for the borane adduct by itself. The magnitude of the downfield shift increased with the trimethylamine concentration, and again depended on the concentration of trimethylamine–borane and on the temperature (Tables I and II).

Table I. Chemical Shift Differences[a] between Trimethylamine (TMA) and Trimethyamine–Borane (TMAB) in Benzene Solution

	δ(TMA) − δ(TMAB), Hz[b]		δ(TMA) − δ(TMAB), Hz[c]	
Temp, °C	Separate components	Mixture	Separate components	Mixture
4	1.6	+1.0	8.4	6.9
16	1.3	>0	6.4	6.2
38	−0.5	−1.7	4.1	4.0
55	−1.8	−2.6	2.4	2.2
64	−2.5	−3.9	1.6	1.5
74	−3.5	−4.8	0.4	

[a] Measured in Hz at 60 MHz. [b] [TMAB] = 0.5 *M*, [TMA] = 0.2 *M*. [c] [TMAB] = [TMA] = 0.01 *M*.

Table II. Effect of $(CH_3)_3N$ on the Chemical Shift[a] of $(CH_3)_3NBH_3$ in Benzene Solution

[TMAB],[b] *M*	[TMA],[c] *M*	δ(TMA) − δ(TMAB), Hz 38°	δ(TMA) − δ(TMAB), Hz 74°
0.9	0	−3.3	−6.1
0.9	0.09	−3.9	−6.2
0.9	0.6	−4.9	−7.1

[a] Measured in Hz at 60 MHz. [b] TMAB = $(CH_3)_3NBH_3$. [c] TMA = $(CH_3)_3N$.

Two observations now can be made concerning the data represented by Figure 1. First, in the absence of an interaction between the two components, the chemical shifts defined by the temperatures and concentrations falling below the trimethylamine curve should behave qualitatively as if exchange were taking place, *i.e.*, the two peaks move closer together as the temperature is raised. Mixtures in fact duplicate this behavior. Reference to Table I shows that an increase in concentration of the components in the mixture also decreases the difference in the chemical shifts, as would be expected as the result of exchange. Second, in the absence of exchange the two peaks should move farther apart for conditions represented by the region above the trimethylamine curve, *i.e.*, at high enough concentrations of amine–borane or at higher temperatures. This is indeed confirmed by the data in Table I, which are representative of a larger number of experiments with mixtures. These data and the ones in Table II show an increase in the peak separation with increasing temperature and are not compatible with the hypothesis that exchange between free and bound amine is taking place on the nmr time scale, whether by a dissociative or by a bimolecular displacement mechanism. Thus, the role of benzene in influencing the nmr behavior does not consist in assisting the exchange kinetics, as previously proposed,[1] but must be related to special and differentiating solvation effects on the separate components of the system.

A clue to the role of benzene is found when the chemical shifts of trimethylamine and of trimethylamine–borane are compared in benzene and in diethyl ether, using tetramethylsilane in either solvent as a common reference. Transfer of trimethylamine from ether to benzene produces an upfield shift of only 3.0 Hz, whereas 0.5 *M* trimethylamine–borane shifts by 30.5 Hz.[3] Apparently benzene solvates trimethylamine–borane in a conformationally much more specific way than it does the free amine, so that the magnetic anisotropy is more fully felt. The larger temperature coefficient of the chemical shift for the borane adduct is then explainable in terms of a reduction of the anisotropy associated with the solvent sphere through averaging over more conformers as the temperature increases. Since trimethylamine–borane is associated to a considerable degree in benzene,[4] high concentration, where association is greatest, should reduce specific solvation and thus would lead to downfield shifts, as is observed. Introduction of magnetically isotropic constituents into the solution which also could associate preferentially with the amine–borane likewise should give downfield shifts. This is indeed observed when trimethylamine is added. An additional confirmation of this notion is found in the fact that diethyl ether, added in small concentrations to trimethylamine–borane in benzene, produces downfield shifts of similar magnitude.

This kind of behavior is rarely predictable. Care must, therefore, be exercised in the interpretation of chemical shifts and their temperature dependence for mixtures. Rapid self-association equilibria and specific solvation effects may very well combine to simulate data expected for rapidly equilibrating solutes.

Acknowledgment. Partial support of this work under Grant GM-13650 provided by the National Institutes of Health to G. E. Ryschkewitsch is gratefully acknowledged.

(3) Tetramethylsilane shifts by 12 Hz upfield going from ether to benzene.

(4) H. Nöth and H. Beyer, *Chem. Ber.*, **93**, 923 (1969).

G. E. Ryschkewitsch
Department of Chemistry
University of Florida, Gainesville, Florida 32601

A. H. Cowley
Department of Chemistry
The University of Texas at Austin, Austin, Texas 78712

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1-Cyano Substituent Effects on 2-Apo- and 2-Apoisobornyl Solvolysis

Sir:

Much work has been devoted to the solvolysis study of the bicyclo[2.2.1]hept-2-yl system.[1] One major problem yet unresolved is whether the considerably large *exo*:*endo* rate ratio is due to σ participation in the transition state of *exo* derivatives or to other factors.[2]

(1) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; J. A. Berson, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 3; B. Capon, *Quart. Rev.* (London), **18**, 45 (1964); P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965; G. D. Sargent, *Quart Rev.* (London), **20**, 301 (1966); J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *J. Amer. Chem. Soc.*, **89**, 2590 (1967); E. J. Corey and R. S. Glass, *ibid.*, **89**, 2600 (1967); A. Nickon and N. H. Werstiuk, *ibid.*, **89**, 3915 (1967); J. M. Jerkunica, S. Borcic, and D. E. Sunko, *Chem. Commun.*, 1488 (1968); C. F. Wilcox, Jr., and R. G. Jesaitis, *Tetrahedron Lett.*, 2567 (1967).

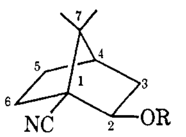
(2) (a) P. v. R. Schleyer, M. M. Donaldson, and W. E. Watts,

Table I. Solvolysis Rates[a] of 1-Cyanoapoiso- and 1-Cyanoapobornyl *p*-Bromobenzenesulfonates

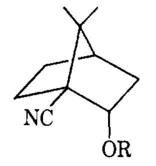
ROBs	Temp, °C	10^6k, sec^{-1}	*exo*/*endo* ratio	$k_{\text{rel-}exo}$[d]	$k_{\text{rel-}endo}$[e]
		Acetic Acid[b]			
exo-**1**-OBs	120.0	29.0			
exo-**1**-OBs	140.0	186			
exo-**1**-OBs	150.0	463			
exo-**1**-OBs	(25.0)[c]	1.32×10^{-4}	2.9	1.71×10^{-7}	
endo-**1**-OBs	150.0	32.7			
endo-**1**-OBs	160.0	76.8			
endo-**1**-OBs	170.0	145			
endo-**1**-OBs	(25.0)[c]	4.57×10^{-5}			2.43×10^{-4}
		Trifluoroacetic Acid[f]			
exo-**1**-OBs	80.0	57			
exo-**1**-OBs	90.0	140			
exo-**1**-OBs	100.0	390			
exo-**1**-OBs	(25.0)[c]	8.0×10^{-2}	83		
endo-**1**-OBs	120.0	61			
endo-**1**-OBs	140.0	360			
endo-**1**-OBs	(25.0)[c]	9.6×10^{-4}			

[a] Acetolysis rates were measured titrimetrically as usual. The nmr absorption of the four aromatic protons in **1**-OBs were well separated from those of the brosylate ion. The trifluoroacetolysis rates were obtained by measuring the decrease of the peak area of the aromatic protons of **1**-OBs against CH_2Cl_2 as reference. [b] [ROBs] 0.019 *M* buffered with 0.02 *M* AcONa. [c] Extrapolated value. [d] Rate ratio for *exo*-**1**-OBs/apoisobornyl-OBs. Rate ratio for *endo*-**1**-OBs/apobornyl-OBs. [f] [ROBs] 0.196 *M*.

Data obtained so far from the solvolysis of 1-substituted bicyclo[2.2.1]hept-2-yl derivatives with electron-releasing groups at the C-1 position do not, as Gassman and Marshall[3a] pointed out, indicate conclusively the existence or nonexistence of σ participation. It is of interest in this connection to investigate the effect of 1 and 7 substituents which destabilize a positive charge upon *exo*:*endo* rate and product ratios in apobornyl systems. Along this line the solvolysis of 7-ketonorbornyl,[3a] 1-carbomethoxyl-*exo*-2-norbornyl,[3b] 1-acetoxyl-*exo*-2-norbornyl,[3b] 7-chloro-2-norbornyl,[3c] and 1-chloro-2-norbornyl[3d] have been reported recently. We have found now that the solvolytic behavior of 1-cyanoapoiso- and 1-cyanoapobornyl brosylates[4] (*exo*- and *endo*-**1**-OBs) exhibits some interesting differences from the parent compounds.



exo-1-OH, R = H
exo-1-OBs, R = Bs
exo-1-OAc, R = Ac



endo-1-OH, R = H
endo-1-OBs, R = Bs
endo-1-OAc, R = Ac

The first-order rate constants for *exo*-**1**-OBs and *endo*-**1**-OBs are given in Table I. Whereas the observed rate decrease for the acetolysis at 25° for *endo*-**1**-OBs ($k_{\text{rel-}endo} = 2.43 \times 10^{-4}$) is close to that[5] calculated by the Taft relation,[7] indicating that the retardation is mainly an inductive one, *exo*-**1**-OBs is found to solvolize much more slowly ($k_{\text{rel-}exo} = 1.71 \times 10^{-7}$). Steric changes resulting from replacement of the 1-hydrogen by a cyano group are not expected to be so important as to exert large effects on the solvolysis rates of apoisobornyl and apobornyl brosylates. Assuming that apoisobornyl brosylate solvolysis is not assisted in the transition state by 1,6 σ participation and that introduction of the 1-cyano substituent results in an inductive effect on the rate only, the rate decrease would be expected to be equal for both *exo*-**1**-OBs and *endo*-**1**-OBs. If this assumption is not correct and 1,6 σ participation is in fact exerted in the parent apoisobornyl brosylate solvolysis but is inhibited inductively by the introduction of a 1-cyano substituent, then the rate decrease for *exo*-**1**-OBs would be expected to be much larger than for *endo*-**1**-OBs, which was actually the case. This indicates 1,6 σ participation in apoisobornyl but not in apobornyl brosylate solvolysis.

Among the structural features of the product pattern shown in Table II, the lack of both acetolysis and trifluoroacetolysis products having a rearranged carbon skeleton is in marked contrast to the case with the parent compounds.[2b] This feature is similar to that noted for the 1-carbomethoxy-*exo*-2-norbornyl derivative,[3b] but somewhat different from results with 7-chloro-2-norbornyl derivatives[3c] (about 9% rearrangement). These results are taken to indicate that in the case of 7-chloro-*exo*-2-norbornyl derivatives there remains the possibility of a partial 1,6 σ participation.

In spite of the lack of a carbon–carbon rearrangement, optical activities of the *exo*-**1**-OH from *exo*-**1**-OBs and of the *endo* epimer, shown in Table III, de-

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J. Amer. Chem. Soc., **87**, 375 (1965); (b) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *ibid.*, **87**, 376 (1965); A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *ibid.*, **87**, 378 (1965); S. Winstein, *ibid.*, **87**, 381 (1965); (c) H. C. Brown, *Chem. Brit.*, 199 (1966); H. C. Brown, *Chem. Eng. News*, **45** (7), 87 (1967); H. C. Brown and M. Rei, *J. Amer. Chem. Soc.*, **90**, 6216 (1968); H. C. Brown and S. Ikegami, *ibid.*, **90**, 7122 (1968); (d) H. L. Goering and K. Humski, *ibid.*, **90** 6213 (1968); H. L. Goering, C. Brown, and C. B. Schewene, *ibid.*, **90**, 6214 (1968).

(3) (a) P. G. Gassman and J. L. Marshall, *ibid.*, **88**, 2822 (1966); (b) J. W. Wilt and W. J. Wagner, *ibid.*, **90**, 6135 (1968); (c) P. G. Gassman and J. M. Hornback, *ibid.*, **91**, 4280 (1969); (d) A. J. Fry and W. B. Farnham, *J. Org. Chem.*, **34**, 2314 (1969).

(4) The synthesis of the model compounds and their structural assignment will be furnished in a full paper. New compounds obtained here gave satisfactory carbon and hydrogen analyses.

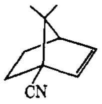
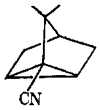
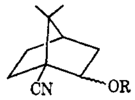
(5) Using $\rho^* = -2.32$[6] and $\sigma^* = +1.30$[7] one obtains $k_{\text{rel-}endo} = 9.64 \times 10^{-4}$. Considering the range over which the ρ^* values reported for *sec*-alkyl acetolyses vary, the agreement is a satisfactory one. Applying the lowest value found in literature for $\rho^* = -3.49$[8] the calculation gives $k_{\text{rel-}endo} = 2.9 \times 10^{-5}$, somewhat smaller than observed.

(6) C. J. Lancelot, J. J. Harper, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 4294 (1969).

(7) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 595.

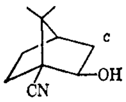
(8) A. Streitwieser, Jr., *J. Amer. Chem. Soc.*, **78**, 4935 (1956).

Table II. Yields of Solvolysis Products[a]

 **2**	 **3**	 sum[b] of *exo*- and *endo*-**1**-OR	*exo*-**1**-OAc: *endo*-**1**-OAc[c]	Unknown substances
		exo-**1**-OBs:AcOH,[d] 130°		
8.6	34	52.4	98.2:1.8	5
		endo-**1**-OBs:AcOH,[d] 160°		
1.0	42.0	57.0	96.9:3.1	
		exo-**1**-OBs:CF_3CO_2H,[e] 100°		
	32.5	64.4		3.1

[a] Obtained by vpc after ten half-lives using the area correction factors 1:1:1.05 for **2**, **3**, and the sum of *exo*- and *endo*-**1**-OR, respectively. [b] Vpc peaks of the *exo* and *endo* epimer overlapped, both in R = Ac and R = CF_3CO. [c] Calculated from *exo*-**1**-OH:*endo*-**1**-OH area ratios in vpc. [d] Buffered with 0.02 *M* NaOAc. [e] Buffered with 0.1 *M* CF_3CO_2Na.

Table III. $[\alpha]_D$ Values[a] of Solvolysis Products from Optically Active 1-Cyanoapoisobornyl *p*-Bromobenzenesulfonate[b] and 1-Cyanoapobornyl *p*-Bromobenzenesulfonate[b]

	exo-**1**-OBs[e] AcOH, 130°	*endo*-**1**-OBs[f] AcOH, 160°	*exo*-**1**-OBs,[e] CF_3CO_2H, 100°
	−7.1 ± 1.5[g]	−12.1 ± 0.4[h]	−4.5 ± 1.7[i]

[a] Measured in MeOH at room temperature. [b] These are derived from optically active ketopinic acid, $[\alpha]^{25}D$ +30.0 ± 0.7° (*c* 1.055, MeOH) [lit. $[\alpha]^{24}D$ +31.2° (alcohol), "Elsevier's Encyclopedia of Organic Chemistry," Vol. 12A, Series III, E. Josephy and F. Radt, Ed., Amsterdam, 1948, p 959]. [c] $[\alpha]^{25}D$ −30.8 ± 0.7° (*c* 1.050), contains no more than 0.2% *endo* epimer.[d] [d] $[\alpha]^{25}D$ +63.6 ± 2.2° (*c* 0.470). [e] $[\alpha]^{26}D$ −20.7 ± 0.4° (*c* 1.640). [f] $[\alpha]^{26}D$ +14.7 ± 0.5 (*c* 1.094). Concentration for the measurements of *exo*-**1**-OH products: [g] *c* 0.309. [h] *c* 0.356. [i] *c* 0.265.

creased to about 23 and 39%, respectively, on acetolysis (the absolute rotation[9] of **2** has not been determined). The higher activity decrease observed on trifluoroacetolysis of *exo*-**1**-OBs compared with that on acetolysis suggests that in trifluoroacetolysis a 6,2-hydride shift occurs much more frequently than does solvent capture of the carbonium ion formed.

The predominance of *exo* orientation of the acetate (98.2% *exo*-**1**-OAc from *exo*-**1**-OBs and 96.9% *exo*-**1**-OAc from *endo*-**1**-OBs), though less than that in the apoiso- and apobornyl (>99.5% *exo*-acetate[2b]) and the norbornyl systems (>99.98% *exo*-acetate[2b]), seems to require an assumption of existence of an assisting group from the *endo* side. This is at present tentatively assigned to C-6 hydrogen bridging[2b] or to a rapidly equilibrating pair of ions.[10] Another interesting fact, the small *exo*-**1**-OBs:*endo*-**1**-OBs rate ratio in acetolysis (2.9 at 25°, 8.3 at 100°), but a larger one (83 at 25°) in trifluoroacetolysis, might also be explained by assuming C-6 hydrogen participation[11] in the ionization of *exo*-**1**-OBs.

Further investigations of the solvolysis of 1-substituted apoisobornyl and its epimer are now in progress.

Acknowledgment. We are grateful to Dr. Hiroshi Tanida for his valuable discussions and encouragement.

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(9) $[\alpha]^{25}D$ for **2** isolated from acetolysis products is −20.0 ± 0.5° (*c* 1.206, MeOH).

(10) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, pp 140–158, 174–168.

(11) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, 76, 4501 (1954); A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 141. Similar rate increases due to hydrogen participation were found in the solvolysis of the primary alkyl tosylate in trifluoroacetic acid,[12] fluorosulfuric acid,[13] and sulfuric acid.[14] But as one of the referees suggested, the dipole–dipole repulsive interaction between the 1-cyano group and the polarized C^+–OBs^- dipole is another interpretation for the *exo*:*endo* rate ratio. This interaction[15] causes the difference of the ground-state energy between the two epimers (*exo*-1-OBs > *endo*-1-OBs) due to the smaller angle between the two dipoles in *exo*-1-OBs compared to that in *endo*-1-OBs.

(12) I. L. Reich, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 5635 (1969).

(13) A. Diaz, I. L. Reich, and S. Winstein, *ibid.*, **91**, 5637 (1969).

(14) P. C. Myhre and K. S. Brown, *ibid.*, **91**, 5639 (1969).

(15) P. E. Peterson, R. J. Bopp, D. M. Chevli, E. L. Curran, D. E. Dillard, and R. J. Kamat, *ibid.*, **89**, 5902 (1967).

Ryonosuke Muneyuki, Toshisada Yano
Shionogi Research Laboratory Shionogi and Company, Ltd.
Fukushima-ku, Osaka, Japan

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Book Reviews

Aromatic Character and Aromaticity. By G. M. Badger, Vice-Chancellor, University of Adelaide. Cambridge University Press, 32 East 57th St., New York, N. Y. 1969. viii + 133 pp. 14 × 22 cm. $6.00.

Aromaticity is a field in which many chemists are interested at present, and in which considerable advances are being made. The monograph by Badger is therefore a timely one.

The book commences with a consideration of benzene, including the application of physical methods and wave mechanics to the benzene problem; polycyclic benzenoid hydrocarbons and heterocyclic aromatic compounds are then dealt with. The second part describes some consequences of aromaticity, including bond lengths, resonance energies, electronic absorption spectra, and induced ring currents. The third part deals with nonbenzenoid hydrocarbons; Hückel's and Craig's rule are considered first, followed by a systematic description of various conjugated monocyclic hydrocarbons (neutral and ionic, bridged and unbridged) containing 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 24, and 30 π electrons. The final part, which considers more complex systems, deals with fulvenes and fulvalenes, metallocenes, and polycyclic compounds.

The book is intended for students in the final year of their undergraduate chemistry course and for those beginning graduate work The subject is therefore not covered exhaustively or in great depth, and only general references to the most important topics are given at the end. The book is very readable and the material is attractively set out. It certainly succeeds admirably in presenting the subject of aromaticity in a relatively simple way.

Some minor criticisms can be made. The order of presentation does not always appear to be completely logical (*e.g.*, aromaticity is defined and some consequences of aromaticity are considered *after* the section on benzene, but *before* that on nonbenzenoid hydrocarbons), and some of the theoretical treatment is rather old-fashioned. Also, the book in places is out-of-date; for instance, it is stated (p 100) that [18]annulene could not be made to undergo electrophilic substitution reactions, whereas the successful nitration and acylation in fact were described in 1967.

In summary, the book is definitely recommended to anybody unfamiliar with the subject, who wishes to become acquainted with the exciting field of aromaticity.

Franz Sondheimer
Chemistry Department, University College
London W.C.1, England