nents for homoaromatic stabilization. In every case the homoaromatic interaction provides the major stabilizing influence and the laticyclic interaction is a second-order effect. This point is emphasized by the results of simple Hückel calculations given in Table III.

Table III. Hückel Stabilization Energies for I and II[a]

y	z = 0	0.2	0.4	0.6
0	0	0	0	0
0.2	114	4	12	36
0.4	348	7	36	86
0.6	710	12	52	122

[a] In units of $10^{-3}\beta$. Assuming $\beta_{23} = \beta_{34} = \beta_{67} = \beta$; $\beta_{27} = \beta_{46} = y\beta$; $\beta_{69} = \beta_{78} = z\beta$. All other interactions were neglected. The values for $z = 0$ correspond to the homoaromatic stabilization of I and the other columns give the *additional* stabilization provided by the 8-9 double bond in II.

It should be noted that we are not ruling out extensive delocalization between the three π bridges, but simply point out that such interaction will not lead to significant net stabilization energy, in contrast to homoaromatic interaction between two π bridges. Similar conclusions have been reached by other workers[12] about the relationship between delocalization and stabilization in bridged π systems. As a result of the work reported here and previous studies, it is our belief that while laticyclic and longicyclic interactions may be of considerable theoretical interest, they have little to contribute to the milieu of ionic stabilization mechanisms by comparison with homoaromatic and other stabilization mechanisms.

[12] (a) P. Bischoff, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **52**, 1745 (1969); (b) H. E. Zimmerman, *Accounts Chem. Res.*, **4**, 272 (1971), and references cited therein.

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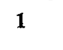
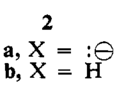
Stabilization and Destabilization of Unsaturated Bicyclo[3.2.2]nonyl Anions

Sir:

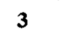
Some time ago, one of us predicted that π-electron stabilization of anion **1a** would exceed that of the bishomoaromatic **2a**, albeit by less than a factor of two.[1] The otherwise unstabilized allylic anion **3a** serves as conventional reference for both.



1



2



3

a, X = :⊖
b, X = H

More recent photoelectron data[2a] have now disqualified one of many theoretical approximations used to achieve such conclusions—explicit neglect of "through-bond" interaction.[2b] Still others remain to be tested.[1b,3] Nor is the peripheral experimental evidence entirely unambiguous in its interpretation.[1b,4]

We are therefore particularly pleased to be able to report quantitative confirmation of the original predictions. As measured by KO-*t*-Bu–Me_2SO-catalyzed detritiation of **1b**-*t*, **2b**-*t*, and **3b**-*t*, stabilization of the trienyl anion **1a** exceeds that of the dienyl **2a** by 4.0 ± 0.3 kcal/mol.[5] The latter, in turn, is stabilized by more than 5.6 kcal/mol. The first value recalls the solvolytically measured 3.7 kcal/mol advantage of the 7-norbornadienyl cation over the 7-norbornenyl.[6] The second may be compared with the solvolytically measured 12.4 kcal/mol stabilization of the 7-norbornenyl cation.[7]

1b was prepared by Na–K reduction of 4-methoxybicyclo[3.2.2]nona-2,6,8-triene;[4b,8,9a] **2b** was similarly obtained from **1b**.[9b] Tritiated dimethyl sulfoxide served to label both under conditions similar to those of subsequent detritiation kinetics. That the label was almost exclusively at C-2 or C-4 (>99% for **1b**, >93% for **2b**) was demonstrated both by pmr analysis of the products of parallel deuterium incorporation experiments and by nonlinear least-squares analysis of detritiation data.[10]

The detritiation k_{obsd} of both hydrocarbons increased with primitive concentration[12] of base to reach a broad maximum between 0.08 and 1.0 *M*.[13] Within this common range of related kinetic investigation,[4c,11,13] k_{obsd} varied by less than 15% and never exceeded 1.2 times its value at 0.057 *M* (Table I).[14]

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[1] (a) M. J. Goldstein, *J. Amer. Chem. Soc.*, **89**, 6357 (1967); (b) M. J. Goldstein and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 6193 (1971); (c) footnote 9 in ref 1a.

[2] (a) M. J. Goldstein, S. Natowsky, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **56**, 294 (1973); (b) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

[3] M. J. S. Dewar and W. W. Schoeller, *Tetrahedron*, **27**, 4401 (1971); S. Yoneda, S. Winstein, and Z. Yoshida, *Bull. Chem. Soc. Jap.*, **45**, 2510 (1972); *Tetrahedron*, **28**, 2395 (1972).

[4] (a) J. C. Barborak, J. Daub, D. M. Follweiler, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 7760 (1969); J. C. Barborak and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 3184 (1970); (b) J. B. Grutzner and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2200 (1972); (c) S. W. Staley and D. W. Reichard, *J. Amer. Chem. Soc.*, **91**, 3998 (1969); (d) P. Ahlberg, D. L. Harris, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 4454 (1970); P. Ahlberg, *Chem. Scr.*, **2**, 231 (1972); (e) M. V. Moncur and J. B. Grutzner, *J. Amer. Chem. Soc.*, **95**, 6449 (1973).

[5] Earlier work[4c] had permitted a 3.9 kcal/mol estimate with the added assumptions of identical $\Delta S^{\ddagger}$ for exchange of **1b** and **2b**, obedience to a common basicity function, and indifference to 3-methyl substitution.

[6] S. Winstein and C. Ordronneau, *J. Amer. Chem. Soc.*, **82**, 2084 (1960). $\Delta S^{\ddagger}$ is assumed constant.

[7] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, 77, 4183 (1955).

[8] M. J. Goldstein and B. G. Odell, *J. Amer. Chem. Soc.*, **89**, 6356 (1967).

[9] (a) Mp 43°. Other data agree with those reported.[4b,9c] (b) Mp 53° (lit. mp 35–36°)[4e]; *m/e* 120; nmr τ (CCl_4) 3.62 (t, 1.03), 4.11 (m, 1.96), 4.73 (d of t, 1.01), and 7.21–8.63 (m, 8.01) ppm. *Anal.* Found: C, 89.82; H, 10.05. (c) M. Jones, Jr., and D. S. Reich, *J. Amer. Chem. Soc.*, **89**, 3935 (1967).

[10] As in the bicyclo[3.2.1]octadienyl series,[11] dimethyl sulfoxide adequately prevents the rearrangements observed in other media.[4b,c]

[11] J. M. Brown and J. L. Occolowitz, *J. Chem. Soc. B*, 411 (1968).

[12] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1970, p 85.

[13] (a) A. Schriesheim and C. A. Rowe, Jr., *J. Amer. Chem. Soc.*, **84**, 3160 (1962); (b) J. E. Hoffmann, R. J. Muller, and A. Schriesheim, *J. Amer. Chem. Soc.* **85**, 3000 (1963); (c) S. B. Tjan, H. Steinberg, and Th. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, **88**, 680 (1969); (d) P. K. Freeman and T. A. Hardy, *Tetrahedron Lett.*, 3939 (1971); (e) M. J. Maskornick, *Tetrahedron Lett.*, 1797 (1972).

[14] A more extensive base dependence study, to be reported subsequently, permits extrapolation to infinite dilution.

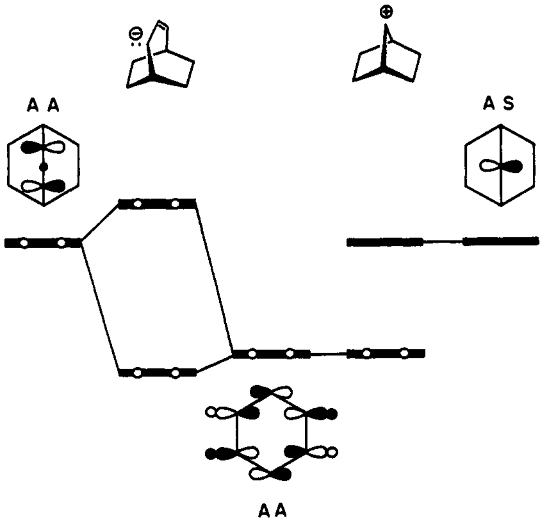

Figure 1. Destabilization and nonstabilization of bicyclic ions.

Table I. Temperature Dependence of k_{obsd}[a]

Temp, °C	10^6k_{obsd}, sec^{-1} Triene **1b**	Diene **2b**
25.0	93 ± 2	0.62 ± 0.02
34.9	206 ± 10	
44.0	424 ± 9	
55.0	906 ± 21	12 ± 1
65.3		28 ± 2
75.6		62 ± 4
85.1		127 ± 4
$\Delta H^{\ddagger}$, kcal/mol[b]	14.0 ± 0.2	18.0 ± 0.1
$\Delta S^{\ddagger}_{0.057\,M}$, cal/(mol deg)	−25.6 ± 0.6	−22.0 ± 0.3

[a] 0.057 M KO-t-Bu–Me_2SO; uncertainties are standard deviations. [b] Negligibly different from those at infinite dilution.

Incorporation of deuterium or tritium into the corresponding monoene **3b**[15] proved to be much more difficult. Quantitative detritiation data were achieved only in competition with concurrent (and heterogeneous) decomposition of the basic solvent. Zero time and base dependence estimates thus provided only an upper limit to the homogeneous k_{obsd} ($<4.27 \times 10^{-7}$ sec^{-1} at 0.057 M and 95°). The reasonable assumption that $\Delta S^{\ddagger}_{0.057\,M}$ approximates a lower limit of −24 cal/(mol deg) (*cf.* Table I and ref 13b,c) then sets $\Delta H^{\ddagger}$ as >23.6 kcal/mol.

The 4.0 kcal/mol discrepancy between $\Delta H^{\ddagger}$ for **1** and **2** is most economically attributed to longicyclic[1b] π-electron delocalization throughout all three unsaturate bridges of the trienyl anion. The expected[1c] and observed greater discrepancy between **2** and **3** (>5.6 kcal/mol) is similarly attributed to bishomoaromatic stabilization of **2a**.

More disconcerting, **3b** is also less reactive than any other simple olefin (whether bicyclic,[4c,11,13d] monocyclic,[11,13c,d] or acyclic[13a]) previously studied in this medium.[16] This behavior recalls that of 7-norbornyl tosylate, the abnormally unreactive reference substrate of the bicyclo[2.2.1]heptyl system.[18] And it can be understood in an entirely analogous way.[19]

Within the framework of naive theory,[1b] cations are stabilized by an occupied, high-lying orbital—anions by a vacant low-lying one—but only if these are of appropriate symmetry. Figure 1 shows that the electron-occupancy and the symmetry conditions cannot both be satisfied, either for the allylic anion of **3a** or for the 7 cation of norbornyl. In the case of **3a**, as elsewhere,[1] interaction between fully occupied orbitals of corresponding symmetry necessarily leads to destabilization. In the case of the 7-norbornyl cation, electron occupancy is appropriate but the symmetry is not; this cation is therefore better described as abnormally nonstabilized.[19]

Although the originally anticipated reactivity pattern remains intact, its quantitative dissection into σ and π contributions thus becomes unresolved, if not indeed unresolvable. Conventional references, such as we and others[4b,c,e,6,7] have used, are clearly inappropriate for such finer distinctions. We therefore content ourselves with the now demonstrated semiquantitative reliability of the original π-electron approach, whatever the ultimate origins of its success.

Acknowledgment. We are grateful to R. Hoffmann for his critical comments, to M. Jones, Jr., for copies of spectra, and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Professor Grutzner graciously agreed to delay publication of ref 4e until this manuscript was available.

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[15] Obtained by methyllithium treatment of the p-toluenesulfonylhydrazone of bicyclo[3.2.2]nonan-2-one: mp 108°; m/e 122; nmr τ (CCl_4) 4.11 (m, 0.99), 4.56 (d of t, 0.99), and 7.54–8.60 (m, 12.02) ppm. *Anal.* Found: C, 87.84; H, 11.81.

[16] More quantitative comparisons must await the reconciliation of different treatments of base dependence[4c,e,11,13] and of conflicting data[11,13c,d] as well as the more frequent study of temperature dependence.[13b,c] Correction for isotope effects should be less important.[17]

[17] J. R. Jones, *Progr. Phys. Org. Chem.*, **9**, 241 (1972); I. O. Shapiro, F. S. Yakushin, I. A. Romanskii, and A. I. Shatenshtein, *Kinet. Kat.*, **9**, 1011 (1968).

[18] J. D. Roberts, F. O. Johnson, and R. A. Carboni, *J. Amer. Chem. Soc.*, **76**, 5692 (1954); W. G. Woods, R. A. Carboni, and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 5653 (1965); P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **83**, 182 (1961); P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1854 (1964); C. S. Foote, *J. Amer. Chem. Soc.*, **86**, 1853 (1964).

[19] R. Hoffmann, P. D. Mollère, and E. Heilbronner, *J. Amer. Chem Soc.*, **95**, 4860 (1973).

[20] NDEA Title IV Fellow, 1966–1969; U. S. Public Health Service. Fellow, 1969–1970, and Trainee, 1970–1971.

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Reductive Removal of Halo and Mesyloxy Groups with a Copper(I) Complex

Sir:

A rather general synthetic problem encountered in another study has necessitated us to search for a method that effects reductive removal of halo and mesyloxy and thus indirectly hydroxy groups.[1] Required of the method are high efficiency, stereospecificity, operational simplicity, and mild conditions. We have found that a reducing system consisting of some Cu(I) species satisfies virtually all those requirements with a

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[1] Methods recently developed for this purpose are: (a) $NaBH_3CN$–HMPA: R. O. Hutchins, B. E. Maryanoff, and C. A. Milewski, *Chem. Commun.*, 1097 (1971); (b) C. W. Jefford, D. Kirkpatrick, and F. Delay, *J. Amer. Chem. Soc.*, **94**, 8905 (1972); (c) $LiBH(C_2H_5)_3$: H. C. Brown and S. Krishnamurthy, *ibid.*, **95**, 1669 (1973); (d) Li–$C_2H_5NH_2$ reduction of diethyl phosphates or tetramethylphosphorodiamides of alcohols: R. E. Ireland, D. C. Muchmore, and U. Hengartner, *ibid.*, **94**, 5098 (1972).