J. Org. Chem. 1988, *53*, 661–675 661

Remote Inductive Effects in the Solvolysis of Secondary and Tertiary 2-Norbornyl Derivatives. Evidence for Nonclassical Stabilization of the 2-Norbornyl Cation

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Received August 1, 1986

This paper deals with evidence for the structure of the 2-norbornyl cation, when it occurs as an intermediate in solvolysis reactions in relatively nucleophilic media. Seen in a wider context, the 2-norbornyl cation has been shown unequivocally to have a bridged structure in isolation and in nonnucleophilic media. Thermochemical comparisons in the gas phase and in superacid media show the secondary 2-norbornyl cation to be exceptionally stable; at high levels of ab initio theory, the symmetrically bridged structure is the only minimum and the classical cation does not even exist. Spectroscopic evidence (e.g., NMR at 4 K, ^{1}H and ^{13}C chemical shift analyses, ESCA, etc.) in superacids clearly favors the nonclassical structure. The same is true for the 2-norbornyl cation as a reactive intermediate. Solvolysis of 2-*exo*-norbornyl tosylate in the very weakly nucleophilic hexafluoroisopropyl alcohol is exceptionally fast, whereas the endo isomer reacts at a normal rate. While high exo/endo ratios also are found for 2-methyl- and 2-aryl-substituted norbornyl systems, effects other than bridging must be responsible, since these tertiary systems are shown to respond differently than the secondary systems with regard to secondary deuterium isotope effects or when additional substituents are introduced. Thus, electronegative substituents at C_5 as well as at C_6 reduce the exo/endo ratio significantly; e.g., a dichloro group at C_5 reduces the parent value of 860 to 9.4. While substituents at C_6 suffer from the potential disadvantage of electronic interaction with the leaving group at C_2, substituents at C_5 are free from this complication. The reduction of exo/endo ratios by deactivating substituents is shown to be stronger in weakly nucleophilic solvents, compared to 60% ethanol. Dipolar interactions between substituents at C_5 and the leaving group at C_2 can be excluded by an analysis of the spatial arrangement of the 5-CN group relative to the brosylate group; different orientations do not affect the relative rates significantly. The rate constants of deactivated 2-norbornyl sulfonates can be correlated by linear free energy relationships (LFER), as also has been shown more extensively by Grob. Rates of *exo*-sulfonates are unique in their exceptionally large response to polar substituents. Since no break is observed in the LFER, including the parent 2-*exo*-norbornyl sulfonate, a graded set of mechanisms proceeding from strong, to weak, to no participation is the most likely explanation for the behavior. The possibility of rapid equilibration between partially bridged 2-norbornyl cation geometries as well as heavy atom tunneling is analyzed in detail and rejected by structural considerations based both on high level ab initio calculations and on Laube's X-ray structure of a partially bridged 1,2-dimethyl-2-norbornyl cation derivative.

The symmetrically bridged structure of the 2-norbornyl cation (1) is now established unambiguously.[1-9] A wealth of spectroscopic information obtained by direct measurements on the stable ion in superacid media rules out the alternative formulation, a rapid equilibration between two enantiomeric cations, 2, with classical geometries (bond lengths and bond angles).[9-11] The experimental evidence, quite different in nature, all leads to the same conclusion.

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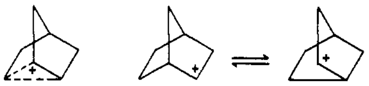
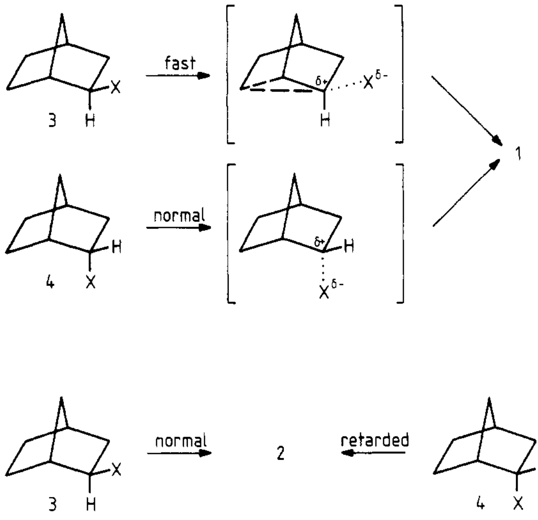
No dynamic NMR equilibrium corresponding to **2** can be frozen out even at liquid helium temperature.[2] Deuterium isotopes should perturb equilibria like **2** ⇌ **2′** much more than is observed experimentally.[3] The ^{13}C and ^{1}H NMR chemical shifts are inconsistent with **2**, but like the other observations, are in full accord with **1**.[1,3,8] An ab initio method (IGLO) for the accurate calculation of ^{1}H and ^{13}C NMR and chemical shifts now differentiates clearly between classical and nonclassical structures; these data "strongly support a symmetrically bridged geometry of the norbornyl cation".[8] ESCA spectra also exclude the rapidly equilibrating classical formulation.[4]


1 **2** **2′**

No direct detailed geometrical information concerning the parent 2-norbornyl cation, e.g., an X-ray crystal structure, is yet available experimentally.[12a] However, increasingly sophisticated calculations, which now have been carried out at near the state of the art ab initio levels, provide geometries, energies, and electron distributions.[6] The use of polarization basis sets and inclusion of electron correlation corrections in the final calculations give results that are unambiguous. No minimum corresponding to **2** can be found on the potential energy surface; thus, the classical 2-norbornyl cation (**2**) can be said not to exist. The only minimum on the 2-cation potential energy surface is the symmetrically bridged structure **1**, and *this single potential well is quite sharp* and not at all flat, as is sometimes discussed. Energetic data, obtained calculationally, agree with those found experimentally in the gas phase.[7] Depending on the choice of reference comparisons, the extra stabilization due to bridging of the 2-nornyl cation is 11–15 kcal/mol. This also corresponds to the energy difference between **1** and assumed models for the hypothetical classical ion, **2**.[5-7]

The most recent papers[7f-h] that analyze the gas-phase data for the 2-norbornyl cation are particularly convincing. Lossing and Holmes have shown through an extensive study that for classes of ions having common structural features (e.g., primary, secondary, etc.), $D(R^+-H^-)$ is a linear function of the logarithm of the number of atoms in R^+. This treatment corrects for "size effects", i.e., energy lowering of charged species by polarization. On this basis, the $D(R^+-H^-)$ value for the 2-norbornyl cation lies 10 kcal/mol below the value it would have as a secondary ion, indicating a special stabilization.[7f] Kebarle et al.[7g] measured the chloride ion affinity of the 2-norbornyl cation and showed that the results lead to essentially the same conclusion as that of the earlier hydride affinity measurements[7a-c] (which were accurately reproduced),[7g] namely, that the 2-norbornyl cation is unusually stable relative to other secondary cations. For example, the 2-norbornyl cation is more stable than the cyclopentyl cation by 12.7 and 11.4 kcal/mol according to hydride and chloride ion transfer measurements, respectively.[7g] The quantitative agreement with the calculations,[6] which show the ion to be bridged, is noteworthy.

Scheme I. Interpretation of Solvolysis Rates of 3 and 4 by Winstein and by Brown, Respectively.



The overwhelming spectroscopic, thermochemical, and theoretical evidence favoring **1**,[1-8] which continues to accumulate, has not been challenged meaningfully[9-11] (for the view of an "innocent bystander" and other reviewers, see ref 5). The first information, necessarily indirect, that led to the nonclassical interpretations was based on solvolysis rates and products. Brown is not convinced that such data requires a bridged ion intermediate in solvolysis media.[9-11] One purpose of this paper is to discuss this aspect of the problem and to answer Brown's objections.

Although the first bridged carbocation formulation was published in 1939,[12] Winstein and Trifan were the first to ascribe the detailed behavior of the 2-norbornyl cation system to the intermediacy of a symmetrical intermediate (Scheme I).[13] Indeed, this interpretation of over 30 years ago has proven to be almost exactly correct. Secondary 2-*exo*-norbornyl derivatives **3** solvolyze hundreds of times faster than the 2-endo epimer **4**. According to Winstein and Trifan, the endo rate was "normal"; it corresponded to that of other typical secondary substrates without neighboring groups. Participation of the C_1–C_6 bonding electrons during ionization led to the accelerated rate of the 2-exo isomer. Scheme I contrasts this interpretation with that later espoused by Brown.[14] He considered the exo isomer **3** to be "normal", but the endo counterpart to be "slow". However, Brown's explanation for the alleged slow solvolysis rate of the endo isomer was based on an assumed model rather than independent evidence and has found no support subsequently.[5]

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(8) Schindler, M. *J. Am. Chem. Soc.* **1987**, *109*, 1020.

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(13) Winstein, S.; Trifan, D. S. *J. Am. Chem. Soc.* **1949**, *71*, 2953; **1952**, *74*, 1147, 1154.

(14) Brown, H. C. *Science (Washington, D.C.)* **1946**, *103*, 385.

Table I. Relative Rates of Solvolysis of Various Aliphatic Tosylates in HFIP at 25 °C[a]

tosylate	rel rate, 25 °C, HFIP	RT ln rel rate, kcal/mol
2-propyl	1.0	0.0
2-butyl	14.3	1.6
2-pentyl	17.4	1.7
3-pentyl	76	2.6
4-heptyl	141	2.9
cyclopentyl	377	3.5
cyclohexyl	24	1.9
pinacolyl	955	4.1
2-adamantyl	134	2.9
2-*endo*-norbornyl	99	2.1
2-*exo*-norbornyl	155, 450	7.1

[a] Reference 16a. For a larger collection of secondary tosylate HFIP solvolysis data, and a quantitative interpretation, see ref 16b.

Most of Winstein's early solvolysis data were obtained in acetic acid, which was then regarded as being a limiting solvent, or nearly so. However, our work starting in 1970[15] established conclusively that nucleophilic solvent assistance contributed appreciably to the acetolysis rates of simple secondary substrates. Instead, highly fluorinated solvents are needed to establish the unassisted rate constants for S_N2-prone substrates. The relative rates of a set of representative secondary substrates in hexafluoroisopropyl alcohol (HFIP), one of the least nucleophilic solvents in which measurements can be made, are presented in Table I.[16] This is the best data currently available. The reader can judge for himself which of the alternative explanations the Scheme I is the more appropriate. The 2-*endo*-norbornyl relative rate is in the middle of the range exhibited by the comparison molecules; "retarded" (see Scheme I) it certainly is not. The 2-*endo*-norbornyl (4) value is somewhat less than that of cyclopentyl, but this reflects the ability of the latter system to relieve eclipsing interactions on ionization.[17] The rigid norbornyl system cannot do this effectively; while the C_2–C_3 eclipsing interaction is relieved on ionization, the staggered C_1–C_2 interaction becomes more nearly eclipsed.[18] Recent force-field calculations, which correlate successfully the rates of solvolysis of a large number of secondary tosylates with the strain relieved upon ionization, estimate that in the ionization of the 2-*endo*-norbornyl tosylate the steric hindrance to the expulsion of the leaving group is less than 1 kcal/mol.[16c,19] Furthermore the same type of analysis shows that the *exo*-2-norbornyl tosylate reacts faster than expected, indicating special stability.[16c,19] Brown's extrapolation of the behavior of isopropyl and cyclopentyl to model 2-*exo*-norbornyl[9–11] is unjustified. More than "size" influences solvolysis rates.

Table II. Exo/Endo Rate Ratio for Secondary and Tertiary 2-Norbornyl Derivatives in Various Solvents

R	X	solvent	k_{exo}/k_{endo} (25 °C)
H	OTs	acetic acid	280[a]
H	OBs	acetic acid	350[a]
H	OBs	acetic acid	1600[b]
H	OTs	60% ethanol	1000[c]
H	OTs	97% TFE	1040[c]
H	OTs	TFA	1120[d]
H	OTs	97% HFIP	1410[e]
H	OBs	97% HFIP	1746[f]
H	OMes	H_2O	1590[g]
CH_3	OPNB	80% acetone	885[h]
CH_3	OPNB	80% acetone	396[i]
C_6H_5	OPNB	80% acetone	127[j]
CH_3	ODNP	80% ethanol	171[j]

[a] Reference 13. [b] Polarimetric value: Winstein, S.; Clippinger, E.; Howe, R.; Vogelfanger, E. *J. Am. Chem. Soc.* **1965**, *87*, 376. [c] Reference 23b. [d] Nordlander, J. E.; Grutzmacher, R. R.; Kelly, W. J.; Jindal, S. P. *J. Am. Chem. Soc.* **1974**, *96*, 181. [e] See Table III. [f] Reference 24. [g] Bentley, T. W.; Bowen, C. T.; Parker, W.; Watt, C. I. F. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1244. [h] Rei, M.-H.; Brown, H. C. *J. Am. Chem. Soc.* **1966**, *88*, 5335. [i] Grob, C. A., private communication. [j] Brown, H. C.; Ravindranathan, M.; Takeuchi, K.; Peters, E. N. *J. Am. Chem. Soc.* **1975**, *97*, 2900. ODNP = 2,4-dinitrophenyl ether. At 100 °C, see ref 22.

It is well to remember that the isomeric 7-norbornyl derivatives solvolyze 10^7 times slower than model secondary substrates.[18] Why does Brown's simple $C_3 \rightarrow C_5 \rightarrow C_7$ extrapolation[9–11] not work there as well?[9–11] As noted above, size effects influence the energies of ions in the gas phase,[7] but this is not expected in solution where solvation is more effective than the polarization stabilization due to alkyl groups.

Brown's central argument concerned the influence of substituents at C_2.[9–11] For example, a 2-methyl and especially a 2-phenyl group should stabilize the corresponding classical carbocation more than the bridged alternative. Tertiary substrates were thus proposed as models for classical behavior. Since product and rate data of exo and endo derivatives are complimentary,[9–11] rate ratio comparisons suffice to make the point. These data have also been refined over the years. The recognition that 2-*endo*-norbornyl solvolysis is somewhat solvent assisted[16] (contrary to Brown's assertion)[9–11,20] has led to a revision of the secondary rate ratio upward. On the other hand, Brown's tertiary 2-methylnorbornyl exo/endo rate ratio[9–11] could not be reproduced and has been revised downward.[21] Table II summarizes the best results. The tertiary exo/endo rate ratios are significantly lower than the secondary ratio, but are still noteworthy in being quite large. This is due to steric effects[9] that are naturally larger in the tertiary derivatives than in the secondaries but may also be due to some residual anchimeric assistance even in the tertiary exo methyl systems.[5,22]

Brown's inference that the tertiary and secondary ratios have the same origin (which he attributes to steric effects) has been refuted by numerous further examples.[9,22–27]

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(16) (a) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5466 and references cited therein. That 2-*endo*-norbornyl is a weak k_s substrate has been confirmed by McMannus et al. (b) McMannus, S. P.; Neamati-Mazraek, N.; Karaman, R. M.; Harris, J. M. *J. Org. Chem.* **1986**, *51*, 4876. (c) Schneider, H.-J.; Becker, N.; Schmidt, G.; Thomas, F. *J. Org. Chem.* **1986**, *51*, 3602.

(17) Cf. (a) Brown, H. C. *J. Chem. Soc.* **1956**, *1248*. (b) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 701.

(18) Cf. ref 17b and 9, pp 119–122; 146–149.

(19) (a) Müller, P.; Blanc, J.; Perlberger, J.-C. *Helv. Chim. Acta* **1982**, *65*, 1418. (b) Müller, P.; Mareda, J. *Ibid.* **1985**, *68*, 119. Also see ref 16c.

(20) (a) Brown, H. C.; Ravindranathan, M.; Chloupek, F. J.; Rothberg, I. *J. Am. Chem. Soc.* **1978**, *100*, 3143. Brown, H. C.; Rao, C. G. *J. Org. Chem.* **1980**, *45*, 2113. (b) Raber, D. J.; Neal, W. C., Jr.; Dukes, M. O.; Harris, J. M.; Mount, D. L. *Ibid.* **1978**, *100*, 8137. (c) Harris, J. M.; Mount, D. L.; Raber, D. J. *Ibid.* **1978**, *100*, 3139.

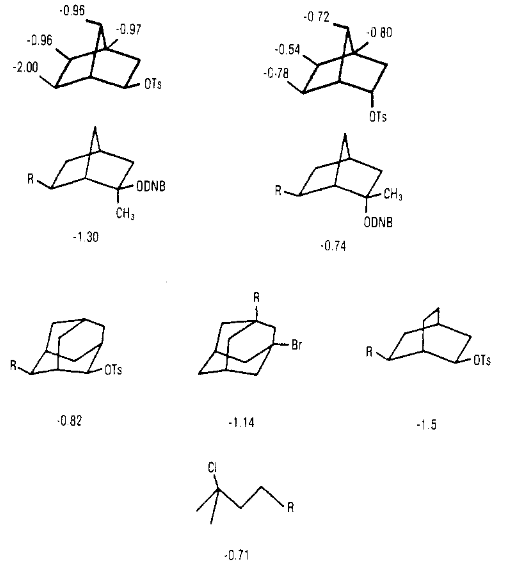
(21) (a) Grob, C. A., private communication. See also: (b) Grob, C. A.; Waldner, A. *Helv. Chim. Acta* **1983**, *66*, 2481.

(22) Grob, C. A.; Sawlewicz, P. *Tetrahedron Lett.* **1984**, *25*, 2973.

(23) (a) Schleyer, P. v. R.; Stang, P. J.; Raber, D. J. *J. Am. Chem. Soc.* **1970**, *92*, 4725. (b) Lenoir, D. *Chem. Ber.* **1975**, *108*, 2055.

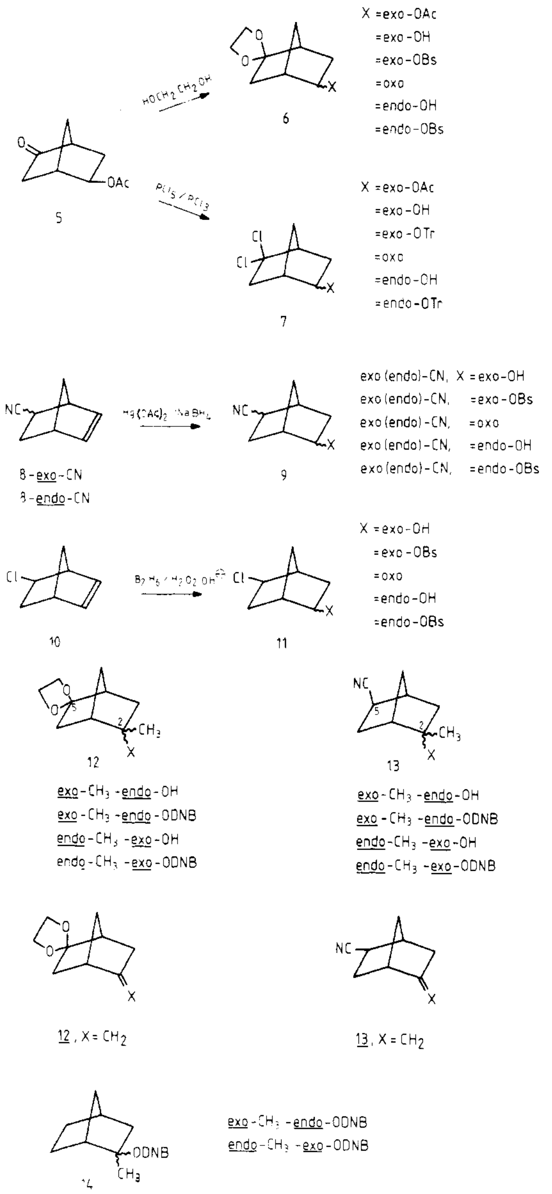
(24) Lenoir, D.; Röll, W.; Weiss, E.; Wenke, G. *Tetrahedron Lett.* **1976**, 1991. Apeloig, Y.; Arad, D.; Lenoir, D.; Schleyer, P. v. R. *Ibid.* **1981**, 879.

Scheme II. Summary of Grob's ρ_I Values[26] Showing the Influence of Substituents at the Position Indicated. Note, in Particular, the Unequally Large Value, -2.0, for the 6-Substituted-2-*exo*-norbornyl System, the Small Exo/Endo Corresponding Tertiary Difference, and the Effects of Groups at the 5-Norbornyl Position.



Secondary deuterium isotope effects differentiate clearly between secondary and tertiary systems and show clearly that bridging is involved in the 2-*exo*-norbornyl solvolysis transition state.[27] To mention only one example, attachment of a five-membered ring at C_5–C_6 (as far away from the reaction site as possible) has very little effect on the tertiary exo/endo ratio.[28] This is consistent with a steric interpretation. However, the effect of the additional ring in this tetrahydrodicyclopentadiene system on the secondary exo/endo ratio, which should be less prone to steric effects, is actually much greater, and the exo/endo ratio is much smaller than that in norbornyl.[28] A different, i.e., electronic, origin of the secondary rate ratios is indicated. Similarly, dimethyl groups can be placed at C_7 or at C_6; these influence the tertiary exo/endo rate ratios enormously; bumping between groups is relieved on ionization.[29] In contrast, the secondary systems are influenced to a much lesser extent and respond in qualitatively different ways. Despite frequent challenges, Brown has not provided a variable rationalization of this and similar behavior, which are perfectly consistent with a bridging interpretation but not with the equilibrating classical ion hypothesis.

Scheme III. Syntheses of Compounds, See Text.[a]



[a] The following abbreviations are used: OAc = $OOCCH_3$; OBs = OSC_6H_4-Br-*p*; OTr = $OSO_2CH_2CF_3$; ODNB = 3,5-$(NO_2)_2C_6H_3CO_2$.

In the late 1960s, the similar phenonium ion controversy was resolved by the use of graded sets of aryl substrates with remote electron-donating and electron-withdrawing substituents.[30] Steric problems were not involved, and the inductive effects of aryl substituents (k_s pathway) could be disected from their ability to encourage or discourage neighboring group participation (k_Δ pathway). We recognized that a similar strategy could be applied to the 2-norbornyl system, and began, along with other investigators, to explore these possibilities some years ago.[23] Along with our preliminary reports,[23,24] other groups have

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(27) (a) Maskill, J. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1889; (b) *J. Am. Chem. Soc.* **1976**, *98*, 8482. (c) Sunko, D. E.; Hehre, W. J. *Progr. Phys. Org. Chem.* **1983**, *14*, 205 and literature cited.

(28) Nordlander, J. E.; Neff, J. R.; Moore, W. B.; Apeloig, Y.; Arad, D.; Godleski, S. A.; Schleyer, P. v. R. *Tetrahedron Lett.* **1981**, *22*, 4921 and literature cited.

(29) Comments by P. v. R. Schleyer, ref 9, p 146, 214. Also see, ref 52. (a) Altmann-Schaffner and Grob (Altmann-Schaffner, E.; Grob, C. A. *Helv. Chim. Acta* **1987**, *70*, 43) have now confirmed the observations in ref 52, but their interpretation does not take the destabilizing effects of alkyl substituents on bridging cations (see ref 55) into account.

(30) Lancelot, C. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1969**, *91*, 4291. Lancelot, C. J.; Harper, J. J.; Schleyer, P. v. R. *Ibid.* **1969**, *91*, 4294. Harris, J. M.; Schadt, F. L.; Schleyer, P. v. R.; Lancelot, C. J. *Ibid.* **1969**, *91*, 7508.

Table III. Solvolysis Rates of 5-Substituted 2-Norbornyl Derivatives

compd	solvent[a]	temp (°C)	k (s^{-1})	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/mol)
3-OBs	60% E	25.0	8.30×10^{-3}		
	97% HFIP	9.2	8.20×10^{-2}		
		−4.7	1.74×10^{-2}	15.6	−8.0
		25.0	3.91×10^{-1}[b]		
3-OTs	97% HFIP	25.0	1.10×10^{-1}[b]		
4-OBs	60% E	74.9	2.28×10^{-3}		
		49.5	1.75×10^{-4}	21.9	−7.9
		25.0	9.67×10^{-6}		
	97% HFIP	50.1	2.54×10^{-3}		
		25.0	2.24×10^{-4}	18.0	−15.0
4-OTs	97% HFIP	25.0	7.80×10^{-6}		
6-*exo*-OBs	60% E	75.3	1.71×10^{-3}		
		50.1	4.84×10^{-5}	25.0	0.3
		25.0	3.30×10^{-6}[b]		
	97% HFIP	52.9	1.34×10^{-3}		
		24.4	6.73×10^{-5}	19.6	−11.7
		25.0	7.21×10^{-5}[b]		
6-*endo*-OBs	60% E	99.4	3.74×10^{-4}		
		75.0	3.13×10^{-5}	25.4	−6.5
		25.0	5.18×10^{-8}[b]		
	97% HFIP	75.0	4.23×10^{-4}		
		49.9	4.11×10^{-5}	20.3	−16.0
		25.0	2.71×10^{-6}[b]		
7-*exo*-OTr[c]	60% E	80.6	9.20×10^{-4}	21.6	−12.8
		55.8	4.76×10^{-5}		
		25.0	1.42×10^{-6}[b]		
7-*endo*-OTr[c]	60% E	99.5	2.10×10^{-4}		
		80.7	2.64×10^{-5}	20.1	−22.0
		55.8	4.65×10^{-6}		
		25.0	1.51×10^{-7}[b]		
9-*exo*-CN-*exo*-OBs	60% E	89.3	2.74×10^{-3}		
		75.0	7.21×10^{-4}	23.5	−5.2
		65.0	2.39×10^{-4}		
		25.0	1.90×10^{-6}[b]		
	97% TFE	100.0	4.00×10^{-4}		
		89.3	1.46×10^{-4}	21.7	−16.5
		75.0	4.51×10^{-5}		
		25.0	1.95×10^{-7}[b]		
9-*exo*-CN-*endo*-OBs	60% E	100.0	3.19×10^{-4}		
		89.6	1.23×10^{-4}	23.9	−10.8
		75.0	2.94×10^{-5}		
		25.0	7.66×10^{-8}[b]		
	97% TFE	100.0	5.24×10^{-5}	24.7	−11.8
		89.3	1.89×10^{-5}		
		25.0	9.10×10^{-9}[b]		
9-*endo*-CN-*exo*-OBs	60% E	75.0	8.39×10^{-4}		
		60.0	1.67×10^{-4}		
		50.3	4.84×10^{-5}	25.1	−0.8
		25.0	1.67×10^{-6}[b]		
9-*endo*-CN-*endo*-OBs	60% E	115.6	5.90×10^{-4}		
		100.0	1.70×10^{-4}		
		89.2	5.95×10^{-5}	23.5	−13.3
		25.0	4.46×10^{-8}[b]		
11-*exo*-OBs	60% E	61.6	8.16×10^{-4}		
		50.0	1.97×10^{-4}	25.0	3.4
		36.2	3.22×10^{-5}		
		25.0	6.50×10^{-6}[b]		
11-*endo*-OBs	60% E	95.0	1.77×10^{-4}		
		75.3	3.28×10^{-5}	19.1	
		25.0	3.09×10^{-7}[b]		
12-*exo*-ODNB	60% acetone	100.0	1.04×10^{-4}		
12-*endo*-ODNB	60% acetone	100.0	4.30×10^{-6}		
13-*exo*-ODNB	60% acetone	125.0	5.52×10^{-4}		
		100.0	4.65×10^{-5}	28.5	−2.5
		25.0[b]	2.38×10^{-9}		
13-*endo*-ODNB	60% acetone	142.6	7.02×10^{-5}		
		125.0	1.50×10^{-5}		
		116.0	6.25×10^{-6}	28.8	−8.9
		100.0[b]	1.19×10^{-6}		
		25.0[b]	5.45×10^{-11}		
14-*exo*-ONDB	60% acetone	100.0	4.20×10^{-3}		
14-*endo*-ONDB	60% acetone	100.0	2.80×10^{-5}		

[a] E = ethanol; HFIP = hexafluoroisopropyl alcohol; TFE = trifluoroethanol. [b] Extrapolated. [c] Tr = $SO_2CH_2CF_3$ (tresylate). A conversion factor of k(OTr)/k(OBs) = 33, based on the solvolysis of the corresponding parent 2-norbornyl derivative, was used.

published their observations as well.[25] Grob's extensive studies are particularly impressive.[21,26,29a]

Using a number of substituents in each case, Grob's group has evaluated the sensitivity of reaction rates, ρ_I, in a variety of norbornyl and model polycyclic and acyclic systems. Scheme II summarizes the data. For the most part, values of ρ_I for β-substituted systems do not vary greatly but tend to be a little larger when the substituent and the leaving group describe "W-like" arrangements. The tertiary norbornyl derivatives with 6-substituents and the secondary 2-*endo*-norbornyl system can be taken as reference standards. The single, outstanding exception in Scheme II is the 6-substituted 2-exo-norbornyl series; the ρ_I value is nearly twice as large as the corresponding tertiary exo ρ_I value.

Brown's steric rationalization for the high exo/endo ratio for the parent secondary 2-norbornyl derivatives is once again negated by Grob's results.[26,29a] An exo substituent at C_6 cannot interfer sterically with reactions at C_2 and yet actual cases of endo compounds solvolyzing faster than exo (inverse exo/endo ratio) have been found by Grob.[26,29a] In contrast, the electronic effects of the 6-substituents influence the C_1–C_6 bonding electrons that become delocalized during departure of the leaving group; the solvolysis rates are influenced markedly. In no other case in Scheme II is the extent of such bridging/hyperconjugation (these are both manifestations of the same type of electronic interaction)[31] involvement so extensive. While we do not agree[24] with some aspects of Grob's detailed interpretations[26,29a] (see Discussion and Conclusions, below), his demonstrations of the special electronic nature of the secondary 2-*exo*-norbornyl system are conclusive: "The inductivity patterns...thus confirm the hypothesis that differential C-participation is responsible for the high *exo*/*endo* rate ratios...".[26c] Recent studies have also demonstrated that the exo/endo rate ratio can be increased to ca. 10^5 by attaching strongly electron-withdrawing groups to C_3.[32] Thus, the tool of "increasing electron demand"[9] applied to secondary systems leads to the conclusion that the origin of the high exo/endo rate ratio in the solvolysis of 2-norbornyl tosylates is electronic, rather than steric.

Although the 6-position is the most sensitive to the influence of substituents, attached groups are involved more directly in the bridging process. For example, Grob has observed extremely fast solvolysis rates accompanied by fragmentations for some (electrofugal) substituents.[26] These data complicate the analysis and had to be omited.[26] We chose the 5-position for our study because of the more straightforward opportunities to interpret the results. The 5-position is the most remote from the 2-position in the norbornane molecules. Both 5-exo and 5-endo substituents should interfer minimally sterically with processes occurring at C_2 and the chief electronic effects should be inductive. By comparing the behavior of corresponding secondary and tertiary derivatives, we also show that the origin of the high exo/endo rate ratios in the secondary 2-norbornyl derivatives is primarily electronic in nature. Recently, Grob[22,26c,f] and Wilcox[25g] have communicated some results on solvolysis of C_5-substituted 2-norbornyl sulfonates, as has Kirmse[25i] on C_5,C_6-disubstituted derivatives.

Table IV. Exo/Endo Rate Ratios of 2-Norbornyl Derivatives

2-norbornyl deriv	solvent[a]	exo/endo rate ratio[b]
3-OBs/**4**-OBs	60% E	860
	97% HFIP	1746
6-OBs	60% E	63.7
	97% HFIP	26.6
7-OTr	60% E	9.4
9-*exo*-CN-OBs	60% E	24.8
	97% TFE	7.6[c]
	97% HFIP	5.0[d]
9-*endo*-CN-OBs	60% E	37.4
	97% HFIP	1.3[d]
11-OBs	60% E	21.0
12-ODNB	60% acetone	24.2[c]
13-ODNB	60% acetone	39.1[c]
		43.7
14-ODNB	60% acetone	150.0[c]

[a] Abbreviations as in Table III. [b] At 25 °C. [c] At 100 °C. [d] Tosylates, ref 25g.

Syntheses

The syntheses of all compounds were straightforward and are summarized in Scheme III. Starting from known **5**,[33] **8**-*exo*-CN, **8**-*endo*-CN,[34] and **10**,[35] the corresponding derivatives **6**, **7**, **9**, and **11** were prepared. The tertiary 2-norbornyl derivatives **12** and **13** were obtained from the corresponding 5-substituted ketones by standard procedures. More details are given in the Experimental Section.

The 6:4 Diels–Alder mixture of **8**-*exo*-CN and **8**-*endo*-CN[34] was separated by spinning band distillation. Oxymercuration–demercuration of **8**-*exo*-CN or **8**-*endo*-CN is both regio- and stereoselective. ^{13}C NMR[36] and more recently X-ray analysis[37] established that the sole products are the *exo*-5-substituted alcohols **9**. The electrophilic mercury attacks preferentially at C_6, thus generating a positive charge at C_5 rather than at C_6, as expected. Oxymercuration–demercuration of **10** yields a complex mixture of products, but hydroboration–oxidation unexpectedly gives **11**-*exo*-OH. The assignment of the structure is based on X-ray analysis[37] and ^{13}C NMR.[38] The reduction of the 5-monosubstituted ketones is generally less stereoselective than that of 2-norbornanone, leading to a ca. 8:2 mixture of the corresponding endo:exo alcohols (see Experimental Section).

Results

The solvolysis rates of the secondary sulfonates **6**, **7**, **9**, and **11** in 60% ethanol (buffered with 2,6-lutidine) were

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(31) Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Parkash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683 and references cited.

(32) (a) Wilcox, C. F., Jr.; Brungardt, B. *Tetrahedron Lett.* **1984**, *25*, 3403. (b) Creary, X.; Geiger, C. C. *J. Am. Chem. Soc.* **1983**, *105*, 7123.

(33) Meinwald, J.; Crandall, J. K. *J. Am. Chem. Soc.* **1966**, *88*, 1292.

(34) Alder, K.; Krieger, H.; Weiss, H. *Chem. Ber.* **1955**, *88*, 144.

(35) Schmerling, L.; Luvisi, J. P.; Welch, R. W. *J. Am. Chem. Soc.* **1956**, *78*, 2819.

(36) The following signals were observed for **9**-*exo*-CN-*exo*-OBs (in ppm): 29.7; 30.4; 33.9; 38.3; 40.6; 41.7; 83.0; 129.0; 132.7. The following absorptions were calculated for the norbornane carbons of **9**-*exo*-CN-*exo*-OBs from the known ^{13}C NMR spectra of 2-cyanobornane and 2-nornanol (see: Grutzner, J. B.; Jautelat, M.; Dence, J. B.; Smith, R. A.; Roberts, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 7107): 29.8 (C_5); 31.2 (C_6); 33.3 (C_7); 40.8 (C_3); 41.3 (C_4); 44.2 (C_1); 72.9 (C_2). Similarly the calculated absorptions of *exo*-6-cyano-*exo*-2-norbornyl brosylate are 24.9 (C_6); 33.3 (C_7); 35.1 (C_5); 35.5 (C_4); 40.3 (C_3); 50.0 (C_1); 72.8 (C_2). The calculated data for the 5-cyano derivative fits more closely the experimental data than that of the 6-cyano derivative.

(37) Arad, D.; Apeloig, Y., unpublished results. Full details of the molecular structure will be published elsewhere.

(38) The absorptions (in ppm) and the assignments (in parentheses) for **11**-*exo*-OBs are the following: 31.8 (C_7); 36.7 (C_6); 37.5 (C_3); 42.2 (C_1); 44.9 (C_4); 59.5 (C_5); 83.4 (C_2). Considerations similar to those in ref 36 show that these data fit more closely the **11**-*exo*-OBs structure than that expected for isomeric *exo*-6-chloro-*exo*-2-norbornyl brosylate.

Table V. Yield of Products (in Percent) from the Solvolysis of 5-Cyano-2-norbornyl Brosylates 9 in 60% Acetone, Buffered with a 2 M Excess of 2,6-Lutidine

	products				
brosylates	9-*exo*-CN-*exo*-OH	9-*endo*-CN-*exo*-OH	9-*exo*-CN-*endo*-OH	8-*exo*-CN	8-*endo*-CN
9-*exo*-CN-*exo*-OBs	53.2	43.7	0.9	1.0	1.0
9-*endo*-CN-*exo*-OBs	52.9	44.4	0.7	0.7	1.2
9-*exo*-CN-*endo*-OBs	67.3	30.7		1.5	0.4
9-*endo*-CN-*endo*-OBs	32.1	66.7	0.1	0.3	0.9

Table VI. Yield of Products (in Percent) from the Solvolysis of 5-Cyano-2-methyl-2-norbornyl Dinitrobenzoates in 60% Acetone, Buffered with a 2 M Excess of 2,6-Lutidine

	products			
substrate	13-*endo*-CH_3-*exo*-OH	13-*exo*-CH_3-*endo*-OH	13-CH_2	23
13-*endo*-CH_3-*exo*-ODNB	32.4	0.5	27.5	39.6
13-*exo*-CH_3-*endo*-ODNB	57.8	2.6	35.7	3.8

measured conductometrically.[39] Good first-order kinetics were observed in all cases. The epimeric **6**-OBs and **9**-OBs rate constants were also determined in 97% trifluoroethanol (97% TFE) as well as the rate constants for the epimeric (parent 2-norbornyl tosylates (**3**-OTs, **4**-OTs) in 97% hexafluoroisopropyl alcohol (97% HFIP). The solvolysis rates of the tertiary dinitrobenzoates **12**, **13**, and **14** were determined by potentiometric titration of the 3,5-dinitrobenzoic acid liberated. Potentiometric titration is more convenient and more accurate than the use of indicators.[40] All solvolysis rates are summarized in Table III. Relative comparisons are generally made at 25 °C (Table IV). For secondary and tertiary 5-cyano-2-norbornyl derivatives, we have also carried out a careful gas chromatographic analysis of the solvolysis products in 60% acetone; the results (see Tables V and VI) will be discussed below.

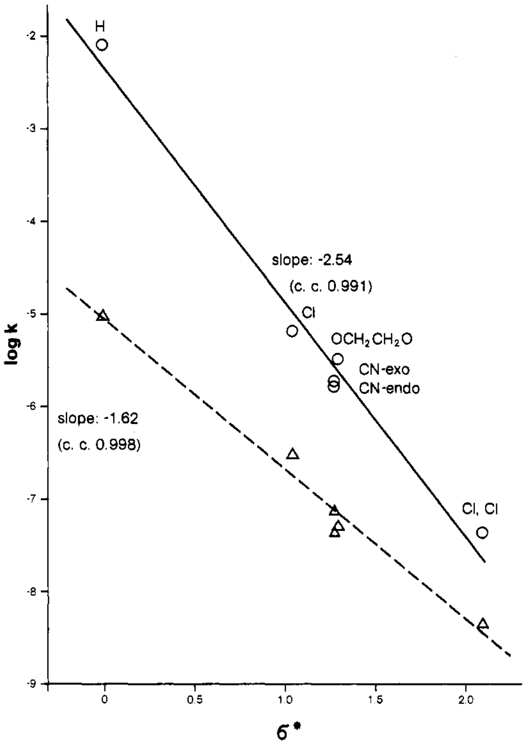

Figure 1. Linear free energy relationship for solvolysis of 5-substituted 2-norbornyl brosylates: solid line, *exo*-brosylates; broken line, *endo*-brosylates.

Discussion

As expected for a cationic process, electronegative substituents at C_5 reduce the solvolysis rates of both the *exo*- and the *endo*-2-norbornyl esters significantly (Table III). Polar substituents at other positions behave similarly.[23-26] The rate-retarding effect of the 5-substituent depends on the system and follows the order secondary exo > secondary endo > tertiary exo > tertiary endo. The largest effect, induced by the *gem*-5-dichloro group, retards the rates of secondary *exo*- and *endo*-2-norbornyl tosylate by ca. 5.2 × 10^6 and 4.7 × 10^4, respectively.

A more general description of substituent effects is provided by linear free energy relationships.[41] Good correlations of the solvolysis rates are obtained with inductive substituent constants, either Taft's σ^*,[41b] σ_I[41b] ($\sigma_I = 0.45\ \sigma^*$),[41a] or Grob's σ_q^I parameters.[42] As neither a σ_I nor a σ_q^I value for the $^-OCH_2CH_2O^-$ group is available, we prefer to use Taft's σ^* values. Our analysis is more extensive for the secondary derivatives where five substituents in addition to hydrogen were investigated. For the tertiaries only two substituents in addition to hydrogen were studied and the calculated reaction constants are approximate. The good correlations that are obtained (Figure 1), despite the necessary temperature extrapolation and the use of different leaving groups, indicate that only inductive effects are operative. Steric effects due to the remote 5-substituent are insignificant. For the 5-substituted *exo*-brosylates series, the reaction constant ρ^* is −2.54; the value for the endo epimers is substantially smaller, −1.62. Grob's ρ_I values[26] (see Scheme II), determined under different conditions, are in fair agreement when the conversion factor (see above) is applied.

The secondary *endo*-2-norbornyl brosylates **4** solvolyze with a small amount of solvent assistance.[16,20b,c] The ρ^* value for solvolysis of substituted 2-*endo*-norbornyl brosylates measures the effect of the substituents on the rate of formation of a nearly classical 2-norbornyl cation. The ρ^* value for the secondary *exo*-2-norbornyl brosylates is much higher. A special electronic effect must be involved in the solvolysis of *exo*-2-norbornyl sulfonates, namely, σ participation of the C_1–C_6 bond. The *uniquely* high ρ_I value of this series is still more pronounced when other systems are considered (see Scheme II). All the various

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[39] Heald, C.; Smith, A. C. K. In *Applied Physical Chemistry*; Macmillan Press: London, 1974.

[40] Cf. Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1955**, *77*, 3619.

[41] (a) Cf. Chapman, N. B.; Shorter, J.; Eds. *Correlation Analysis in Chemistry, Recent Advances*; Plenum Press: New York, London, 1978; and references cited therein. (b) Taft, R. W. In *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; Wiley: New York, 1956; Chapter 13.

[42] Grob, C. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 569. Grob, C. A.; Schaub, B.; Schlageter, M. G. *Helv. Chim. Acta* **1980**, *63*, 57.

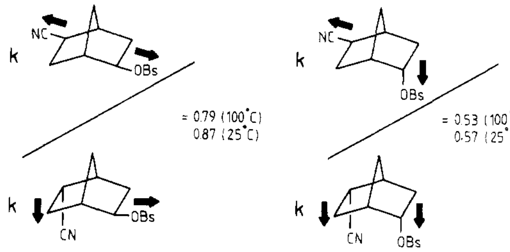
ρ_I values in Scheme II fall within the range of -0.54 to -1.5; only one system, the secondary 2-*exo*-norbornyl, system deviates significantly. The ρ_I value of -2.00 is far larger than one expects on the basis of its W-shape structure or strain alone. Participation of the C_1–C_6 σ-bond is responsible. More electron-withdrawing substituents decrease the ability of the C_1–C_6 bonding electrons to participate. An estimation of the magnitude of the anchimeric assistance for secondary 2-*exo*-norbornyl solvolysis cannot be deduced with confidence from the Hammett–Taft plots. Since a k_s vs. k_Δ mechanistic continuum is expected in solvolysis, no break in the Hammett–Taft plot is found as in, e.g., phenonium ion systems.[30]

While the high value of ρ_I differentiates the behavior of secondary *exo*-norbornyl sulfonate, some tendency toward participation is shown by other W-form systems in Scheme II. This is true in particular for the 6-substituted tertiary 2-*exo*-norbornyl series ($\rho_I = -1.30$) and for the 6-substituted 2-bicyclo[2.2.2]octyl system ($\rho_I = -1.5$). However, the parent members of these systems cannot give symmetrically bridged carbocation intermediates, and participation is less effective than in the secondary norbornyl case.

Exo/Endo Rate Ratios. The high exo/endo solvolysis rate ratio of the secondary 2-norbornyl sulfonates is central to the nonclassical ion controversy. Is the same effect responsible for the exo/endo ratios in the secondary and in the tertiary derivatives as Brown claims?[9–11] Both ratios are reduced by electron-withdrawing substituents (Table IV), but the effect is *much larger* in the secondaries (note the ρ^* values). In 60% ethanol, the exo/endo ratio is reduced from 860 in the parent 2-norbornyl system to 9.4 in the dichloro derivative, **7**. An even larger (236-fold) reduction in the exo/endo rate ratio is found in 97% TFE (see below). In the tertiaries, the exo/endo rate ratio is reduced only 3.8-fold by a 5-cyano substituent (100 °C, 60% acetone). The reduction in the exo/endo rate ratio is larger (i.e., 20) if the rate constants are compared at 25 °C. However, comparison at 25 °C involves the use of an unreliable extrapolation over a wide range of temperatures especially as the data for the parent system is based on rate measurements at only two temperatures.[43] Furthermore, Grob has remeasured the exo/endo rate ratio of the parent system **14** in 60% acetone and found a value of 396 at 25 °C.[21a] For the dinitrophenyl ether the rate ratio is only 171 in 80% ethanol at 100 °C.[21b] Thus, the above estimates of the rate retardations in the tertiary systems probably are overestimated. Even so, the behavior is quantitatively quite different from that of the secondaries.

The results of Table IV rule out Brown's argument that the high exo/endo ratio is steric in origin. If this were true, distant substituents at C_5 would be expected to have only a small influence on this rate ratio. In contrast we find a large change in the secondary 2-norbornyl derivatives. Thus, electronic effects must be primarily responsible for the high exo/endo rate ratio in secondary 2-norbornyl derivatives. In the tertiary derivatives, the high exo/endo rate ratio of the parent system reflects steric effects to a large extent and indeed a 5-substituent reduces this ratio only moderately. Grob has observed even larger reductions in the exo/endo rate ratio in secondary 6-substituted 2-norbornyl tosylates and has also concluded that the origin of the secondary high exo/endo rate ratio is electronic and that steric effects play a minor role.[26,29a]

Scheme IV. Spatial Orientation of Cyano and Brosylate Dipoles in 5-Substituted-2-norbornyl Brosylates.



The exo/endo rate ratios are known to depend on the solvent. For the parent system the **3**/**4** ratio increases as the nucleophilicity of the solvent decreases and as its ionizing power increases.[9] In 60% ethanol, for example, the exo/endo rate ratio for the **3**/**4** brosylates is 860 and it increases to 1746 in 97% HFIP (Tables III and IV). A value of 1590 was reported by Bentley et al. for the hydrolysis in pure water of the epimeric 2-norbornyl mesylates.[44] Interestingly, in the 5-substituted 2-norbornyl derivatives the exo/endo rate ratio is lower in the nonnucleophilic fluorinated solvents than in aqueous ethanol. For the **5**-*exo*-cyano system (**9**), for example, the exo/endo rate ratio at 25 °C (Table IV) is 24.8 in 60% ethanol, 7.6 in 97% TFE, and 5.0[32a] in 97% HFIP (the latter using tosylate as the leaving group). The apparently contradictory behavior of the parent and the 5-substituted derivatives can be understood. Two major changes occur when the solvent is changed from aqueous ethanol to fluorinated solvents. First, nucleophilic solvent assistance in the transition state of the endo sulfonate[16] is reduced, thus causing an increase in the exo/endo rate ratio. Second, as the ionizing power of the solvent increases and its nucleophilicity decreases, the transition state resembles more closely the intermediate cation so that σ-participation becomes more pronounced and the exo/endo ratio increases. In agreement with this interpretation, the ρ^* values of solvolysis reactions are usually smaller in aqueous ethanol than in fluorinated alcohols.[16,26e] For example, in the solvolysis of $RCH(OTs)CH_3$, $R = CH_3$, C_2H_5, C_3H_7, C_5H_{11}, ρ^* is -1.17 in 80% ethanol, -5.24 in 97% TFE, and -9.14 in 97% HFIP.[16a] Hence, in the 2-norbornyl derivatives with electron-withdrawing substituents in the 5-position the retardation of the solvolysis rate is larger in the exo than in the endo isomer. Therefore the exo/endo rate ratio is expected to be reduced more strongly in 97% TFE (or 97% HFIP) than in 80% ethanol; indeed, this is observed (Table IV).[45]

Dipolar Effects. The possibility that dipolar effects may be responsible for the low exo/endo rate ratios in the deactivated secondary 2-norbornyl derivatives[46] was examined by comparing the different orientation of polar groups in system **9**. The approximate directions of the dipole alignments in these systems are shown in Scheme IV. Comparisons of the solvolysis rate constants given show clearly that dipole orientation effects are small. Thus, **9**-*exo*-cyano- and **9**-*endo*-cyano-2-*exo*-norbornyl-OBs solvolyze at similar rates although the C_5–CN and the

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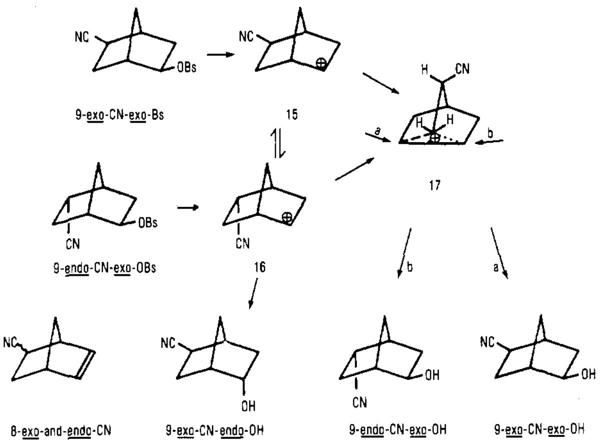
[43] See: Brown, H. C.; Igegami, S. *J. Am. Chem. Soc.* **1980**, *90*, 7122.

[44] Bentley, T. W.; Bowen, C. T.; Parker, W.; Watt, C. I. F. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1244.

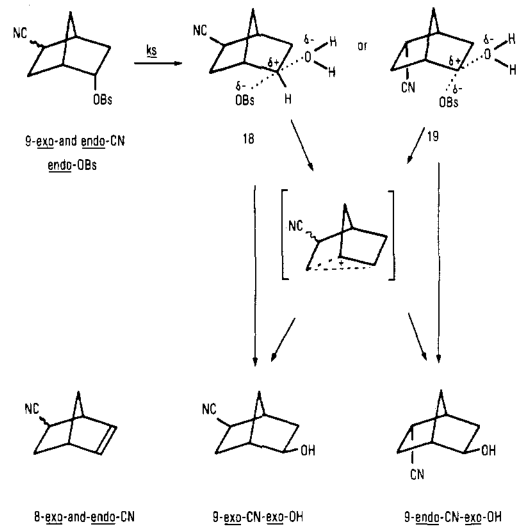
[45] Grob has reported[26e] that the $\rho_q{}^I$ of the 6-substituted-2-*endo*-norbornyl tosylate is larger in 97% TFE than in 80% ethanol but that the $\rho_q{}^I$ value of the 6-substituted 2-*exo*-norbornyl tosylate is essentially unchanged. Thus in the 6-substituted series exo/endo rate ratios are generally higher in 97% TFE than in 80% ethanol. Unfortunately similar extensive studies for the 5-substituted derivatives were not reported.

[46] See the discussion by Brown, ref 11.

Scheme V. Solvolysis of 9-*exo*- and 9-*endo*-CN-*exo*-OBs (See Text).



Scheme VI. Solvolysis of 9-*exo*- and 9-*endo*-CN-*endo*-OBs (See Text).



C_2–OBs bond dipoles are nearly antiperiplanar in the former compound, but nearly perpendicular in the latter (Scheme IV). The dipolar effect is somewhat larger, although still smaller than a factor of 2, in 9-*endo*-CN-*endo*-OBs where repulsion in the transition state between the negatively charged OBs and cyano groups slows the solvolysis (Scheme IV). However, dipolar orientation effects are much too small to account for the large reduction of the exo/endo rate ratios in secondary 2-norbornyl derivatives by electron-withdrawing substituents. Grob has come to similar conclusions by analogous arguments.[22,26]

Solvolysis Products. The solvolysis products of the 5-cyano-2-norbornyl derivatives (9), both secondary (i.e., *exo*- and *endo*-CN-*exo*-OBs and *exo*- and *endo*-CN-*endo*-OBs, Schemes V and VI) and tertiary (i.e., 13-*exo*- and 13-*endo*-ODNB, Scheme VII) were studied by gas chromatography in 60% acetone buffered with 2,6-lutidine. The results are presented in Tables V and VI. All products were found to be stable under the reaction conditions.

(a) Secondary Derivatives. Alcohols are the major products for solvolysis of all the secondary derivatives. Only ca. 2% of the elimination products, *exo*- and *endo*-8, are observed. A sharp distinction is found between the solvolysis products of the isomeric pair 9-*exo*-CN-*exo*-OBs and 9-*endo*-CN-*endo*-OBs on one hand, and the isomeric pair, 9-*exo*-CN-*endo*-OBs and 9-*endo*-CN-*endo*-OBs, on the other hand. In the 9-*exo* series the same product composition is formed from either epimer. The initial orientation of the 5-cyano substituent is unimportant. This can be explained (Scheme V) by invoking a common bridged cation, 17, or a rapidly equilibrating pair of classical cations (15 $\rightleftharpoons$ 16) as the product-forming intermediates. These two alternatives cannot be distinguished on the basis of product studies. Thus, the conclusion is that even in the presence of the strongly electron-withdrawing cyano group the C_1–C_6 Wagner–Meerwein rearrangement is still faster than capture by the solvent or alternatively that partial bridging and thus anchimeric assistance still occurs.[47] The later possibility is supported by the fact that the exo/endo rate ratio can be reduced further as in 7, pointing to a residual σ participation in 9. Bridging plays a diminished role in the product-determining intermediate in deactivated 2-norbornyl cations like 17, which represents a weakly bridged unsymmetrical cation.[31] However, a significant degree of exo stereoselectivity (retention of configuration) can still be found in solvolytic processes where weakly bridged secondary cations like unsubstituted or substituted 2-adamantyl cations are the product-forming intermediates.[48] The observation of ca. 99:1 exo/endo product ratios found in hydrolysis of the *exo*-brosylates (Table V) is in line with these arguments. Grob[49] has found that in the solvolysis of the closely related *exo*- and *endo*-6-cyano-2-*exo*-norbornyl tosylates each isomer gives a *different* product composition in 70% dioxane. The fast equilibration of the ions corresponding to 15 and 16 is inhibited when the cyano substituent is attached directly to the C_1–C_6 bond.[49] The 6-cyano-2-norbornyl derivatives also give much higher amounts of endo alcohols (and elimination products) than the 5-cyano derivatives.[49] The formation of significant yields of the endo products (30% in the case of the 6-cyano-2-norbornyl tosylate[49]) supports our suggestion that 17 is a weakly bridged unsymmetrical intermediate and that the exo/endo product ratio is also controlled by electronic effects although steric effects also contribute.[9] The cyano group at C_1 also leads to preferred exo solvolysis products.[23b]

On the contrary, the isomeric 2-*endo*-brosylates, 9-*exo*-CN-*endo*-OBs and 9-*endo*-CN-*endo*-OBs, do not yield the same product mixtures on solvolysis in 60% acetone (see Table V). The former gives 67.3% of 9-*exo*-CN-*exo*-OH and 30.7% 9-*endo*-CN-*exo*-OH, while the reverse ratio, 32.1% 9-*exo*-CN-*exo*-OH and 66.7% 9-*endo*-CN-*exo*-OH, is obtained from the latter. This shows that these epimeric brosylates do not solvolyze through a common intermediate (see Scheme VI). Solvolysis of either brosylate proceeds with predominant inversion of configuration at C_2. A solvent-assisted pathway (k_s) shown already for the parent sulfonate[16] can accommodate the results.[50] But still some Wagner–Meerwein rearrangement can occur at the intimate ion pair stage (18 $\rightleftharpoons$ 19) as shown in Scheme VI.

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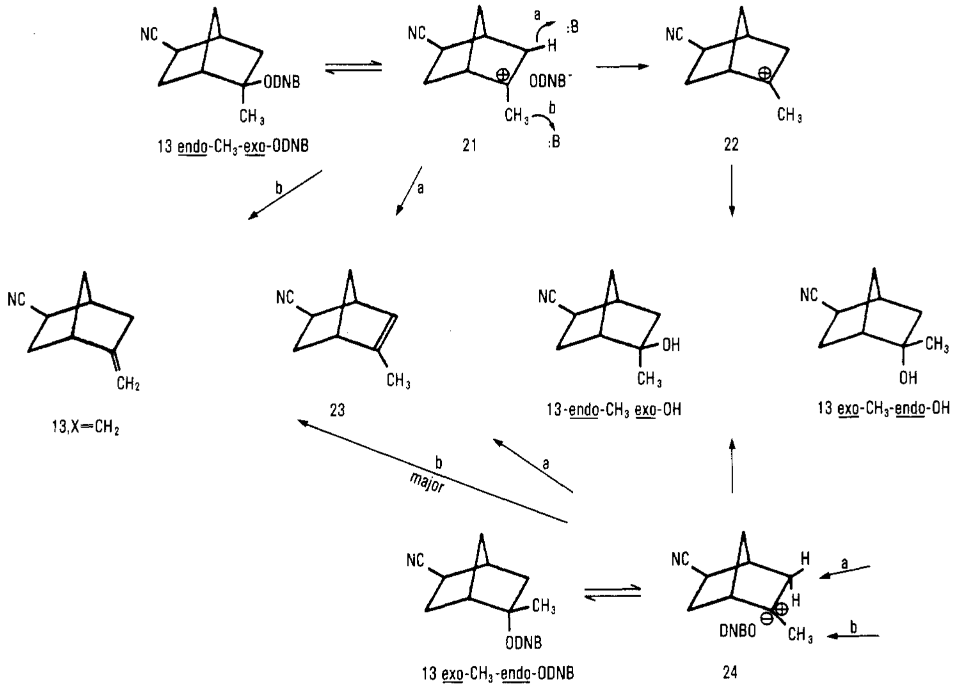
[47] The Wagner–Meerwein shift can be totally inhibited by the presence of four fluorine or trifluoromethyl groups in the 5- and 6-positions.[25i]

[48] Lenoir, D.; Raber, D. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 2149 and references cited therein. Goeckel, P. Diplomarbeit, Erlangen. See also: Le Noble, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 1598.

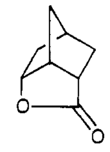
[49] Grob, C. A.; Herzfeld, D. *Helv. Chim. Acta* **1982**, *65*, 2443.

[50] See also the results of Banert and Kirmse (Banert, K.; Kirmse, W. *J. Am. Chem. Soc.* **1982**, *104*, 3766.

Scheme VII. Solvolysis of 13-*exo*- and 13-*endo*-ODNB (See Text).



In 97% HFIP the products are different. Wilcox has reported that both the 5-cyano and the 6-cyano-2-norbornyl tosylates yield the 2,6-lactone **20** as the main product.[25g] This lactone was assumed to result from fast hydrogen shifts that convert the 5-cyano to the 6-cyano-2-norbornyl cation followed by hydrolysis and cyclization to give the thermodynamically stable lactone. These results are consistent with a free, longer lived cationic intermediate in 97% HFIP than in 60% acetone. A higher degree of rearrangement in fluorinated alcohols than in aqueous solvents was found in other cationic rearrangements.[51]



20

(b) Tertiary Derivatives. *exo*- and *endo*-**13**-OBs lead to different amounts of the same products (see Table VI). In contrast to the secondary brosylates, the tertiary esters yield considerable amounts of elimination products, i.e., **23** and the exocyclic olefin **13**-CH_2. The parent tertiary *p*-nitrobenzoates **14**-OPNB, 6,6-dimethyl-*exo*-2-methyl-*p*-nitrobenzoate,[52] and other 6-*exo*-substituted-2-methyl(*exo* and *endo*)norbornyl 2,4-dinitrophenyl ethers[53] also give mostly elimination products. Elimination evidently is not enhanced significantly by the electron-withdrawing cyano group at C_5.

The *exo*-dinitrobenzoate yields a much higher percentage of elimination products than the endo isomer; i.e., 67% and 39%, respectively. The composition of the olefins is also different. **13**-*exo*-ODNB yields 40% of **23** and 28% of **13**-CH_2, while with **13**-*endo*-ODNB this ratio is 3.8%/36%. The product data are consistent with the participation of ion pairs as the major product-forming intermediates (Scheme VII). The exo ion pair **21** is sterically hindered to nucleophilic solvent attack from the exo face. Elimination thus competes favorably with dissociation to the free ion (or solvent separated ion pair) **22**, which is captured to give mainly the exo alcohol. The endo ion pair **24** is less hindered to solvent attack than **21**, and exo substitution products predominate. The composition of the elimination products can be understood if it is assumed that elimination occurs in the ion-pair stage and that syn elimination including a 3-exo hydrogen is preferred over anti elimination, as observed previously.[54] In the exo ion pair the solvent, serving as a base, can abstract a proton syn to the dinitrobenzoate anion from either C_3 or the 2-methyl group leading to **23** or to **13**-CH_2, respectively (Scheme VII). On the other hand, the syn endo hydrogen at C_3 in the endo ion pair **24** is strongly hindered and the solvent abstracts a proton mainly from the 2-methyl group, giving **13**-CH_2 as the major product. Similar trends were reported for the products distributions in the solvolysis of some 6-*exo*-substituted-2-methyl(*exo* and *endo*) norbornyl esters, but no rationalization was offered for these observations.[53]

Both **13**-*endo*- and -*exo*-ODNB, yield small amounts of the endo alcohol **13**-*exo*-CH_3-*endo*-OH (2.5% and 0.5%, respectively). Higher exo/endo product ratios for tertiary dinitrobenzoates result from electronic effects. Since a more stable tertiary cation is involved in this process, no Wagner–Meerwein rearrangement occurs.

Conclusions

The major conclusion from the results of our study, combined with the overwhelming amount of diverse data (summarized in the Introduction), is that the parent 2-

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[51] Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic Press: New York, 1979; pp 395–432.

[52] Schleyer, P. v. R.; Donaldson, M. M.; Watts, W. E. *J. Am. Chem. Soc.* **1965**, *87*, 375.

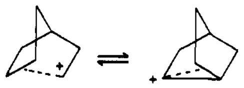
[53] Grob, C. A. Also see ref 29 a. Sprecher, G.; Waldner, A. *Helv. Chim. Acta* **1983**, *66*, 2656.

[54] Sicher, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 200.

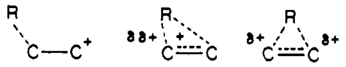
norbornyl cation is *symmetrically* bridged as was brilliantly deduced by Winstein and Trifan nearly 40 years ago.[13] The origin of the high exo/endo rate ratio in the solvolysis of secondary 2-norbornyl sulfonates is electronic and not steric. Secondary and tertiary 2-norbornyl derivatives respond differently to the inductive effects of substituents, the latter being much less influenced. In contrast to the secondaries, the exo/endo rate ratios in the parent tertiary 2-norbornyl solvolyses are controlled much more by steric effects.[16c] However, Grob's work and our own have shown that these ratios in tertiary systems also are influenced significantly by remote substituents. Hence, electronic effects contribute there as well.

Grob's extensive studies, which used a similar strategy to ours, also lead him to favor C-participation as the factor responsible for the high exo/endo rate and product ratios in secondary 2-norbornyl solvolyses.[26,29a] However, Grob suggests that the electronic interactions involved do not lead in the parent case to symmetrical bridging. According to Grob the C_6 carbon participates *directly* through space, much like an atom possessing a lone pair, *without* involving the C_1–C_6 bonding electrons.[26,29a] From a molecular orbital viewpoint, Grob's electron delocalization mechanism is unacceptable. The LUMO of the 2-norbornyl cation (depicted in Figure 6.5 p 97, of ref 9) shows quite the opposite: the largest contribution involves orbitals at C_6 polarized along the C_1–C_6 bond. Numerous theoretical studies have established that a cation is stabilized most effectively by β-CC bonding electrons when they are antiperiplanar (180° dihedral angle relationship) to the developing carbocationic 2p orbital.[55] Beautiful experimental studies by Traylor et al.[56] have clearly demonstrated this angular relationship which is inconsistent with Grob's model.[26,29a] According to Grob the substituent donates (or withdraws) electrons through the back lobe of the σ(C–R) orbital and in this manner it affects the charge which is transfered to the cationic center. This does not agree with the charge-transfer mechanism suggested by theory[55] and by Traylor's[56] experiments. In particular, a $-CH_2SnMe_3$ substituent at C_1 accelerated 2-*exo*-norbornyl solvolysis by 6×10^5.[56d] Furthermore, the 6-*exo*-D- and 6-*endo*-D-2-*exo*-norbornyl secondary isotope effects are nearly identical.[27] This speaks against the interaction of a CD bond (or its backside lobe) with the carbocation center, which should lead to significant differences.[27c] Thus, Grob considers the C-6-*exo*-H electrons to be particularly important,[26b] but there is no independent evidence for this. Our view of the role of the substituent is different: The substituent withdraws (or donates) electrons from the C_1–C_6 *bond* by a simple "through-bond" inductive (or dipolar) mechanism, thus attenuating the electron density of this bond and its ability to participate in the ionization process. The inductivities (ρ_I values) that Grob has reported for exo substituents at C_6 (−2.0), C_5 (−0.96), and C_7 (−0.96)[26,29a] are easily understood on this basis. Both C_7 and C_5 are separated by one CC bond from the C_1–C_6 bond and substituents at these positions affect the reactivity of the *exo*-2-norbornyl tosylate to a similar degree.

Since the late 1960s,[56–58] the possibility has been considered *that rapid equilibration* occurs between two equivalent unsymmetrically bridged 2-norbornyl cation structures, **25** and **25′** (also see discussion below). Grob favors this model,[26] but there is no supportive spectroscopic or ab initio calculational evidence for this postulate for the parent secondary ion. However, we pointed out some years ago that there is a continuum from weak hyperconjugation without significant distortion toward bridging, to unsymmetrical bridging, to strong symmetrical bridging.[9,31]



25 **25′**



Gradations of behavior are thus expected, even though the extremes—classical and nonclassical—can be recognized clearly. The interaction with a vacant carbocation p orbital involves the σ-CC bonding electrons; if this interaction is strong the β-carbon responds by moving toward or into a bridging position.[31] This is demonstrated by model ab initio calculations.[55] The extent to which bridging occurs depends on the particular system. For example, several of the examples in Scheme II have β-CC bonds antiplanar to the leaving group, but exhibit lower ρ_I values than secondary 2-*exo*-norbornyl. Sophisticated calculations[6] and a wealth of spectroscopic evidence[1–4] indicate the 2-norbornyl cation not only to prefer a symmetrical bridged structure, but to favor it strongly: The calculated potential energy surface toward $C_1C_6C_2$ angle bending is quite sharp.[6] How do substituents at remote locations on the norbornyl skeleton affect this structure? Due to the reduction of symmetry substituents at C_6 or C_5 will render the corresponding cations (e.g., **17**) unsymmetrical, but usually only slightly so: there is still only a single minimum. As the substituents become more electron withdrawing, the structure becomes more unsymmetrical and the degree of anchimeric assistance is reduced correspondingly. At the extreme, an appropriately substituted 2-norbornyl cation can have a "classical", unbridged structure. For example, this has now been shown directly by an X-ray structure of a 2-methoxy-substituted cation derivative based on camphor.[59]

As we discussed many years ago, much of the strain in the bicyclo[2.2.1]hexyl system would be relieved in the bridged cation due to the long C···C partial bonds. "This relief of strain may be the chief factor responsible for the favored bridged structure of the 2-norbornyl cation in contrast to the behavior of simple secondary (and other polycyclic) cations where such strain-relief opportunities are not present (or are diminished)."[60]

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[55] For model ab initio studies of the effects of substituents on bridging carbons in nonclassical carbocations, see: Saunders, M.; Chandrasekhar, J.; Schleyer, P. v. R. *Rearrangements in Ground and Excited States*; De Mayo, P., Ed.; Academic: New York, 1980; Vol. 1, p 39. Davidson, E. R.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1980**, *108*, 3135. For a general discussion also see: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab. Initio Molecular Orbital Theory*; Wiley: New York, 1986; Chapter 7. See also: Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 5901 and references therein.

[56] (a) Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, N. A.; Brown, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 5715. (b) Clinton, N. A.; Brown, R. S.; Traylor, T. G. *Ibid.* **1970**, *92*, 5230. (c) Eaton, D. E.; Traylor, T. G. *Ibid.* **1970**, *96*, 1226. (d) Hartmann, G. D.; Traylor, T. G. *Ibid.* **1975**, *97*, 6147. (e) Traylor, T. G.; Berwin, H. J.; Jerkvica, J.; Hall, M. L. *Pure Appl. Chem.* **1972**, *30*, 599 and references therein.

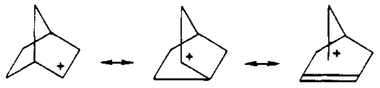
[57] Jensen, F. R.; Smart, B. E. *J. Am. Chem. Soc.* **1969**, *91*, 5686, 5688.

[58] Kosower, E. M. *An Introduction to Physical Organic Chemistry*; Wiley: New York, 1968; p 137.

[59] Montgomery, L. K.; Grendze, M. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4749.

[60] Radom, L.; Pople, J. A.; Buss, V.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 311.

The chief confusion in the interpretation of the effects of 6-substituents on the solvolysis rates of 2-*exo*-norbornyl derivatives is due to the misunderstanding of the nature of change distribution in carbonium (nonclassical) ions. Resonance depictions, **26a–c**, in particular **26c**, are misleading, since C_6 in the norbornyl cation (like the central carbon in CH_5^+) actually is *negatively* charged.[8,55] Hence, substituents cannot be expected to behave (as often as been argued by Brown) as if they were attached to carbenium ion (classical cation) centers. As Grob has demonstrated experimentally, and as we have shown from model calculational studies,[55] the *inductive* effects of substituents on a bridging carbon should predominate.

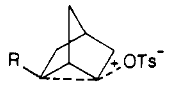

26a **26b** **26c**

We also agree with Grob that substituents at C_6, depending on their electron-withdrawing character, should result in a spectrum of structures with varying degrees of bridging. However, we find his model for the electron delocalization of these ions to be vague, and unsupported quantum-mechanically. The degree of bridging in these species should be very important energetically, as the two are directly related. Even ions inherently unsymmetrical because of their constitution (e.g. lacking a C_s point group) may exhibit a nearly symmetrical bridging geometry when strong interactions are present.

Fortunately, the recent X-ray structure of Laube[61] dispels much of the speculative cloud associated with this problem. Laube's result on a 1,2-dimethyl-2-norbornyl cation derivative showed a *partially bridged* structure, with a significantly shortened C_1–C_2 bond (1.44 Å) and distances between C_6 and C_1 and C_2 of 1.74 and 2.09 Å, respectively. These distances may be compared with those calculated (6-31G* basis set) for the symmetrical 2-norbornyl cation, 1.38 and 1.88 Å (both bonds to the bridging carbon), respectively. Very little additional movement is needed to achieve symmetrical structure **1**. The 1,2-dimethyl-2-norbornyl cation[2b,31] is known to be rapidly equilibrating from trapping experiments[62] and from the freezing out of the NMR at 4 K.[2b] Hence, the X-ray result confirms conclusions based on an analysis of the ^{13}C chemical shifts[31] and on isotopic perturbation[3] that the structure is partially bridged. Rather than being classical, as has often been assumed,[9] this implies that the 2-methyl-2-norbornyl cation has a partially bridged structure as well.

All available evidence indicates (and this has been generally accepted) that the secondary 2-norbornyl cation, relative to the 2-methyl or the 1,2-dimethyl tertiary ions, exhibits a greater degree of bridging and nonclassical character.[2,9,31] Since the 1,2-dimethyl species is now known to be partially bridged with an average deviation of C_6 of only 0.18 Å from a symmetrical position,[61] it is hard to imagine that the 2-norbornyl cation can exhibit any significant distortion from perfect C_s symmetry. Indeed, this is exactly what the ab initio calculations demonstrate.[6]

Postscript: The Possibility of Rapidly Equilibrating, Partially Bridged 2-Norbornyl Cations Laid To Rest. Since the late 1960s, it has been suggested from time to time that rapid equilibration might occur between two equivalent unsymmetrically bridged 2-norbornyl cation structures. Kosower,[58] Jensen,[57] and Traylor[56] considered this possibility as a way to reconcile the rapid, degenerate Wagner–Meerwein rearrangement with what was perceived to be a relatively small magnitude of anchimeric assistance. Some stabilization was provided hyperconjugatively by the C_1–C_6 bonding electrons, but relatively small movement of the atoms (e.g. toward a bridging situation) was involved. Structures like **25**, **27**, and **28** were employed to depict the situation envisioned, in order to differentiate clearly from a symmetrical intermediate transition state represented by a resonance hybrid of the canonical forms **26a** and **26b**.



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In 1972, Hoffmann, Radom, Pople, Schleyer, Hehre, and Salem stated "on theoretical grounds there is no dichotomy between participation with and without bridging. The hyperconjugative interaction will *always* be accompanied by geometrical adjustment, but the extent of that deformation may be small or large".[63]

That "there should be a continuum from hyperconjugation without significant motion towards bridging, to unsymmetrical bridging, to symmetrical bridging"[64] has been emphasized, e.g., by Olah,[65] ever since. Examples of partial bridging have been found calculationally which illustrate this principle. However, some of these, like the earlier quantum mechanical results on the 2-norbornyl cation which appeared to favor unsymmetrical structures,[66] proved to be artifacts of the inadequate levels or insufficiencies in the theory employed.[6,67]

As the spectroscopic evidence indicating a symmetrical 2-norbornyl cation accumulated, a further ingenious possibility was suggested first by Fong[68] and then by Brickmann:[69] heavy atom tunneling involving partially bridged species might be so rapid as to result in a kind of effective or "pseudo"-symmetry, at least on the NMR time scale.

Following these suggestions of Fong[68] and Brickmann,[69] Dewar has proposed that the 2-norbornyl cation is unsymmetrically bridged and that the symmetrical NMR spectrum observed at 4 K can be explained by rapid equilibration due to heavy atom tunneling (HAT).[70] This possibility was examined experimentally by Myhre et al., who found no evidence for HAT in the NMR spectra behavior of the 1,2-dimethyl-2-norbornyl cation.[2b] In agreement with classical expectations, the rapid Wagner–Meerwein rearrangement could be slowed down and frozen out when the temperature was decreased to 8 K. The quite different behavior of the secondary 2-norbornyl cation[2a] demonstrated its structure to be symmetrically bridged.

Dewar recently rejected this arguent as "fallacious".[70] He continues, "HAT is expected to be significant only when the motions and the corresponding barrier is ex-

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[61] Laube, T. *Angew. Chem.* **1987**, *99*, 580; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 561.

[62] Goering, H.; Humski, K. *J. Am. Chem. Soc.* **1968**, *90*, 6213.

[63] Hoffmann, R.; Radom, L.; Pople, J. A.; Schleyer, P. v. R.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1972**, *94*, 6221.

[64] Reference 9, comments on p 161.

[65] Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1973**, *95*, 3792.

[66] E.g. MINDO/3: Dewar, M. J. S.; Haddon, R. C.; Kormornicki, A.; Rzepa, H. *J. Am. Chem. Soc.* **1977**, *99*, 377.

[67] A detailed critical analysis has demonstrated the fatal shortenings of MINDO/3 for the norbornyl cation problem, see: Wenke, G.; Lenoir, D. *Tetrahedron* **1977**, *35*, 489.

[68] Fong, F. K. *J. Am. Chem. Soc.* **1974**, *96*, 7638. Fong, F. K., submitted for publication. We thank Prof. Fong for a preprint of this paper.

[69] Brickmann, J. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 106.

[70] Dewar, M. J. S.; Merz, K. M., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 5634.

pected to be much higher". Dewar's argument is invalid on both these counts. It is instructive to compare the 1,2-dimethyl-2-norbornyl cation with cyclobutadiene in this context. Carpenter[71] pointed out that the movement of carbon atoms in the automerization of cyclobutadiene is only about 0.2 Å, and his proposal that HAT predominates at lower temperatures has received strong support from Dewar.[72] However, the energy differences between rectangular cyclobutadiene and the square transition state, assumed to be 8.1 kcal/mol by Dewar in his treatment (even larger values are found by ab initio calculations), clearly is *much* greater than the classical barrier for the 1,2-dimethyl-2-norbornyl cation interconversion. NMR measurements show the latter to be less than 2.5 kcal/mol.[2b] Hence, on the basis of the classical barrier height, the 1,2-dimethyl-2-norbornyl cation should be much more prone to HAT than cyclobutadiene.

Laube's X-ray structure of the 1,2,4,7-tetramethyl-2-norbornyl cation[61] now provides us with important calibrating data. The two extra 4- and 7-*anti*-methyl groups are not expected to distort the geometry appreciably from that expected for the parent 1,2-dimethyl-2-norbornyl cation. Laube's structure clearly substantiates the conclusions reached earlier based on analysis of ^{13}C chemical shifts[2b] and on the degree of isotopic perturbation[73] that this species has a partially bridged structure: the critical bond lengths, C_1–C_2 = 1.44 (2), C_1–C_6 = 1.74 (2), and C_2–C_6 = 2.09 (2) Å, deviate markedly from the values found in norbornane (C_1–C_2 = C_1–C_6 = 1.55 and C_2–C_6 = 2.5 Å).

The symmetrically bridged 2-norbornyl structure has been calculated at several ab initio levels,[6] the highest employing the polarized split valence 6-31G* basis set.[6c] It has also been possible to optimize the geometry of the bridged bicyclo[2.1.1]hexyl cation at both 6-31G* and at the correlated MP2/6-31G* levels.[6e] If the (relatively small) effects of electron correlation on the geometry are the same in the [2.2.1] and the [2.1.1] species, the central bond lengths in the symmetrically bridged 2-norbornyl cation should be about C_1–C_2 = 1.39 and C_1–C_6, C_2–C_6 = 1.83 Å (the corresponding values at 6-31G* are 1.38 and 1.88 Å). Similar distances are expected in the symmetrically bridged transition structure for the 1,2-dimethyl-2-norbornyl cation, as the influence of the methyl groups should be small. Hence, the average displacements expected for C_1, C_2, and C_6 of this cation in going from the partially bridged minimum (X-ray structure) to the bridged transition structure for the degenerate rearrangement should only be about 0.15 Å. This is less than average displacement of about 0.2 Å discussed for the cyclobutadiene automerization. The other atoms in the 1,2-dimethyl-2-norbornyl cation are expected to undergo small or negligible movement.

We conclude both on the basis of the classical barrier height and the degree of geometry alteration, that cation 1 should be even more prone to heavy atom tunneling (if this were to occur) than cyclobutadiene. That no evidence for HAT in 1 is found experimentally[2b] contradicts Dewar[70] and supports Myhre et al.'s conclusion that a static symmetrical geometry rather than HAT is responsible for the 5 K NMR spectrum of the 2-norbornyl cation.[2] Saunders and Johnson also have rejected HAT in the latter ion.[73] If HAT were taking place in the 2-norbornyl cation at 5 K, as they point out, a different NMR spectrum than that observed would be expected.

The 2-norbornyl cation has a symmetrically bridged structure and a *sharp* (not flat) single well potential energy surface both in the gas phase and in solution.[6e] This is just what Winstein and Trifan envisaged nearly 40 years ago.[13] We have learned much in the meantime—Brown's steric effects are important indeed in more crowded systems[16c]—but the best way to interpret the solvolytic behavior of 2-*exo*- and 2-*endo*-norbornyl arenesulfonates has hardly changed at all.

Experimental Section

Melting points were determined in sealed capillaries and are uncorrected. ^{1}H NMR spectra were determined with a Varian A60A spectrometer with CDCl$_3$ as the solvent and Me$_4$Si as internal standard. ^{13}C NMR spectra were recorded on a Bruker HX-90 in CDCl$_3$. IR spectra were recorded on a Perkin-Elmer Model 131 apparatus. Satisfactory elemental analyses were obtained for all new compounds. Products generally were worked up by washing the organic phase with NaHCO$_3$ solution (10%) and H$_2$O and then drying over MgSO$_4$ and evaporating the solvent.

The 6:4 Diels–Alder mixture of 8-*exo*-CN and 8-*endo*-CN was separated by distillation on a spinning band column at 84–85 °C and 87–89 °C (13 Torr), respectively. Only 8-*endo*-CN solidifies upon cooling to 0 °C.

Preparation of 6-*exo*-OAc, 6-*exo*-OH, 7-*exo*-OAc, 7-*exo*-OH, 9-*exo*(*endo*)-CN-*exo*-OH, and 11-*exo*-OH. 6-*exo*-OAc. Ketone 5[33] (8.0 g) was refluxed with 3.0 g of ethylene glycol in 30 mL of benzene in the presence of catalytic amounts of *p*-toluenesulfonic acid for 5 h. The product was distilled in vacuo. bp 79 °C (0.7 Torr), to give 8.1 g (80%) of a colorless oil.

6-*exo*-OH. Acetate 6-*exo*-OAc (2.5 g) was refluxed for 3 h in 30 mL of methanol containing 0.1 g of sodium methylate. Distillation in vacuo, bp 78 °C (0.3 Torr), yielded 2.1 g (83%) of a colorless oil.

7-*exo*-OAc. Ketone 5[33] (90 g) was dissolved in 20.0 g of PCl$_3$; 14.5 g of PCl$_5$ was added gradually at 0 °C and the mixture was stirred at 0 °C for 2 h. Ice was added and the product was extracted with CH$_2$Cl$_2$. Distillation in vacuo, bp 67 °C (1 Torr) gave 10.8 g (90%) of a colorless oil.

7-*exo*-OH. The alcohol was prepared in 60% yield from acetate 7-*exo*-OAc by using the procedure described for 6-*exo*-OH.

9-*exo*-CN-*exo*-OH. Nitrile 8-*exo*-CN (11.0 g) was oxymercurated/demercurated[74] starting with 29.3 g of Hg(OAc)$_2$ in a mixture of 100 mL of H$_2$O and 100 mL of THF by the standard procedure. Crude 9-*exo*-OH, 10.5 g (85%), obtained as an oil, was used without further purification.

9-*endo*-CN-*exo*-OH. The nitrile 8-*endo*-CN was converted into 9-*endo*-CN-*exo*-OH in an analogous procedure described for the epimer. Yield: 83% as a colorless oil.

11-*exo*-OH. The chloro compound 10[35] (40.0 g) was hydroborated/oxidized by the standard procedure.[75] The product was distilled in vacuo, bp 115–120 °C (12 Torr); 17.0 g (45%) of crude material obtained as an oil was used without further purification.

Preparation of Ketones 6-oxo, 7-oxo, 9-*exo*-CN-oxo, 9-*endo*-CN-oxo, and 11-oxo. All ketones were prepared by Jones oxidation (in acetone, 5–15 h, 25 °C) starting from the corresponding exo alcohols (Jones reagent: 70 g of CrO$_3$, 100 mL of H$_2$O, 112 g of H$_2$SO$_4$). Yields were ca. 80%; except for ketone 11-oxo (15%).

Preparation of Endo Alcohols 6-*endo*-OH, 7-*endo*-OH, 9-*exo*-CN-*endo*-OH, 9-*endo*-CN-*endo*-OH, and 11-*endo*-OH. All endo alcohols were obtained by reduction of the corresponding ketones with NaBH$_4$. The preparation of 9-*exo*-CN-*endo*-OH is typical: to 2.0 g of 9-*exo*-CN-*oxo* dissolved in 5 mL of ethanol is added 2.6 g of NaBH$_4$ dissolved in 35 mL ethanol, and the

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Table VII. Physical Properties of Compounds 6, 7, 9, 11, 12, and 13

compd	mp or bp (torr) [°C]	Ir [cm^{-1}]	^{1}H NMR [δ]
6-*exo*-OAc	79 (0.7)	1730	1.3–1.8 (m, 6 H), 2.1–2.4 (m, 2 H), 2.00 (s, 3 H), 3.92 (m, 4 H), 4.75 (H-2)
6-*exo*-OH	78 (0.3)	3600	1.1–2.3 (m, 8 H), 3.2 (H-2), 3.95 (4-H)
6-*exo*-OBs	64–65		1.2–2.5 (m, 8 H), 3.85 (4-H), 5.55 (dd, H-2), 7.70 (4-H)
6-oxo	86 (1.2)	1740	1.7–2.3 (m, 6 H), 2.50 (m, 2 H), 3.50 (s, 4 H)
6-*endo*-OH	72		
6-*endo*-OBs	84–85		1.4–2.9 (m, 8 H), 3.85 (4-H), 4.8–5.2 (H-Z), 7.75 (4 H)
7-*exo*-OAc	67 (1)	1730	1.6–2.6 (m, 8 H, 2.00 (s, 3 H), 4.6–4.8 (m, 1 H)
7-*exo*-OH	89–91	3300	1.9–2.9 (m, 8 H), 3.9 (m, 1 H)
7-*exo*-$OSO_2CH_2CF_3$	44–45		1.8–2.3 (m, 6 H), 2.7–2.9 (m, 2 H), 3.90 (g, J = 8.5 Hz) (2 H), 4.67 and 4.80 (d, 1 H)
7-oxo	(194–195; (2,4-dinitrophenyl)hydrazone)	1750	1.2–2.4 (m, br)
7-*endo*-OH	86–88	3600	1.2–3.1 (m, 8 H), 4.20 (m, 1 H)
7-*endo*-$OSO_2CH_2CF_3$	57–59		1.7–2.7 (m, 8 H), 3.90 (g, J = 8.5 H_3, 2 H), 5.1 (m, 1 H)
9-*exo*-CN-*exo*-OH		3400, 2237	1.0–2.1 (m, 4 H), 2.1–2.3 (m, 2 H), 2.4–2.7 (m, 1 H), 3.0–3.3 (m, 1 H), 3.5–3.9 (m, 1 H)
9-*endo*-CN-*exo*-OH		3400, 2235	1.0–2.4 (m, 8 H), 2.4–2.7 (m, 1 H), 3.74 (1 H), 3.7–3.9 (m, 1 H)
9-*exo*-CN-*exo*-OB_s	131–132	2230, 1575	1.5–2.86 (m, 8 H), 2.56–2.86 (m, 1 H), 4.46–4.7 (t, 1 H), 7.83 (s, 4 H)
9-*endo*-CN-*exo*-OB_s	108–109	2228, 1585	1.07–2.9 (m, 9 H), 4.4–4.8 (d, 1 H), 7.83 (s, 4 H)
9-*exo*-CN-oxo	97–98	2240, 1750	1.33–2.5 (m, 7 H), 2.5–2.9 (m, 2 H), 2.95–3.16 (m, 1 H)
9-*endo*-CN-oxo	109	2240, 1760	1.60–2.17 (m, 3 H), 2.3–2.6 (m, 3 H), 2.66–2.93 (m, H), 2.93–3.4 (m, 2 H)
9-*exo*-CN-*endo*-OH		3590, 2240, 1610	1.32–2.08 (m, 5 H), 2.22–2.58 (m, 5 H), 4.04–4.84 (m, 2 H)
9-*endo*-CN-*endo*-OH		3590, 2240	1.03–2.96 (m, 9 H), 3.36–3.7 (s, 1 H), 4.0–4.23 (m 1 H)
9-*exo*-CN-*endo*-OBs	141–142	2235, 1580	1.1–2.83 (m, 9 H), 4.73–5.13 (m, 1 H), 7.9 (s, 4 H)
9-*endo*-CN-*endo*-OBs	88–90	2240, 1582	1.4–3.1 (m, 9 H), 4.8–5.2 (m, 1 H), 7.76 (s, 4 H)
11-*exo*-OH	115–120 (12)	3500–3200	1.4–1.9 (m, 6 H), 2.3–2.5 (m, 2 H, H-4.5), 3.70 (s, H-Z), 3.70–3.85 (m, 3 H)
11-*exo*-OBs	108–110		1.5–1.85 (m, 6 H), 2.35–2.58 (m, 2 H), 3.6–3.82 (Zr, 1 H), 4.32–4.5 (tr. 1 H), 7.74 (m, 4 H)
11-oxo	(oil)	1760	1.85–2.35 (m, 6 H), 2.57–2.95 (m, 2 H), 4.05–4.28 (m, 1 H)
11-*endo*-OH	(oil)	3500	1.25–2.1 (m, 6 H), 2.18–2.55 (m, 2 H), 2.98 (s, 1 H), 3.92–4.25 (m, 2 H)
11-*endo*-OBs	121		1.20–2.05 (m, 6 H), 2.33–2.65 (m, 2 H), 3.97–4.05 (m, 1 H), 4.87–4.96 (m, 1 H), 7.92 (4 H)
12-*exo*-CH_3-*endo*-OH	84–86 (1)	3600	1.5–2.3 (m, 6 H), 1.32 (s, 3 H), 3.95 (4-H), 3.1 (br.OH).
12-*exo*-CH_3-*endo*-ODNB	145–146		1.4–2.3 (m, 6 H), 1.72 (s, 3 H), 3.92 (4-H), 9.20 (m, 3 H)
13-CH_2	70–75 (15)	1650	1.0–2.4 (m, 6 H), 2.5–2.8 (m, 2 H), 3.90 (s, 4 H), 4.65 and 4.84 (dd, 2 H)
12-*endo*-CH_3-*exo*-OH	96–98 (1)	3600	1.0–2.2 (m, 8 H), 1.30 (s, 3 H), 3.92 (s, 4 H)
12-*endo*-CH_3-*exo*-ODNB	110–112		1.5–2.4 (m, 6 H), 1.85 (s, 3 H), 3.95 (s, 4 H), 9.3 (3 H)
13-*exo*-CH_3-*endo*-OH	76	3575, 2225	1.30 (s, 3 H), 1.4–2.4 (m, 5 H), 2.4–2.62 (m, 3 H)
13-*exo*-CH_3-*endo*-ODNB	140–143	2220, 1730	1.80 (s, 3 H), 1.7–2.17 (m, 6 H), 2.17–2.80 (m, 3 H), 2.97–3.27 (m, 1 H), 8.49–8.83 (m, 3 H)
13-CH_2	230 (760)	2235, 1670	1.53–2.30 (m, 5 H), 2.33–2.67 (m, 2 H), 4.63–5.06 (dd, 2 H)
13-*endo*-CH_3-*exo*-OH	60 (subl)		1.26 (s, 3 H), 1.43–2.30 (m, 8 H), 2.43–2.66 (m, 1 H)
13-*endo*-CH_3-*exo*-ODNB	177	2220, 1735	1.75 (s, 3 H), 1.7–2.7 (m, 6 H), 2.73–3.0 (m, 1 H), 3.0–3.3 (m, 1 H), 8.4–8.7 (m, 3 H)

mixture is stirred for 24 h. NaCl solution is added and the product extracted with $CHCl_3$. After usual workup 2.0 g (96%) of a crude product was obtained which consisted of a 75:25 mixture of epimeric alcohols 9-*exo*-CN-*endo*-OH and 9-*exo*-CN-*exo*-OH. Pure endo alcohols can be obtained by chromatography or by repeated crystallizations.

Preparation of Sulfonates 6-*exo*-OBs, 6-*endo*-OBs, 7-*exo*-$OSO_2CH_2CF_3$, 7-*endo*-$OSO_2CH_2CF_3$, 9-*exo*-CN-*exo*-OBs, 9-*exo*-CN-*endo*-OBs, 9-*endo*-CN-*exo*-OBs, 9-*endo*-CN-*endo*-OBs, 11-*exo*-OBs, and 11-*endo*-OBs. All brosylates were prepared from the corresponding alcohols by the standard procedure. Tresylates 7-*exo*-$OSO_2CH_2CF_3$ and 7-*endo*-$OSO_2CH_2CF_3$ were prepared following the method of Shiner et al.[76] Sulfonates were crystallized from *n*-pentane/$CHCl_3$ several times until analytically pure material was obtained. Table VII summarizes some physical properties of the sulfonates.

Preparation of Tertiary 2-Norbornyl Derivatives 12 and 13 and the Methylene Compounds (X = CH_2). The tertiary alcohols 12-*exo*-CH_3-*endo*-OH and 13-*exo*-CH_3-*endo*-OH were

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[76] Crossland, R. K.; Wells, W. E.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 4217.

prepared from the corresponding ketones with CH_3MgI. The preparation of 12-*exo*-CH_3-*endo*-OH is typical. To the Grignard reagent, prepared from 0.5 g of Mg and 3.0 g of CH_3I in 15 mL of absolute ether is added 3.0 g of ketone 6-oxo, and the mixture is refluxed for 2 h. After the usual workup, the crude product is purified by distillation in vacuo, bp 84 °C (1 Torr) to give 2.5 g (76%) of an oil.

The methylene compounds 12-CH_2 and 13-CH_2 were prepared from the corresponding ketones by the Wittig reaction. The preparation of 13-CH_2 is typical. The Wittig reagent was prepared from 11.5 g of triphenylphosphonium bromide and 30 mL of *n*-butyllithium (15%) in 100 mL of absolute THF under an N_2 atmosphere. 6-oxo, 4.0 g, dissolved in 80 mL of absolute THF is added and the mixture stirred for 25 h at room temperature. H_2O is added and the product extracted with ether. After the usual workup, distillation in vacuo, bp 71–75 °C (15 Torr), gave 2.0 g (51%) of a liquid product.

Tertiary alcohols 12-*endo*-CH_3-*exo*-OH and 13-*endo*-CH_3-*exo*-OH are obtained from the corresponding methylene compounds by oxymercuration/demercuration using the standard procedure described above.

The four 3,5-dinitrobenzoates 12-*exo*-CH_3-*endo*-ODNB, 12-*endo*-CH_3-*exo*-ODNB, 13-*exo*-CH_3-*endo*-ODNB, and 13-*endo*-CH_3-*exo*-ODNB were prepared from the corresponding alcohols by the standard procedure. They were crystallized several times from ligroin. Some of the physical properties of the compounds are summarized in Table VII.

Acknowledgment. A travel scholarship from the DAAD to one of us (Y.A.) was helpful for this work. The work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Registry No. 3-OBs, 840-88-0; 3-OTs, 959-42-2; 4-OBs, 840-89-1; 4-OTs, 840-90-4; 6-*exo*-OBs, 60494-06-6; 6-*endo*-OBs, 60537-04-4; 6-*exo*-OAc, 67594-59-6; 6-*exo*-OH, 67594-60-9; 7-*exo*-OTr, 60494-07-7; 7-*endo*-OTr, 60494-08-8; 7-*exo*-OAc, 111718-77-5; 7-*exo*-OH, 111718-78-6; 9-*exo*-CN-*exo*-OBs, 78376-59-7; 9-*exo*-CN-*endo*-OBs, 78419-47-3; 9-*endo*-CN-*exo*-OBs, 78419-48-4; 9-*endo*-CN-*endo*-OBs, 78376-60-0; 9-*exo*-CN-*exo*-OH, 60178-80-5; 9-*endo*-CN-*exo*-OH, 60209-06-5; 11-OBs, 111718-76-4; 11-OH, 111819-64-8; 12-*endo*-ODNB, 60537-05-5; 13-ODNB, 111819-63-7; 14-*exo*-ODNB, 60494-09-9; 14-*endo*-ODNB, 60494-10-2; 2-norbornyl cation, 24321-81-1.

Notes

Addition of Fluorenylidene to Hexafluorobenzene and an Answer to the Question: How Does Hexafluorobenzene Influence the Reactions of Diazofluorene with Olefins?

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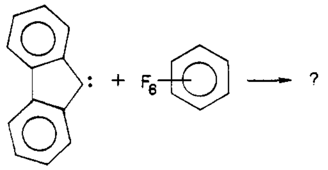
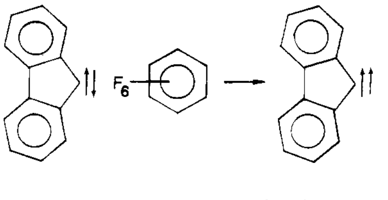
Received May 26, 1987

The structure of the product of addition of fluorenylidene to hexafluorobenzene is of interest in relation to the question: How does hexafluorobenzene influence the reactivity of fluorenylidene toward olefins?



Jones and Rettig suggested that hexafluorobenzene was an inert moderator, increasing the number of nonreactive collisions of the carbene and thus enhancing the relaxation of excited singlet to ground-state triplet fluorenylidene.[1]



That hexafluorobenzene is *not* inert to fluorenylidene, however, is clear from the report by Griller et al. that an adduct is formed in ca. 20% yield, but no structural information was provided.[2] Direct kinetic measurements on triplet fluorenylidene by Griller and Schuster established that hexafluorobenzene is ca. 1–2 orders of magnitude *less* reactive toward the carbene than more traditional trapping agents such as monoolefins, dienes, and alcohols.[2,3] The reaction of fluorenylidene with hexafluorobenzene is, however, quite rapid, the lifetime of the triplet carbene in C_6F_6 being only 95 ns.[3]

We have found that the presence of hexafluorobenzene dramatically alters the stereochemistry of fluorenylidene addition to *cis*-1,2-dichloroethylene.[4] We also observed that chemical combination of fluorenylidene and hexafluorobenzene at low temperature leads to a species whose ESR spectrum could be recorded, but whose structure could not be assigned from the spectrum.[4] These observations led to the suggestion that the role of hexafluorobenzene might be to reversibly form a complex that could act as a carbenoid, mimicking a triplet carbene.[4] Such a complex could also give rise to the previously uncharacterized stable adduct of fluorenylidene to hexafluorobenzene noted by Griller and ourselves,[2,4] and we thus set out to establish its structure.

Results and Discussion

Irradiation of 0.05 M solutions of diazofluorene in hexafluorobenzene with the uranium glass-filtered radiation from a 450-W medium-pressure mercury lamp yielded two major products, bifluorenylidene (40%), and 2,3,4,5,6,7-

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