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Bishomoaromatic Stabilization of Bicyclic Anions[†]

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The pK_a's per hydrogen of bicyclo[3.2.1]octadiene (1), bicyclo[3.2.1]octene (2), bicyclo[3.2.2]nonadiene (5), and bicyclo[3.2.2]nonatriene (6), as measured in cyclohexylamine, were 31.4, >40.5, 34.0, and 32.0, respectively. The enhanced acidity of diene 1 corresponds to a stabilization of at least 12.2 kcal relative to the anion of 2, thus emphasizing the importance of homoaromaticity for suitable allylic anions.

The concept of aromatic stabilization has been extended to include interacting π systems containing one or more insulating groups.[1,2] The magnitude of bishomoaromatic stabilization of the norbornadienyl and related cations has been established by solvolytic data and direct measurements of the activation barrier for bridge flipping.[1] Supporting evidence, summarized below, for the corresponding extension of this concept to anionic systems has been based on interpretations of kinetic data and ^{1}H NMR chemical shifts. This paper provides the first quantification of anionic homoaromatic stabilization.

Brown and Occolowitz attributed the $10^{4.5}$ enhanced rate of exchange of bicyclo[3.2.1]octadiene (1) relative to bicyclo[3.2.1]oct-2-ene (2) to extended charge delocalization of the bicyclo[3.2.1]octadienyl anion (3) as represented by **3a**.[3] The bishomocyclopentadienyl character of anion 3 was also indicated by NMR studies.[4] The existence of a diatropic ring current was inferred from the δ 2.3 upfield shift of the C_6 and C_7 hydrogens of 3 relative to bicyclo[3.2.1]oct-3-enyl anion (4).


3a

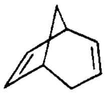
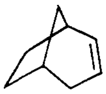
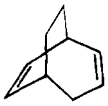
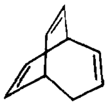

3b


4

Similar enhanced rates of exchange were observed for benzobicyclo[3.2.1]octadiene, bicyclo[3.2.2]nona-2,6-diene (5), and bicyclo[3.2.2]nonatriene (6).[5,6] Goldstein estimated that for the [3.2.2] system bishomoaromaticity contributed at least 5.6 kcal of stabilization, based on the relative rates of detritiation of diene 5 and bicyclo[3.2.2]non-2-ene. Furthermore these kinetic studies also indicated that the anion of triene 6 was 4 kcal more stable than that of 5.[6b] Concurrently Grutzner concluded from a study of the decomposition rates of the anions of 5 and 6 that the anion of 6 was 2.4 kcal more stable.[6a] Although the two authors differed concerning the importance of bicycloaromatic charge delocalization, they concurred with respect to bishomoaromaticity.

These conclusions concerning homoaromaticity began to be questioned when Trimitsis and Tumcay reported that the C_6 and C_7 hydrogens of 2,4-diphenylbicyclo[3.2.1]octadienyl anion resonated δ 1.4 upfield of the analogous protons of the 2,4-diphenylbicyclo[3.2.1]oct-3-enyl anion despite the fact that the kinetic acidities of the two hydrocarbons differed by 3.3.[7] In view of these findings, the upfield chemical shift of anion 3 could no longer be interpreted as unambiguous evidence for a diatropic ring current.[8]

Table I

Hydrocarbon	$pK_a{}^{a}$	Anionic stabilization relative to allylic model (kcal)
 1	31.4 ± 0.3^{a}	>12.2
 2	>40.5	0
 5	34.0 ± 0.3	$>8.7^{b}$
 6	32.0 ± 0.3	$>11.4^{b}$
	16.25^{24}	41.2
	47^{15}	0

[a] pK_a per hydrogen. [b] Value assumes pK_a of bicyclo[3.2.2]non-2-ene > 40.5.

Recently, two theoretical papers dealing with anionic homoaromaticity concluded that the archetypical bis-

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[†] Work first presented at the 175th National Meeting of the American Chemical Society at Anaheim, CA, March 1978.

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(1) (a) Winstein, S. *Q. Rev. Chem. Soc.* **1969**, *23*, 141; *Spec. Publ. Chem. Soc.* **1967**, *No. 21*, 5. (b) Olah, G. A., Schleyer, P. R., Eds. "Carbonium Ions"; Interscience: New York, 1972; Vol. 3. (c) Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 106.

(2) For theoretical studies, see: (a) Goldstein, M. J.; Hoffman, R. *J. Am. Chem. Soc.* **1971**, *93*, 6193. (b) Hehre, W. J. *Ibid.* **1974**, *96*, 3644. (c) Jorgensen, W. L. *Ibid.* **1976**, *98*, 6784.

(3) Brown, J. M.; Occolowitz, J. L. *J. Chem. Soc., Chem. Commun.* **1965**, 376.

(4) (a) Brown, J. M. *J. Chem. Soc., Chem. Commun.* **1967**, 638. (b) Winstein, S.; Ogliaruso, M.; Sakai, M.; Nicholson, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 3656.

(5) (a) Rosenthal, J. W.; Winstein, S. *Tetrahedron Lett.* **1970**, 2683. (b) Brown, J. M.; Cain, E. N.; McIvor, M. C. *J. Chem. Soc. B* **1971**, 730.

(6) (a) Moncur, M. V.; Grutzner, J. B. *J. Am. Chem. Soc.* **1973**, *95*, 6449. (b) Goldstein, M. J.; Natowsky, S. *Ibid.* **1973**, *95*, 6451. (c) Staley, S. W.; Reichard, D. W. *Ibid.* **1969**, *91*, 3998.

(7) Trimitsis, G. B.; Tuncay, A. *J. Am. Chem. Soc.* **1976**, *98*, 1997.

(8) The general role of extended bonding is currently being reexamined. For example: (1) the bicyclo[3.2.1]octadienyl radical is not delocalized;[9] (2) in closed systems homoconjugative interactions of neutral fragments are destabilizing;[10] (3) the bicyclo[6.2.1]undecatrienyl dianion is localized despite the existence of a 10-π-electron bishomoaromatic ensemble.[11]

(9) Sustman, R.; Gellert, R. W. *Chem. Ber.* **1978**, *111*, 42.

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homoaromatic anion **3** would be 3–4 kcal more stable than the octenyl anion **4** in the gas phase.[12] In the absence of any computational evidence for extended charge delocalization using STO-3G basis set, the authors concluded that (1) the MINDO/3 optimized structure of the bicyclooctadienyl anion is best represented as **3b** and (2) the stabilization reflects the polarizability and inductive effects of the vinyl bridge. The authors suggested that homoaromaticity is a phenomenon characteristic of only a selected class of bridged carbocations and not of anions, radicals, or neutral species.

We directly addressed this question by measuring the equilibrium pK_a's of hydrocarbons **1**, **2**, **5**, and **6** in cyclohexylamine (CHA) containing cesium cyclohexylamide. The pK_a values reported in Table I are the average for a series of measurements in which at least two different polyarylmethanes were used as standards.

Bicyclo[3.2.1]octadiene (**1**) is a suprisingly acidic hydrocarbon; the pK_a of **1** is 31.7 (31.4 per hydrogen after statistical correction), i.e., approximately that of triphenylmethane (31.45)[13] in CHA. The pK_a of bicyclo[3.2.1]octene (**2**) was determined to be greater than 40.5, the upper limit for this method.[14] The pK_a's of bicyclononadiene **5** and bicyclononatriene **6** are 34.3 and 32.0 (34.0 and 32.0 per hydrogen), respectively. These values correspond to a 3.2 kcal difference in stability of the corresponding anions, a value in good agreement with the 2.4–4.0 kcal inferred from the kinetic studies.

To confirm that the above hydrocarbon anions were formed, 4-deuteriobicyclo[3.2.2]nonatriene was prepared and treated with CsCHA/CHA, and the product reisolated. The anionic solution decomposed to generate barbaralane (tricyclo[3.3.1.0^{4,6}]nona-2,7-diene) with a half-life of ~4 h. By ^{2}H NMR the label was scrambled after 30 min as follows due to isomerization to the barbaralyl anion followed by ring opening to regenerate the trienyl anion: 60% at C_2 and C_4; 20% at C_6, C_7, C_8, and C_9; and 20% at C_1 and C_5. The ~45 min half-life for this degenerate rearrangement in CHA at 20 °C is consistent with the 10-min half-life reported in THF at 28 °C.[16]

The stabilization of anion **3** resulting from the remote double bond is greater than 9.1 pK_a units or 12.2 kcal relative to the allylic anion derived from **2**. Comparison of this value to the stabilization of a simple allylic or benzylic anion due to direct conjugation of a phenyl ring or double bond is informative. The pK_a's of toluene and diphenylmethane are 41.2[17] and 33.4,[13] implying 10.5 kcal stabilization from the second phenyl ring. Likewise the pK_a difference of cycloheptene (44[15]) and cycloheptatriene (36[18]) suggests that an additional conjugated double bond would provide at least 10.7 kcal of stabilization to an allylic anion. Thus the stabilization due to the isolated double bond of **3** is greater than the ~11 kcal obtained by direct conjugation of a double bond or phenyl ring to an allylic or benzylic anion.

From these models the relative importance of structures **3a** and **3b** as representive of the chemical bonding of anion **3** can be evaluated. For **3b** the 11 kcal of stabilization of an allylic anion produced by conjugation to a second double bond would be substantially reduced due to (1) the absence of any extended charge delocalization and (2) attenuation of the polar effect of the additional unsaturated unit. Since we were unable to measure the pK_a of 6,7-bismethylenebicyclo[3.2.1]oct-2-ene (**7**)[19] to determine this effect directly for this system, the increase in stability of a carbanion resulting from a noninteracting homoconjugated double bond was estimated from the equilibrium pK_a's of 3-cyclopentenecarbonitrile (**9**) and cyclopentanecarbonitrile (**10**) in CHA. The pK_a's of **9** and **10** are 30.8 and 33.9, respectively, corresponding to 4.1 kcal of stabilization[22]—a value in good agreement with the theoretical predictions of 3–4 kcal for a noninteracting double bond.

However, the observed magnitude of the differential stability of the octadienyl anion **3** vs. octenyl anion **4** is incompatible with structure **3b** because the difference is not only greater than that predicted but also is larger than that of a double bond conjugated to an allylic anion.[23] Only the extended bishomoaromatic charge delocalization represented by structure **3a** would account for the enhanced stability of **3**. The acidities of diene **5** and triene **6** further support this conclusion.

Depending on the exact pK_a of bicyclooctene **2**, the homoaromatic charge delocalization of **3** provides at least 12.2 kcal and as much as 20 kcal of stabilization. In conclusion, contrary to the theoretical predictions, bishomoaromaticity can provide substantial stabilization for carbanions; in fact, the resonance stabilization of the bishomocyclopentadienyl anion **3** is at least 30% of that of the parent cyclopentadienyl anion.[24]

Experimental Section

Proton magnetic resonance spectra were recorded on a Varian EM-390 or a UCB 180 MHz FT superconducting spectrometer. UV spectra were recorded on a Carey 118 spectrometer. Mass spectra were obtained by using either an Atlas MS-12 or a Consolidated 12110B mass spectrometer. All GLPC work used columns packed with 5% SE-30 on Chrom G.

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[11] Paquette, L. A.; Kukla, M. J.; Ley, S. V.; Traynor, S. G. *J. Am. Chem. Soc.* **1977**, *99*, 4756.

[12] (a) Grutzner, J. B.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 1372. (b) Kaufmann, E.; Mayr, H.; Chandrasekhar, J.; Schleyer, P. R. *Ibid.* **1981**, *103*, 1375.

[13] Streitwieser, A.; Murdoch, J. R.; Hafelinger, G.; Chang, C. *J. Am. Chem. Soc.* **1973**, *95*, 4248.

[14] The pK_a of **2** can be estimated to be as great as 44–46 based on the pK_a's assigned to cyclohexene (46) and cycloheptene (44) from kinetic acidity measurements.[15]

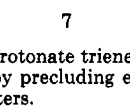
[15] Streitwieser, A.; Boerth, D. W. *J. Am. Chem. Soc.* **1978**, *100*, 755.

[16] Grutzner, J, B.; Winstein, S. *J. Am. Chem. Soc.* **1972** *94*, 2200.

[17] Streitwieser, A.; Granger, M. R.; Mares, F.; Wolf, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 4257.

[18] (a) Dauben, H.; Rifi, M. *J. Am. Chem. Soc.* **1963**, *85*, 3041. (b) Breslow, R.; Chu, W. *Ibid.* **1973**, *95*, 411.

[19] Triene **7**[20] was prepared from 5,6-bis(chloromethyl)bicyclo[2.2.1]hept-2-ene (**8**)[21] to evaluate the polar contribution of the sp^2 hybridized carbons at C_6 and C_7 to the stability of anion **3**. From symmetry considerations the butadiene moiety cannot interact with the allylic anion fragment. Treatment of **8** sequentially with (tribromomethyl)phenylmercury in refluxing benzene, zinc in acetic acid at 40 °C, *tert*-butyllithium in THF at -100 °C, and *t*-BuOK in THF at 20 °C generated **7**.



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To date, all attempts to deprotonate triene **7** in CHA have irreversibly destroyed the triene, thereby precluding efforts to quantify the polar effect of the remote sp^2 centers.

[20] ^{1}H NMR (CCl_4) 1.7 (m, 2 H), 2.1 (m, 1 H), 2.4 (m, 1 H), 2.85 (m, 2 H), 4.02 (s, 1 H), 4.4 (s, 2 H), 4.7 (s, 1 H), 4.75 (m, 1 H), 5.25 (m, 1 H); mass spectrum, *m/e* 132.

[21] Bowe, M. A. P.; Miller, R. G. J.; Rose, J. B.; Wood, D. G. M. *J. Chem. Soc.* **1960**, 1541.

[22] Washburn, W. N.; Batstone-Cunningham, R., unpublished work.

[23] The difference in stability between anions **3** and **4** contains contributions due to the differential solvation energies of the ions as well as the nature of the ion pair that each formed. However, these factors would not be expected to be the origin of a significant fraction of the 12.2 kcal or greater energy differential observed.

[24] Streitwieser, A.; Nebenzahl, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 2188.

Preparation of Hydrocarbons. Bicyclo[3.2.1]octene (2) and bicyclo[3.2.1]octadiene (1) were prepared according to the procedure reported by Moore.[25] Bicyclo[3.2.2]nonatriene (6) was prepared from cycloheptatriene as described by Grutzner and Winstein.[16] Bicyclo[3.2.2]nonadiene (5) was synthesized from bicyclo[3.2.2]non-6-en-2-one (11).[26] Ketone 11 was reacted sequentially with $NaBH_4$, TosCl, and *t*-BuOK/18-crown-6-ether in THF at 25 °C. All the hydrocarbons were purified by preparative GLPC.

Acidity Measurements. The procedures devised by Streitwieser[27] were used in which a weighed amount of a polyarylmethane, whose pK_a and anionic extinction coefficient had been determined, was added at 20 °C to CHA containing cesium cyclohexylamide. The UV spectrum of the resulting solution was recorded, a weighed amount of a GLPC purified hydrocarbon of unknown pK_a was added, and the spectrum was recorded. The polyarylmethanes (pK_a's in parentheses)[13] used for the acidity determinations are listed below with the pK_a value measured for hydrocarbons 1, 2, 5, and 6 prior to statistical correction.

Diene 1: triphenylmethane (31.45), pK_a 32.0 ± 0.3; *p*-biphenyldiphenylmethane (30.2), pK_a 31.4 ± 0.3.

Diene 5: tri-*p*-tolylmethane (33.0), pK_a 34.1 ± 0.3; *o*-biphenylphenylmethane (33.5), pK_a 34.5 ± 0.3.

Triene 6: triphenylmethane (31.45), pK_a 32.1 ± 0.3; tri-*p*-tolylmethane (33.0), pK_a 32.0 ± 0.3; *p*-biphenyldiphenylmethane (30.2), pK_a 31.9 ± 0.3.

Octene 2: *p*-biphenylmethane (39.0), pK_a > 40.5.

Acknowledgment. I thank Prof. A. Streitwieser for making available the equipment necessary to measure the pK_a's and W. Schriver for technical assistance. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Registry No. 1, 4096-95-1; 1 anion, 87508-61-0; 2, 823-02-9; 5, 14993-07-8; 5 anion, 87481-57-0; 6, 16216-91-4; 6 anion, 87462-59-7; 1,3-cyclopentadiene anion, 87507-94-6.

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Nucleophilic Aromatic Substitutions of Unactivated Aryl Halides by Methyl Selenide Anions. Synthesis and Selective Dealkylations of Aryl Alkyl Selenides

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Lithium methyl selenide, easily prepared from powdered gray selenium and MeLi, reacts with unactivated aryl halides, in DMF, to afford the aryl methyl selenides as a result of a nucleophilic aromatic substitution. The aryl methyl selenides are rapidly dealkylated in the reaction medium by MeSeLi to give the aryl selenide anions. Addition of an alkyl halide or of cyanogen iodide gives rise to the formation of aryl alkyl selenides or aryl selenocyanates in good yields. From competitive experiments, carried out on compounds of the type ArClSeR and ArClSR, it has been shown that an RSe group is as efficient as an RS group in activating the nucleophilic aromatic substitution of a chlorine atom by MeS or MeSe anions in DMF. (Alkylthio)phenyl and alkoxyphenyl alkyl selenides can be selectively dealkylated by nucleophilic aliphatic substitution with MeSNa or MeSeLi in DMF or by electron transfer with sodium in HMPA. In the first case the easiness with which the dealkylation occurs follows the order ArSeMe > ArOMe > ArSMe, whereas in the second case the order is ArSeR > ArSR > ArOR. The synthetic utility of these reactions is exemplified and discussed.

In previous papers we have reported that alkanethiolate and alkoxy anions easily react with unactivated aryl chlorides or bromides to give the products of nucleophilic aromatic substitutions. These reactions are made possible by the use of HMPA as the solvent. More recently, however, we have found that similar results can be obtained also in DMF, thus avoiding the use of the carcinogenic HMPA.[1] Thus very simple and useful procedures have been developed for the synthesis of aryl alkyl ethers,[2] thioethers,[1,3] phenols,[2] aromatic thiols,[1,4] and aryl thiocyanates[5] from aryl halides, as well as for the synthesis of alkoxyphenols,[2] alkoxyaryl alkyl sulfides,[1,6] alkoxythiophenols,[1,7] (alkylthio)phenols,[1,7] hydroxythiophenols,[1,7] poly(alkylthio)benzenes,[1,8] and polymercaptobenzenes[1,9] from polychlorobenzenes.

We now report that similar nucleophilic aromatic substitutions of unactivated aryl halides can be effected also by the alkyl selenide anions. These reactions thus represent a convenient synthesis of aryl alkyl selenides 2 from

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