclic voltammetry experiments were performed on a Princeton Applied Research Model 1170 electrochemistry system, using a Sargent-Welch sce reference electrode and a hanging mercury drop working electrode. The solvent was dimethyl sulfoxide dried over Linde 4A molecular sieves, containing 0.1 *M* tetrabutylammonium perchlorate (MCB). We did not correct for ir drop, and ΔE_p values of 68–80 mV were observed at the 200-mV/sec scan rates employed.

Esr spectra were simulated using a program similar to Stone and Maki,[23] but modified (originally by Professor J. Harriman) to plot on a Calcomp plotter and employ a Univac 1108 computer for calculations. The values quoted in Table I are those used in the simulations which best fit the experimental spectra. Splittings were calibrated with Fremy's salt.

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Cation–Anion Combination Reactions. XI. Reactions of Cations with Amines[1]

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Abstract: The reactions of a wide variety of amines, and of sulfite and hypochlorite ions, with triarylmethyl, tropylium, and aryldiazonium ions in aqueous solution have been studied using stop-flow spectrophotometry. With the exceptions of methoxylamine and hydrazine, all of the nucleophiles studied show constant selectivities toward the various cations. Thus, these nucleophiles follow the relationship: log $k_n = N_+ + \log k_0$, which we have previously shown to correlate the rates of cation–anion combination reactions. Values of N_+ newly assigned are: glycine, 4.95; ethylenediamine, 5.04; hydrazine, 5.60; ethylamine, 4.88; glycylglycine, 4.28; phenylhydrazine, 4.36; glycine ethyl ester, 3.99; 2-ammonioethylamine, 3.94; semicarbazide, 3.32; methoxylamine, 3.96; 2,2,2-trifluoroethylamine, 3.04; hydroxylamine, 4.95; diethylamine, 5.87; piperidine, 6.25; methylhydrazine, 5.70; hydroperoxide ion, 8.4; hypochlorite ion, 7.0; and sulfite ion, 7.6. With an extensive range of nucleophiles for which we now have N_+ values, it is possible to examine the application of the correlation of reactivities of reactions of carbonyl compounds. We find that the reactions of acetoxy- and acetylpyridinium ions with nucleophiles are excellently correlated by the N_+ values.

The previous papers in this series[1a] have described the results of our studies of the reactions of nucleophiles with aryldiazonium ions, tropylium ions, and triarylmethyl cations. The entire body of rate data was shown to be well correlated by

$$\log k_n/k_0 = N_+ \qquad (1)$$

where k_n is the rate constant for reaction of a given nucleophilic system (*i. e.*, a given nucleophile in a given solvent) with a cation, k_0 is a constant characteristic only of the cation, and N_+ is a parameter characteristic of the given nucleophilic system independent of the cation. Values of N_+ were obtained by setting $N_+ = 0$ for water in water, and by the use of *p*-nitro(Malachite Green) as the standard cation.

All of the reactions were studied under closely analogous conditions of low ionic strength and 23°. Most of the nucleophiles studied were mononegative ions, only water and methanol being included as examples of neutral nucleophiles.

The purpose of the present work is to extend our studies to include nucleophiles of various charge type, particularly amines, and to initiate an attempt to extend eq 1 to reactions of electrophiles other than simple organic cations. For the latter purpose, we shall utilize the extensive data which have been reported by Jencks[2] for the reactions of nucleophiles with carbonyl compounds.

Bruice[3] has recently reported studies of the reactions of primary amines with Malachite Green [bis(*p*-dimethylaminophenyl)phenylmethyl cation] in aqueous solution. The use of high ionic strength (1.0 *M*) and a temperature of 30°, unfortunately, made direct comparisons with our studies somewhat uncertain.

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