methyl ketone **11**, trace amounts of cyclopentyl acetone (**12**) resulting from the exchange-initiated cyclization sequence are observed along with a small amount of **14**, the product resulting from the direct conjugate addition of *n*-BuLi, but the major product **13** arises from direct 1,2-carbonyl addition. Under similar conditions, unsaturated amide **15** also gives a small amount of cyclic amide **16** (15%) along with unidentified polar condensation products and **17**, which apparently arises from direct conjugate addition to the olefinic link followed by intramolecular alkylation of the resulting enolate. Direct uncatalyzed conjugate additions of alkyllithium reagents to unsaturated amides have been reported.[15]

Our success in achieving cyclizations with unsaturated esters suggests the possibility of executing a variety of new cyclization reactions where the lithium-halogen exchange rate exceeds the rate of the direct reaction of the metalating agent with an internal electrophilic center. We are presently investigating such possibilities.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

Registry No. **1a**, 88931-70-8; **1b**, 88931-71-9; **1c**, 88931-72-0; **1d**, 88931-73-1; **1e**, 88931-74-2; **4a**, 88931-75-3; **4b**, 88931-76-4; **4c**, 79033-94-6; **4e**, 16537-06-7; **7**, 88931-77-5; **8**, 88931-85-5; **9**, 88945-39-5; **10**, 88931-78-6; **11**, 88931-79-7; **12**, 1122-98-1; **13**, 88931-80-0; **14**, 88931-81-1; **15**, 88931-82-2; **16**, 88931-83-3; **17**, 88931-84-4; *tert*-butyl (*E*)-3-heptenoate, 88931-86-6; 7-butyl-7-hydroxy-5-undecene, 88931-87-7; *tert*-butyl 3-butylheptanoate, 88931-88-8.

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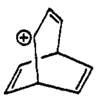
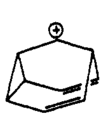
On the Stability of the Phenalenyl Cation Incorporated into a Bicyclo[3.2.2]nona-2,6,8-trienyl Framework[1]

Summary: In order to evaluate the thermodynamic stability of the elusive bicyclo[3.2.2]nona-2,6,8-trienyl cation (**1**), the phenalenyl cation incorporated into a bicyclo[3.2.2]nona-2,6,8-trienyl framework such as **3a** has been synthesized; from the examination of ^{1}H and ^{13}C NMR spectra and the reduction potential of **3a**, it is suggested that **3a** is stabilized to some extent by a positive charge delocalization from the phenalenyl part into the etheno bridges.

Sir: The concept of bicycloaromaticity proposed by Goldstein and Hoffmann[2] in 1971 has stimulated development of the longicyclic carbocations and anions. In contrast to the vast amount of literature concerning the highly stabilized 7-norbornadienyl cation,[3] very little has been revealed about its higher vinylogue, the bicyclo[3.2.2]nona-2,6,8-trienyl cation **1**.[4] Many attempts to generate **1** even under conditions of long life have failed owing to its facile rearrangement into energetically favored 9-barbaralyl cation **2**.[5] The well-known stable phenalenyl cation **3c**[6] consists of an antisymmetric nonbonding molecular orbital (NBMO) (A) similar to that of the allyl cation (B). In this regard the chemical and physical behaviors of the phenalenyl cation incorporated into a bicyclo[3.2.2]nona-2,6,8-trienyl framework, **3a**, in which no energetically economical path to the corresponding barbaralyl cation is available, are of particular interest. We now report the synthesis of **3a** together with the evidence that **3a** is more stable than the progenitor cation **3c**.



1



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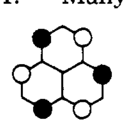
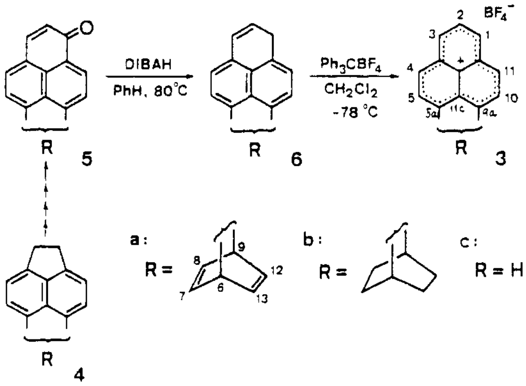


A

B

The etheno-bridged phenalenyl cation **3a**[7] was prepared by starting from the phenalenone **5a**[8] as shown in Scheme I.[9] The ethano-bridged cation **3b**[7] as a reference compound is also prepared from **5a** through diimide reduction (KOOCN=NCOOK/HOAc in MeOH + CH_3CN, room temperature) to **5b** followed by the same manner as in the preparation of **3a**.

Scheme I



The ^{1}H and ^{13}C NMR chemical shifts[10] of **3a–c**[11] are

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[1] The Chemistry of Phenalenium Systems. 36. For part 35, see: Nakasuji, K.; Yoshida, K.; Murata, I. *J. Am. Chem. Soc.* **1983**, *105*, 5136.

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[5] (a) Grutzner, J. B.; Winstein, S. *J. Am. Chem. Soc.* **1970**, *92*, 3186. (b) Paquette, L. A.; Oku, M.; Farnham, W. B.; Olah, G. A.; Liang, G. *J. Org. Chem.* **1975**, *40*, 700. Goldstein, M. J.; Dinnocenzo, J. P.; Ahlberg, P.; Engdahl, C.; Paquette, L. A.; Olah, G. A. *Ibid.* **1981**, *46*, 3751. (c) For the anion: Grutzner, J. B.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 2200. Grutzner, J. B.; Jorgensen, W. L. *Ibid.* **1981**, *103*, 1372. Kaufmann, E.; Mayr, H.; Chandrasekhar, J.; Schleyer, P. v. R. *Ibid.* **1981**, *103*, 1375.

[6] For reviews, see: Reid, D. H. *Q. Rev. Chem. Soc.* **1965**, *19*, 274. Murata, I. In "Topics in Nonbenzenoid Aromatic Chemistry"; Nozoe, T., Breslow, R., Hafner, K., Ito, S., Murata, I., Eds.; Hirokawa: Tokyo, 1976; Vol. 1, p 159.

[7] **3a**: a red solid, mp 190 °C (dec in a sealed tube); UV (CH_3CN) λ_{max} nm (log ϵ) 248 (4.04), 275 (sh, 3.61), 356 (3.97), 420 (4.31), 500 (sh, 3.33), 539 (sh, 3.25). Anal. ($C_{19}H_{13}BF_4$) C, H. **3b**: a yellow solid, mp 180 °C (dec in a sealed tube); UV λ_{max} nm (log ϵ) 228 (4.50), 379 (sh, 4.18), 415 (4.64), 457 (sh, 3.58). Anal. ($C_{19}H_{15}BF_4$) C, H.

[8] Sugihara, Y.; Hashimoto, K.; Yoshikawa, M.; Murata, I. *Tetrahedron Lett.* **1982**, *23*, 1925.

[9] Due to their structures consisting of phenalene skeletons, **6a** and **6b** were highly contaminated with the corresponding double-bond isomers.

[10] ^{1}H NMR spectra were measured in CF_3COOD for **3a–c** and in $CDCl_3$ for **4a**, **5a**, **6a**, **4b**, **5b**, and **6b**.

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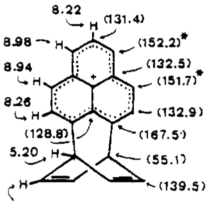
Table I. Reduction Potentials of 3a–c

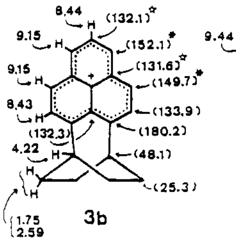
cation salt	$E_1^{\text{red.}}$ ($R^+/R\cdot$)	$E_2^{\text{red.}}$ ($R\cdot/R^-$)	ΔE
3a[a]	0.21	−1.11[b]	−1.32
3b[a]	0.11	−1.18[b]	−1.29
3c[c]	0.7	−0.9	−1.6

[a] Potentials are determined in CH_3CN with 0.1 M n-Bu_4NBF_4 as supporting electrolyte at -78 °C and are given in volts vs. SCE. [b] Irreversible. [c] Data taken from ref 14.

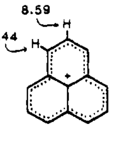
shown alongside the following structures where the values in parentheses denote carbon shift (starred values may be interchanged). All the protons attached to the phenalenyl



3a



3b



3c

skeleton of both **3a** and **3b** appear at rather high field compared to the parent cation **3c**. The upfield shifts are more pronounced in **3a** than **3b**.[12] Furthermore, all aromatic protons of **3a** are about equally shielded from those of **3b** (Δδ for H-1, -2, -4, and -5 are 0.17, 0.22, 0.21, and 0.17 ppm, respectively). Since the chemical shifts of the most remote protons, H-2, from the bridges are at least not considered to be influenced by the anisotropy difference between etheno and ethano bridges, the observed upfield shift in **3a** implies an additional electron supply (besides inductive effect of the alkyl bridge) from the etheno bridge in **3a**. Of the phenalenyl carbons in **3a** and **3b**, the marked upfield shifts of C-5a, C-9a, and C-11c are observed in **3a**. However, this strong shielding cannot be accounted for in terms of electron delocalization from the etheno bridge in **3a** since same shielding is observed in the etheno-bridged acenaphthylene **4a** (δ 130.5) compared to the ethano-bridged one (δ 143.8). Although the chemical shifts of remaining phenalenyl carbons in **3a** and **3b** show no significant difference,[13] those of the etheno and ethano carbons (C-7, -8, -12, and -13) need comment. Within the comparison between **4**, **5**, and **3**, the signals of ethano-bridge carbons are shifted to higher field in the order of **4b** (δ 29.0), **5b** (δ 27.2), and **3b** (δ 25.3), whereas the appearance of the etheno-bridge carbon signal in **3a** (δ 139.5) approximately 5 and 7 ppm to lower field than those in **5a** (δ 134.0, 134.3) and **4a** (δ 132.2), respectively, is seemed to be the deshielding arising from charge delocalization in **3a**.

Measurements of the reduction potentials of **3a** and **3b** by cyclic voltammetry showed first reversible and second irreversible reductions. The results are summarized in Table I together with those for **3c**.[14] The second reduction potentials ($R\cdot/R^-$) of **3a** and **3b** are found to be approximately −1.1 V, which are valid for the reduction potentials of the neutral species having either nonbonding LUMO or SOMO.[15] Taking into account the first reduction potentials as a measure of the thermodynamic stability of a series of cations, **3a**, not to mention **3b**, is substantially more stable than **3c**.[16] Although the pK_{R^+} of **3a** and **3b** could not be determined due to the irreversible disproportionation of the corresponding carbinols that occured under the conditions employed, the observed pK_{BH^+} data for a series of phenalenones, **5a** (−0.8),[8] **5b** (+0.2), and the parent ketone (−1.4),[8] which reflect mainly the stability of the corresponding hydroxyphenalenyl cations, are compatible with the electrochemical data.

In conclusion, the available experimental data suggest that the cations **3a** and **3b** are more stable than **3c** and the ^1H and ^{13}C NMR spectra of **3a** are indicative of charge delocalization into the etheno bridge to some extent.[17]

Registry No. **3a**$^+\cdot BF_4^-$, 88887-56-3; **3a**·, 88980-87-4; **3a**$^-$, 88887-57-4; **3b**$^+\cdot BF4^-$, 88887-59-6; **3b**·, 88980-88-5; **3b**$^-$, 88887-60-9; **3c**$^+\cdot BF_4^-$, 88887-61-0; **4a**, 82655-70-7; **4b**, 88887-62-1; **5a**, 82655-78-5; **5b**, 88887-63-2.

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(11) Prinzbach, H.; Freudenberger, V.; Scheidegger, U. *Helv. Chim. Acta* **1967**, *50*, 1087.

(12) Although a referee has suggested that small differences in ^1H NMR absorption values in **3c**, **3b**, and **3a** could also be rationalized as resulting from reduced delocalization as a result of deviation from planarity caused by increased strain in going from **3c** to the ethano to the etheno structures, it should be stressed that differences in chemical shifts of aromatic protons between ethano- (**4b**, **6b**) and etheno-bridged intermediates (**4a**, **6a**) are less than 0.1 ppm.

(13) A referee has pointed out that ^{13}C values for ring carbons of **3a** offer no evidence of charge delocalization. However, it has been claimed that correlations between ^{13}C NMR shifts and atomic populations of aromatic compounds should not be interpreted in terms of π-electrons only. See: Fliszár, S.; Cardinal, G.; Beraldin, M.-T. *J. Am. Chem. Soc.* **1982**, *104*, 5287.

(14) Haddon, R. C.; Wudl, F.; Kaplan, M. L.; Marshall, J. H.; Cais, R. E.; Bramwell, F. B. *J. Am. Chem. Soc.* **1978**, *100*, 7629.

(15) Dietz, R.; Peover, M. E. *Trans. Faraday Soc.* **1966**, *62*, 3535.

(16) Inductively, the stabilizing effect of the etheno bridge in **3a** is weaker than that of the ethano bridge in **3b** (Nakazawa, T.; Niimoto, Y.; Kubo, K.; Murata, I. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 545. Nakazawa, T.; Kubo, K.; Murata, I. *Ibid.* **1981**, *20*, 189). Nevertheless, the comparable stability observed for **3a** and **3b** suggests that the unfavorable stabilizing effect in **3a** is offset by the electron delocalization in **3a**.

(17) Spectral data of new compounds. **4a**: colorless needles, mp 116–117 °C; UV (CH_3CN) λ_{max} nm (log ε) 229 (4.57), 299 (3.89), 311 (4.03), 325 (3.89); ^1H NMR ($CDCl_3$) δ 3.21 (s, 4 H), 4.01 (m, 2 H), 6.43 (m, 4 H), 6.97 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 30.2, 45.3, 118.6, 124.5, 126.0, 130.5, 132.2, 141.3, 145.2. **4b**: colorless crystals, mp 171–172 °C; UV (CH_3CN) λ_{max} nm (log ε) 236 (4.90), 291 (3.96), 303 (4.04), 314 (3.91), 320 (3.89), 334 (3.74); ^1H NMR ($CDCl_3$) δ 1.88–2.17 (m, 8 H), 3.07 (m, 2 H), 3.33 (s, 4 H), 7.08 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 29.0, 30.3, 39.7, 119.2, 124.8, 130.8, 141.0, 143.4, 143.8. **5a**: for mp, IR, UV, and ^1H NMR, see ref 8; ^{13}C NMR ($CDCl_3$) δ 47.6, 48.0, 124.9, 125.7, 126.9, 127.2, 127.4, 128.9, 129.7, 130.0, 130.7, 134.0, 134.3, 139.6, 141.9, 143.0, 185.1; ^{13}C NMR (CF_3COOD) δ 52.0, 52.3, 119.3, 123.1, 127.5, 128.2, 129.3, 129.9, 137.6, 140.5, 145.4, 153.6, 156.6, 159.8, 178.4. **5b**: yellow crystals, mp 155–156 °C; IR (KBr) 1631 cm^{-1}; UV (CH_3CN) λ_{max} nm (log ε) 267 (4.34), 324 (3.47), 366 (3.82), 411 (4.13); UV (60% H_2SO_4) 210 (4.47), 223 (4.49), 263 (3.97), 365 (4.13), 415 (4.10), 459 (4.17), 477 (4.21); ^1H NMR ($CDCl_3$) δ 1.70–2.28 (m, 8 H), 3.35 (m, 2 H), 6.69 (d, J = 9.8 Hz, 1 H), 7.32 (d, J = 7.2 Hz, 1 H), 7.52 (d, J = 7.6 Hz, 1 H), 7.62 (d, J = 7.2 Hz, 1 H), 7.71 (d, J = 9.8 Hz, 1 H), 8.57 (d, J = 7.6 Hz, 1 H); ^1H NMR (CF_3COOD) δ 1.87 (m, 4 H), 2.52 (m, 4 H), 4.00 (m, 2 H), 7.74 (d, J = 8.9 Hz, 1 H), 8.09 (d, J = 7.8 Hz, 1 H), 8.20 (d, J = 8.1 Hz, 1 H), 8.72 (d, J = 7.8 Hz, 1 H), 8.82 (d, J = 8.9 Hz, 1 H), 9.45 (d, J = 8.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 27.2, 41.9, 42.2, 125.4, 126.3, 126.7, 128.1, 128.5, 129.4, 131.1, 131.7, 131.9, 141.9, 153.4, 156.5, 185.6; ^{13}C NMR (CF_3COOD) δ 25.9, 26.0, 45.8, 46.2, 119.4, 122.6, 127.2, 127.3, 130.6, 131.4, 132.1, 141.7, 146.9, 152.6, 172.2, 174.8, 176.6.

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A Reiterative Route to Chiral *all-syn*-1,3-Polyols

Summary: An efficient, enantioselective procedure for obtaining *syn*-1,3-polyols is described. The method relies on a reiterative two-step protocol involving stereoselective homoallylic alcohol epoxidation followed by ring opening via a higher order, mixed organocuprate.

Sir: Among the myriad advances in synthetic methodology reported over the past 2 decades, those concerned with

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