Structural Effects in Solvolytic Reactions. 21. Solvolysis of 2-Aryl-2-norbornyl and 2-Aryl-2-camphenilyl *p*-Nitrobenzoates. A Critical Examination of the Importance of σ-Participation in the Solvolysis of Tertiary 2-Norbornyl Derivatives by the Application of the Tool of Increasing Electron Demand[1]

Herbert C. Brown,* Ken'ichi Takeuchi,[2] and M. Ravindranathan[3]

Contribution from the Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907. *Received September 28, 1976*

Abstract: *exo*- and *endo*-2-aryl-2-norbornyl and 2-aryl-2-camphenilyl *p*-nitrobenzoates with representative substituents in the aryl ring were synthesized and their rates of solvolysis measured in 80% aqueous acetone. The exo:endo rate ratio in the 2-aryl-2-norbornyl system does not reveal an appreciable increase with increasing electron demand at the cationic center over a wide range of reactivity: 284 for *p*-CH_3O, 232 for *p*-CH_3, 127 for *p*-H, 187 for *p*-CF_3, and 176 for 3,5-$(CF_3)_2$. The exo:endo rate ratios in 2-aryl-2-camphenilyl derivatives also fail to reveal any increase with increasing electron demand: 44 000 for *p*-CH_3O, 49 000 for *p*-H, and 24 000 for *p*-CF_3. The greatly increased exo:endo rate ratios in 2-aryl-2-camphenilyl derivatives arise largely from large decreases in the rates of the endo isomers, ascribed to the increased steric difficulties in the solvation of the anion and its departure. Both *exo*- and *endo*-2-aryl-2-norbornyl derivatives yield almost identical ρ^+ values: −3.82 for the exo isomers and −3.72 for the endo isomers. The ρ^+ values for *exo*- and *endo*-2-aryl-2-camphenilyl derivatives are −3.65 and −3.47, respectively. The solvolysis of 2-aryl-*exo*-norbornyl chlorides in the presence of sodium borohydride yields substitution products with more than 98% of the capture of the hydride by the cation occurring from the exo direction. The *exo*- and *endo*-2-aryl-2-camphenilyl *p*-nitrobenzoates give the exo alcohols as the predominant solvolysis product. Failure to observe increasing exo:endo rate ratios with increasing electron demand clearly establishes that σ-participation is not a factor in the observed high exo:endo rate ratios. It is concluded that the tool of increasing electron demand fails to confirm σ-participation in these 2-norbornyl derivatives as the factor responsible for the observed high exo:endo rate and product ratios. The high exo:endo rate and product ratios in these derivatives must instead arise from the unique steric characteristics of the norbornyl system.

Ever since the σ-bridged formulation of the 2-norbornyl cation (**1**) by Winstein and Trifan,[4] various approaches have

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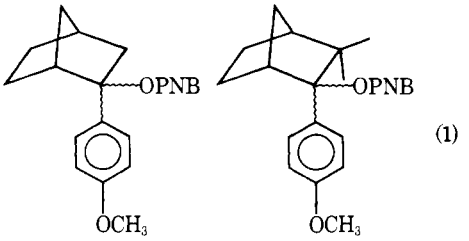
been made by physical organic chemists to confirm the existence of such a species in solvolytic media. The high exo:endo rate and product ratio observed in the solvolysis of 2-norbornyl brosylate was attributed to the driving force associated with the formation of a stabilized σ-bridged species (**1**) in the transition state.[4] The observation that highly stabilized tertiary 2-norbornyl derivatives, such as 2-*p*-anisyl-2-norbornyl (**2**) and 2-*p*-anisyl-2-camphenilyl (**3**) (1), are also capable of exhibiting such high exo:endo rate and product ratios failed to support the original conclusion.[5] The high exo:endo rate ratios in these systems (**2, 3**) are possibly a consequence of the steric characteristics of the norbornyl system (1).[5]

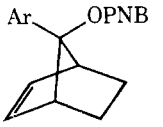


(1)

2 **3**

exo:endo	284	44 000

A basic tenet of carbonium ion chemistry is that the more stable a carbonium ion center, the less demand that center will make on neighboring groups for additional stabilization through participation.[6] An elegant demonstration of this postulate was made by Gassman and Fentiman[7] in the study of the solvolysis of 7-dehydronorbornyl derivatives (**4**). They



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observed that the participation from the π electrons of the double bond is a linear function of the electron demand of the incipient carbonium ion.[7] We have utilized this tool of increasing electron demand to estimate σ- and π-electronic contributions in a large number of representative systems.[8]

Of course, the main objective of this study was the 2-norbornyl system. Would the tool of increasing electron demand reveal σ-electronic contributions from the norbornyl system in the manner that it had detected σ-electronic contributions from the cyclopropyl ring in cyclopropylcarbinyl derivatives[9] and π-electronic contributions in the 5-methyl-2-norbornenyl system?[10]

Accordingly, we undertook a detailed rate and product study of 2-aryl-2-norbornyl *p*-nitrobenzoates (**5**) over a wide range of reactivity (*p*-CH_3O, *p*-CH_3, *p*-H, *p*-CF_3, and 3,5-$(CF_3)_2$). The tool of increasing electron demand was also applied to the 2-aryl-2-camphenilyl system (**6**) by synthesizing *exo*- and *endo*-2-arylcamphenilyl *p*-nitrobenzoates and studying their rates of solvolysis (2).

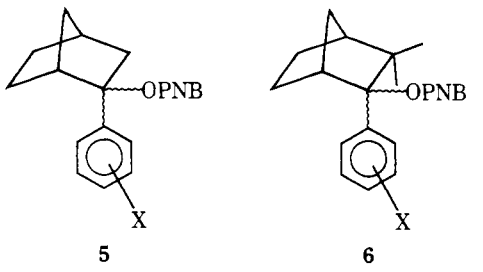
Results

Synthesis. The Grignard reagents prepared from appropriate bromobenzenes were added to norcamphor (**7**) to yield the

Table I. Rates of Solvolysis of 2-Aryl-2-norbornyl and 2-Aryl-2-camphenilyl *p*-Nitrobenzoates in 80% Aqueous Acetone

Substituent	System[a]	Isomer	Rate constant, $k_1 \times 10^6$ s^{-1} T_2, °C	T_1, °C	25 °C	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	Exo:endo at 25 °C
p-CH_3O	N	Exo			11 400[b]			
								284
	N	Endo		1.17 (0)	40.2	22.3	−3.8	
	C	Exo			12 100[c]			
								44 000
	C	Endo	171 (75)	8.77 (50)	0.273[d]	26.0	−1.6	
p-CH_3	N	Exo			131			
								232
	N	Endo	297 (75)	16.5 (50)	0.564[d]	25.3	−2.4	
p-H	N	Exo		179 (50)	7.56	23.6	−2.7	
								127
	N	Endo	364 (100)	30.2 (75)	0.059[d]	25.1	−7.4	
	C	Exo		595 (50)	22.9	24.4	1.9	
								49 000
	C	Endo	162 (125)	12.7 (100)	4.73×10^{-4} [d]	29.5	−2.5	
p-CF_3	N	Exo	400 (100)	29.4 (75)	0.0427[d]	26.4	−3.8	
								187
	N	Endo	70.1 (125)	5.62 (100)	2.27×10^{-4} [d]	29.2	−4.7	
	C	Exo	81.5 (75)	3.67 (50)	0.098[d]	27.1	0.4	
								24 000
	C	Endo	46.2 (150)	4.07 (125)	4.17×10^{-6} [d]	31.9	−3.5	
3,5-$(CF_3)_2$	N	Exo	36 (125)	29.3 (100)	0.0012[d]	29.2	−1.5	
								176
	N	Endo	49.2 (150)	4.63 (125)	6.88×10^{-6} [d]	31.1	−5.4	
	C	Exo			0.0042[e]			
								27 000
	C	Endo			1.59×10^{-7} [e]			

[a] N, 2-aryl-2-norbornyl; C, 2-aryl-2-camphenilyl. [b] Calculated by multiplying the rate of the benzoate by the factor of 20.8.[5] [c] Calculated by multiplying the rate of the benzoate by the factor of 23.5.[5] [d] Calculated from data at higher temperatures. [e] Calculated from the log k–σ^+ plot for other derivatives.



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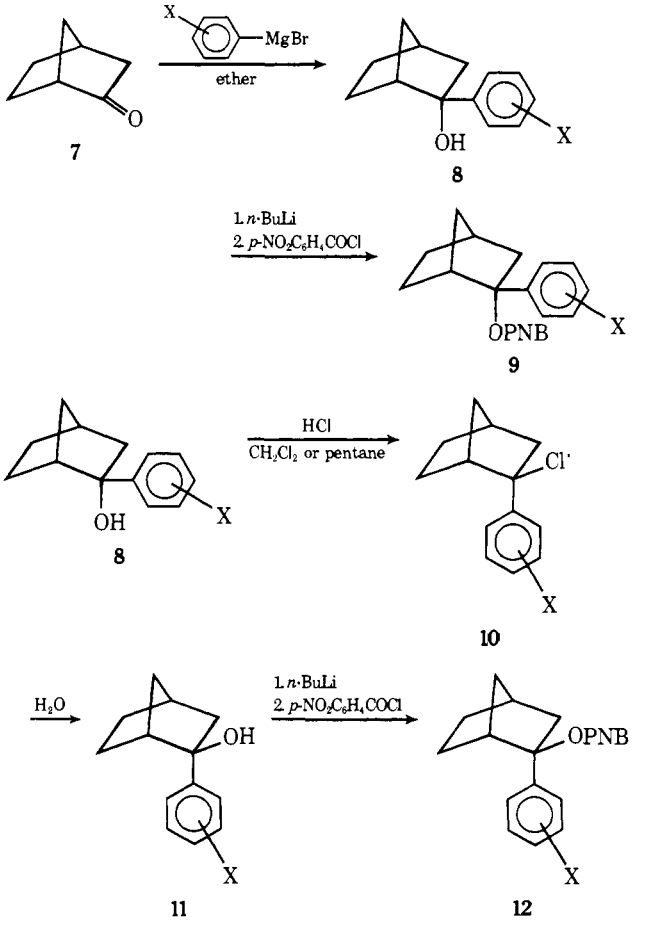


7 8 9 8 10 11 12

endo alcohols (**8**). The endo alcohols (**8**) were converted to the exo chlorides (**10**) by treating them with dry hydrogen chloride in methylene chloride or pentane.[11] Hydrolysis of the chlorides in buffered aqueous acetone afforded 2-aryl-*exo*-norbornanols (**11**). The *p*-nitrobenzoates (**9, 12**) were prepared by treating the lithio derivatives of the alcohols (**8, 11**) with *p*-nitrobenzoyl chloride in THF[12] or by the pyridine method (see Experimental Section). The properties of the tertiary alcohols (Table IV) and *p*-nitrobenzoates (Table V) are summarized in the Experimental Section. The 2-aryl-2-camphenilyl *p*-nitrobenzoates (**6**) were synthesized from camphenilone following the same sequence of reactions (Tables IV, V).

Solvolytic Studies. The rates of solvolysis of the *p*-nitrobenzoates were determined in 80% aqueous acetone. The 2-*p*-anisyl-*exo*-norbornyl (**12**, X = *p*-CH_3O) and 2-*p*-anisyl-*exo*-camphenilyl *p*-nitrobenzoates could not be synthesized owing to their exceedingly high reactivity and hence the rate constants for these derivatives were calculated from the rate constants of the benzoates using the factors of 20.8 and 23.5, respectively.[5] The rate data together with activation parameters for the two systems are tabulated in Table I.

Product Studies. The carbonium ions derived from 2-aryl-*exo*-norbornyl chlorides (*p*-CH_3O, *p*-H, and *p*-CF_3) were

Table II. Trapping of the Carbonium Ion by Sodium Borohydride in the Solvolysis of the 2-Aryl-*exo*-norbornyl Chlorides in 70% Diglyme at 25 °C

Substituent	Yield of 2-arylnorbornane, %[a]	2-Arylnorbornane, %[b] Exo H	Endo H
p-CH_3O	68	≥98	≤2
p-H	82	≥98	≤2
p-CF_3[c]	32	≥97	≤3

[a] GLC analysis. [b] Analysis by ^{1}H NMR. [c] Mp 51.0–51.5 °C.

trapped by sodium borohydride in 70% diglyme.[13] The 2-arylnorbornanes were analyzed by ^{1}H NMR (Table II). The product distribution in the solvolysis of substituted 2-aryl-2-camphenilyl *p*-nitrobenzoates (**3**) in 80% aqueous acetone was determined by ^{1}H NMR and is listed in Table III.

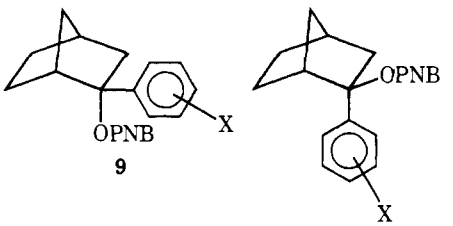
Discussion

The high exo:endo rate ratio of 284 and predominant exo substitution observed in the solvolysis of the 2-*p*-anisyl-2-norbornyl esters (**2**) cannot be attributed to σ-participation.[5] These characteristics have been attributed to steric effects.[14] These factors must also be present in the parent 2-norbornyl and must therefore contribute to the high exo:endo rate and product ratios. However, it is presently not possible to conclude that σ-participation may not also contribute in the parent secondary derivative, even though it cannot be a significant factor in the 2-anisyl system. The problem is how to bridge the gap between the highly stabilized 2-anisyl-2-norbornyl and the corresponding secondary system without introducing uncertain corrections for the differences in the ground state energies.[15]

The Hammett approach offers excellent promise for such cases. By introducing appropriate substituents into the aromatic ring, it is possible to vary the reactivity over a wide range, ultimately approaching or even exceeding the reactivity of the parent secondary 2-norbornyl itself.[16] By restricting these substituents to the meta and para positions, changes in the steric factors can be avoided.

Consequently, as the aromatic ring is deactivated, thereby increasing the electron demand at the carbonium ion center, we should observe increasing σ-participation and increasing exo:endo rate ratios, providing such σ-participation is a significant factor.

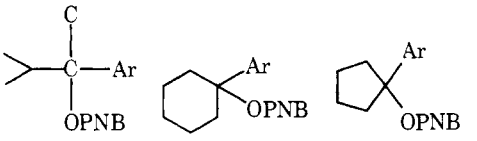
Exo:Endo Rate Ratios in 2-Aryl-2-norbornyl. The data presented in Table I reveal an essentially constant exo:endo rate ratio in the 2-aryl-2-norbornyl system, a ratio which does not change significantly with increasing electron demand (3). Consequently, it is clear that σ-participation cannot be a significant factor in the high exo:endo ratios in these derivatives.



9 **12** (3)

X = *p*-CH_3O	1.00	284
p-CH_3	1.00	232
p-H	1.00	127
p-CF_3	1.00	187
3,5-$(CF_3)_2$	1.00	176
2-H	1.00	280

The data for the 2-aryl-2-norbornyl derivatives yield an excellent log k–σ^+ relationship.[17] The exo derivatives (**12**) yield a value of ρ^+ of −3.82 (correlation coefficient 0.999) and the endo derivatives yield one of −3.72[18] (correlation coefficient 0.999) (Figure 1). The similarity in the value of ρ^+ for exo and endo should be noted, as well as the similarity to the value for cyclopentyl[19] ($\rho^+ = -3.82$). On the other hand, the ρ^+ values for isopropyl[9] (**13**) and cyclohexyl (**14**)[20] are more negative, −4.76 and −4.60, respectively (4). These values suggest that cyclopentyl, *exo*-norbornyl, and *endo*-norbornyl supply electrons to the electron-deficient center more effectively than do the isopropyl and cyclohexyl groups and, more significantly, that there are no significant electronic contributions in these derivatives from *exo*-norbornyl that are not present in *endo*-norbornyl or cyclopentyl. Perhaps the strain in these three systems makes them better able to hyperconjugate and thereby stabilizes the electron-deficient center. However, it is of the utmost importance for the nonclassical ion problem that *endo*-norbornyl is, if anything, slightly more effective than *exo*-norbornyl in thus stabilizing the electron-deficient center, as measured by ρ^+.



13 **14** **15** (4)

ρ^+	−4.76	−4.60	−3.82

Recently Battiste has argued that the original proposal of Winstein that the rate comparison of exo with endo be abandoned.[21] He therefore compares *exo*-norbornyl and *endo*-norbornyl with isopropyl and concludes that both *exo*-norbornyl (the C_1–C_6 bond) and *endo*-norbornyl (the C_1–C_7 bond) are capable of supplying σ electrons to the cationic center under the demand of the tertiary carbonium ion center. High exo:endo rate ratios have long been considered diagnostic of nonclassical ions and σ-participation has not been considered to be a significant factor in endo derivatives.[3] It is difficult to

Table III. Product Distribution in the Solvolysis of 2-Aryl-2-camphenilyl *p*-Nitrobenzoates in 80% Aqueous Acetone

Substituent	Isomer	Product distribution, %[a] Exo OH	Endo OH	Apocyclene	Crude product mp, °C
p-CH_3O	Exo[b]	≥99.5	≤0.5	0.0	79–80
	Endo	≥99.5	≤0.5	0.0	76–77
p-H	Exo	≥99.5	≤0.5	0.0	51–54
	Endo	≥99.5	≤0.5	0.0	54–55
p-CF_3	Exo[c]	87	≤0.4	13	
	Endo[d]	41	≤1.0	58	

[a] Analysis by ^{1}H NMR. [b] Benzoate. [c] GLC analysis showed 85% exo OH and 13% apocyclene derivative with 2% unidentified product (secondary OH?). [d] GLC analysis indicated 45% exo OH and 55% apocyclene derivative.

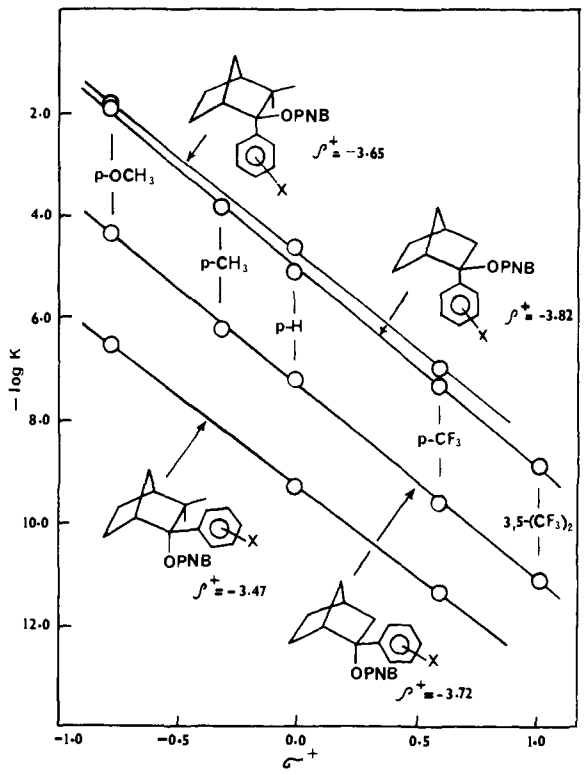


Figure 1. Log k–σ^+ plot for the tertiary 2-aryl-2-norbornyl and 2-aryl-2-camphenilyl *p*-nitrobenzoates in 80% aqueous acetone at 25 °C.

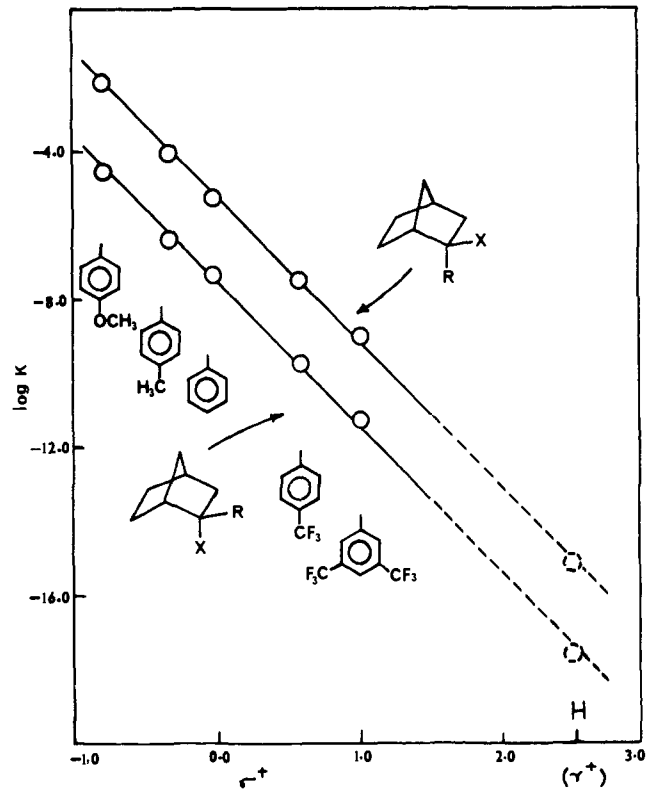


Figure 2. Correlation of the tertiary 2-norbornyl derivatives with the secondary.

understand why the cyclopentane system, where both the carbonyl frequencies in the ketone and the bond opposition forces in the parent system are similar, is not a better model for *exo*- and *endo*-norbornyl.

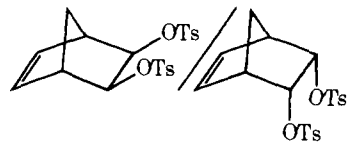
The 2-aryl-2-norbornyl cations have been studied under stable ion conditions.[22,23] From a detailed ^{1}H NMR examination of the 2-aryl-2-norbornyl cations in superacid media, Farnum and co-workers have recently concluded that the 2-phenyl-2-norbornyl cation is a classical ion with no evidence for σ-bridging.[22] However, they report that they do observe the onset of some sort of electronic delocalization in those 2-aryl-2-norbornyl cations involving more electron-demanding aryl groups.[23] Whatever might be the origin of these electronic effects in superacid media—inductive, field, hyperconjugative, or σ-bridging—they are clearly not effective in altering the exo:endo rate ratio in the solvolysis of the 2-norbornyl derivatives. This result points to the need for caution in extrapolating data from superacid media to solvolytic media.[24]

Extrapolation of the Data from Tertiary 2-Norbornyl to Secondary and Beyond. The absence of σ-participation as a significant factor in the high exo:endo rate ratios in these stabilized tertiary derivatives appears to be generally accepted.[25] The problem is whether these results can be extrapolated to account for the high exo:endo rate and product ratios in the secondary derivative. In this connection, Peters has recently estimated a substituent constant for hydrogen (γ^+) which permits the secondary derivative to be included in a linear free energy plot against σ^+ of the tertiary aryl derivatives.[26] Indeed, when *endo*-2-norbornyl is so plotted, an excellent linear relationship is realized. The question is the behavior of the exo derivative. Will the point for 2-*exo*-norbornyl lie far above the line, revealing a large enhancement of rate attributable to σ-participation? However, the data (Figure 2) reveal no such effect.

A recent elegant study by Lambert and Mark used inductively enhanced electron demand to extend the range of test for σ-participation beyond that of the simple secondary.[27] The introduction of a tosyl group into the 3 position of *endo*-norbornyl tosylate decreases the rate of acetolysis by a factor of 100 000 attributed to the strong −I effect of the substituent. They argued that the substituent must increase the electron demand at the developing carbonium ion center and should result in enhanced exo:endo ratios in systems where participation can occur.

Indeed, they observed an increase in the exo:endo rate ratio from 2900 for 2-norbornenyl to 140 000 for 2,3-ditosylnorbornenyl (5).[27] On the other hand, no such major increase in

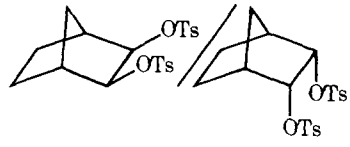
exo:endo 2900 (5)



exo:endo 140 000

the exo:endo rate ratio was observed in the corresponding saturated derivative (6). Consequently, they conclude that even

exo:endo 280 (6)



exo:endo 48

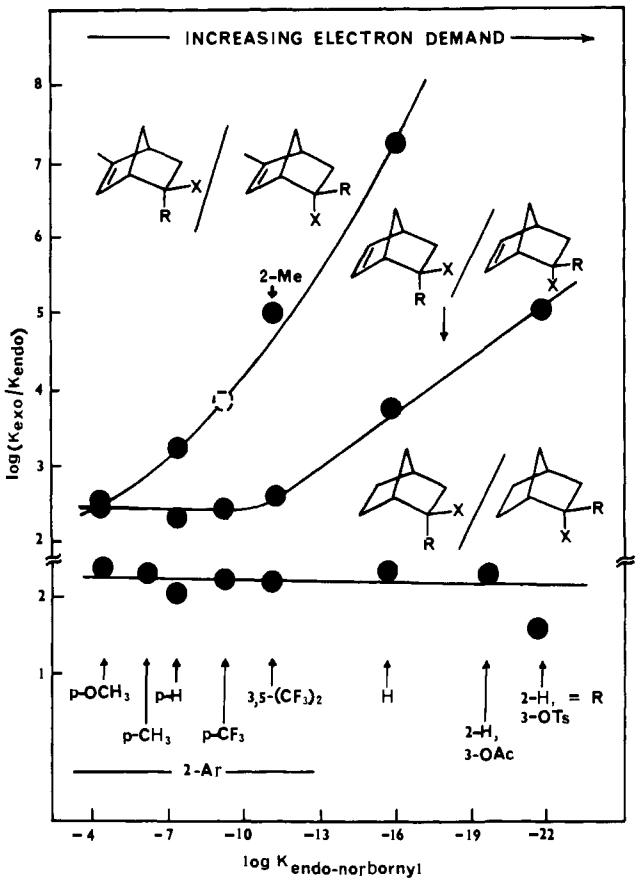
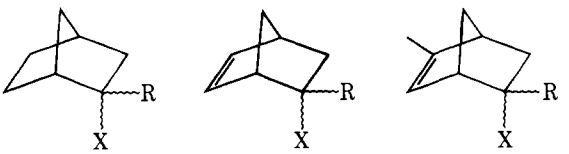


Figure 3. Effect of increasing electron demand on the exo:endo rate ratio in 2-norbornyl, 2-norbornenyl, and 5-methyl-2-norbornenyl derivatives.

under the inductively enhanced electron demand in the solvolysis of these derivatives, σ-participation does not contribute significantly to the exo:endo rate ratio.[27]

It is of interest to compare the effect of increasing electron demand in three related systems, **16, 17,** and **18.** In 5-

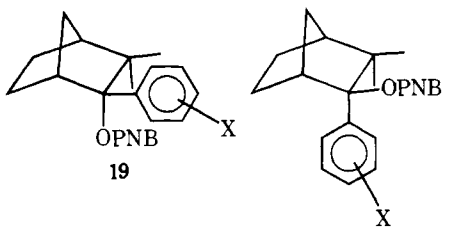


16 **17** **18**

methyl-2-norbornenyl, π-participation is clearly important and the exo:endo rate ratio increases regularly with increasing electron demand[10] (Figure 3). In 2-norbornenyl π-participation is absent until we reach the higher levels of electron demand.[28] Then there is observed a minor increase in the exo:endo rate ratio[28] (Figure 3). Finally, in 2-norbornyl, the exo:endo rate ratio remains sensibly constant over the full range of electron demand explored (Figure 3). Clearly, the absence of significant σ-participation is indicated.

Exo:Endo Rate Ratios in 2-Aryl-2-camphenilyl. The exo:endo rate ratios in 2-aryl-2-camphenilyl *p*-nitrobenzoates (**19, 20**) are much higher, but there is no observable increase in the exo:endo rate ratios as the electron-withdrawing substituents are introduced into the aromatic ring over the range examined (7).

A perusal of the actual rate constants (Table I) reveals that the 2-aryl-*exo*-camphenilyl derivatives (**20**) undergo solvolysis at a rate quite comparable with the corresponding 2-norbornyl derivatives. The greatly increased exo:endo rate ratios in this system arise as a consequence of a sharp decrease in rate of 2-aryl-*endo*-camphenilyl derivatives (**19**). Consequently, as discussed earlier, the slow rate of endo isomers (**19**) could be



19 **20** (7)

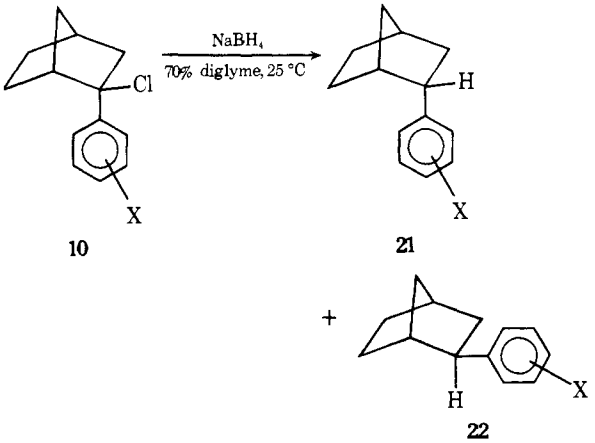
X = *p*-CH_3O	1.00	44 000
p-H	1.00	49 000
p-CF_3	1.00	24 000

accounted for in terms of more major steric difficulties in the solvation of the incipient anion and its departure than are present in the parent 2-norbornyl system.[5]

The value of ρ^+ in the solvolysis of 2-aryl-*exo*-camphenilyl derivatives (**20**) is -3.65 (correlation coefficient 0.999). This compares with a σ^+ value of -3.47 (correlation coefficient 0.999) for the corresponding endo isomers (**19**) (Figure 1). The similar values of ρ^+ confirm the conclusion that σ-participation is not an appreciable factor in the solvolysis of these derivatives.

Exo:Endo Product Ratios in 2-Aryl-2-norbornyl and 2-Aryl-2-camphenilyl. In our earlier study of 2-*p*-anisylnorbornyl derivatives, the great instability of the parent alcohols made it impossible to obtain an accurate determination of the solvolytic products. Consequently, we relied on trapping the cations with sodium borohydride and analyzed the resulting 2-arylnorbornanes by ^{1}H NMR.

The solvolysis of 2-aryl-*exo*-norbornyl chlorides in 70% diglyme in the presence of sodium borohydride gives *endo*-2-arylnorbornanes (**21**) as the predominant product, arising from the capture of hydride from the exo direction (8) (Table



10 **21** **22** (8)

II). Consequently, these tertiary 2-arylnorbornyl derivatives also exhibit the remarkable stereoselectivity observed in the norbornyl itself.

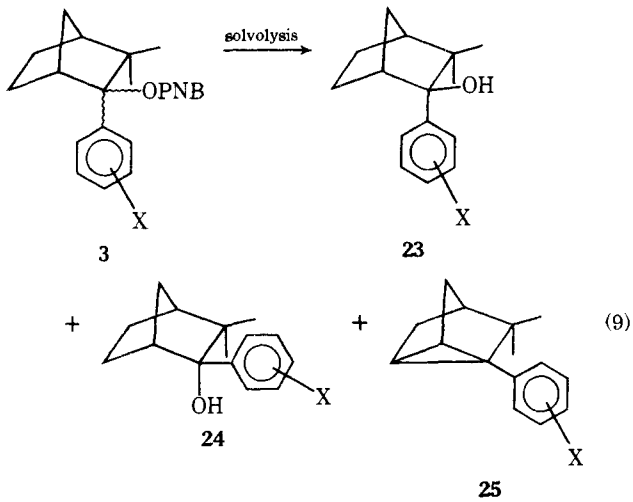
However, it still appeared desirable to establish the nature of the products realized in the reactions of stabilized 2-norbornyl cations with the solvent. For this purpose, the corresponding camphenilyl derivatives (**19, 20**) offered promise because of their markedly greater stability than the parent norbornyl compounds. Presumably, the absence of hydrogen in the 3 position avoids the fast dehydration to the olefin observed in the parent system.

The 2-aryl-2-camphenilyl *p*-nitrobenzoates (**3**) undergo solvolysis in 80% aqueous acetone to give the exo alcohols only (Table III). The formation of the endo alcohols was insignificant, less than the experimental uncertainty ($\leq$0.5%). In the case of the *p*-trifluoromethyl derivative (**18, 19,** X = *p*-CF_3), the apocyclene (**25**) constituted an appreciable fraction of the product (9). This is quite unexpected. Possibly the solvolysis

Table IV. Properties of 2-Aryl-2-norbornanols and 2-Aryl-2-camphenilols

Substituent	System[a]	Isomer	Observed mp or bp, °C	Lit. mp or bp, °C	Anal.
p-CH_3O	N	Exo[b]			
	N	Endo	135–138 (2.5 mm)	160–170 (2.5 mm)[c]	
	C	Exo	77.5–78	76–78[d]	
	C	Endo	113.5–114	115.5–116[d]	
p-CH_3	N	Exo[b,e]			
	N	Endo	113–115 (0.3 mm)	135–150 (2–2.5 mm)[c]	
p-H	N	Exo	65–66.5	61–62[f]	
	N	Endo	44.5–46	44.2–44.6[c]	
	C	Exo	56–57.5		C, H
	C	Endo	134–137 (3.5 mm)	130–131 (5.5 mm)[g]	
p-CF_3	N	Exo	82.5–83		C, H
	N	Endo	65–66		C, H
	C	Exo	108–110 (1 mm)		C, H
	C	Endo	54.5–55		C, H
3,5-$(CF_3)_2$	N	Exo	74–75	75–76.5[h]	
	N	Endo	71–72		C, H, F

[a] N, 2-aryl-2-norbornyl; C, 2-aryl-2-camphenilyl. [b] Syrupy oil at 0 °C, used for benzoate preparation without further purification. [c] D. C. Kleinfelter, Ph.D. Thesis, Princeton University, 1960. [d] P. D. Bartlett, E. R. Webster, C. E. Dills, and H. G. Richey, Jr., *Justus Liebigs Ann. Chem.* **623**, 217 (1959). [e] ^1H NMR showed the presence of 21% olefin. [f] H. C. Brown and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 1246 (1964). [g] S. S. Nametkin and G. A. Serebrennikov, *J. Gen. Chem. USSR (Engl. Transl.)*, **15**, 195 (1945); *Chem. Abstr.*, **40**, 1814 (1946). [h] Reference 23.



(9)

proceeds through a competitive γ-elimination along with the true S_N1 process. If so, this would halve the observed rate to give the true rate for the conversion to carbonium ion, and would increase the exo:endo rate ratio from the observed value of 24 000 to a value of 48 000, in much closer agreement with the value observed for other derivatives.

Conclusion

It has long been customary to interpret high exo:endo rate ratios in bicyclic systems in terms of σ-participation leading to the formation of σ-bridged norbornyl cations. It appears certain at this time that stabilized tertiary 2-norbornyl derivatives such as 2-*p*-anisyl-2-norbornyl and 2-*p*-anisyl-2-camphenilyl are essentially classical with no evidence for σ-bridging. Yet these derivatives exhibit high exo:endo rate and product ratios.[5] Failure to observe increasing exo:endo rate ratios with increasing electron demand in 2-aryl-2-norbornyl (**2**) and 2-aryl-2-camphenilyl derivatives (**3**) reveals that σ-participation is not significant in the high exo:endo rate ratios. These high exo:endo rate ratios are presumably the result of decreased rates of reaction in the sterically hindered endo direction of the U-shaped norbornane structure.[14] Extrapolation of data from the tertiary to the secondary system fails to provide evidence for σ-participation in the secondary.[26,27] It follows that even in norbornyl steric effects must contribute a major, if not the only, important factor in the high exo:endo rate and product ratios.

Experimental Section

2-Aryl-*endo*-norbornanols (8). These alcohols were prepared by the addition of the appropriate Grignard reagents to norcamphor. The tertiary alcohols were purified by distillation or crystallization. The properties of the alcohols are listed in Table IV.

2-Aryl-*exo*-norbornanols (11). The 2-aryl-*endo*-norbornanols were hydrochlorinated in an automatic hydrochlorinator using pentane or methylene chloride as solvent.[11] The tertiary chlorides were hydrolyzed in aqueous acetone containing 10% molar excess of sodium bicarbonate to yield the exo alcohols. The physical properties and analytical data are summarized in Table IV.

2-Aryl-*endo*-camphenilols (24). These alcohols were synthesized by the addition of the appropriate Grignard reagents to camphenilone (Table IV).

2-Aryl-exo-camphenilols (23). Hydrochlorination of the endo alcohols in pentane or methylene chloride afforded the chloride mixture (secondary and tertiary). Hydrolysis of the chloride mixture gave the crude exo alcohols. The pure exo alcohols were obtained by crystallization or distillation (Table IV).

Preparation of *p*-Nitrobenzoates and Benzoates. The *p*-nitrobenzoates and benzoates were prepared by the *n*-butyllithium method.[12] Some of the more stable *p*-nitrobenzoates were prepared by treating the alcohol with *p*-nitrobenzoyl chloride in pyridine.[29] The following procedure is representative. To the tertiary alcohol (5 mmol) dissolved in pyridine (10 mL) was added *p*-nitrobenzoyl chloride at room temperature under stirring. In 15–30 min, pyridine hydrochloride began to separate. After 3 h of stirring at room temperature, the reaction mixture was poured into 80 mL of cold water. Precipitated product was collected by filtration, washed with cold water and small amounts of pentane, and dried in a vacuum desiccator over Drierite. Recrystallization from a suitable solvent gave pure *p*-nitrobenzoate. Generally, yields are 50–60%.

The properties of 2-aryl-2-norbornyl and 2-aryl-2-camphenilyl *p*-nitrobenzoates are tabulated in Table V.

Trapping of 2-Aryl-2-norbornyl Cations by Sodium Borohydride. A typical experiment was described earlier.[5] GLC analysis (Varian Aerograph Hi-Fi 1200, 6-ft FFAP column at 150 °C) of the trapping product from 2-phenyl-*exo*-norbornyl chloride indicated 82% of 2-phenylnorbornane, 8% of 2-phenylnorbornene, and 10% of 2-phenyl-*exo*-norbornanol. In order to remove the olefin, the product was hydroborated. The trapping product was separated by column chro-

Table V. Properties of 2-Aryl-2-norbornyl and 2-Aryl-2-camphenilyl *p*-Nitrobenzoates

Substituent	System	Isomer	Mp, °C	Anal.
p-CH_3O	N	Exo[a]	91-91.5	C, H
	N	Endo[b]	115 dec	C, H, N
	C	Exo[a]	127.5-128.5	C, H
	C	Endo[c]	133.8-134.8	
p-CH_3	N	Exo	112 dec	C, H, N
	N	Endo	142-144 dec	C, H, N
p-H	N	Exo[d]	107.5	
	N	Endo[d]	137	
	C	Exo	124 dec	C, H, N
	C	Endo	144.8-145.3	C, H, N
p-CF_3	N	Exo	127.5-128	C, H, N, F
	N	Endo	135-135.5	C, H, N, F
	C	Exo	156.5-157	C, H, N
	C	Endo	137.8-138.5	C, H, N
3,5-$(CF_3)_2$	N	Exo	150.5-151	C, H, N, F
	N	Endo	136-136.5	C, H, N, F

[a] Benzoate. [b] Lit. mp 90-105 °C. D. C. Kleinfelter, Ph.D. Thesis, Princeton University, 1960. [c] Lit. mp 129.5-135 °C. P. D. Bartlett et al., *Justus Liebigs Ann. Chem.*, **623**, 217 (1959). [d] D. L. Vander Jagt, Ph.D. Thesis, Purdue University, 1967.

matography over alumina and eluted with pentane, $n^{20}D$ 1.5472. The products from the *p*-methoxy derivative were separated by preparative GLC. The ^1H NMR spectra of the trapping products from the *p*-H and *p*-CF_3 derivatives were taken for neat samples. The exo:endo ratio was calculated by measuring the peak area exhibited by the C_2 protons. The exo proton appeared in these derivatives at δ 3.1-3.2 ppm and the endo protons at δ 2.6-2.7. The exo:endo product ratios in the trapping 2-arylnorbornanes are summarized in Table II.

Products of Solvolysis in 2-Aryl-2-camphenilyl *p*-Nitrobenzoates. The procedure was described earlier.[5] One millimole of *p*-nitrobenzoate was solvolyzed in 25 mL of 0.08 M solution of sodium acetate or sodium bicarbonate in 80% acetone for 10 half-lives. The products were analyzed by ^1H NMR by comparing the heights of methyl signals appearing at δ 0.44 -0.48 (endo OH) and 0.74-0.80 (exo OH). The results are summarized in Table III.

Kinetic Measurements. The rate constants for the solvolysis of 2-aryl-2-norbornyl and 2-aryl-2-camphenilyl derivatives were measured in 80% aqueous acetone following the titrimetric procedure described earlier.[12,30]

References and Notes

(1) Preliminary accounts of portions of these studies have been published: K. Takeuchi and H. C. Brown, *J. Am. Chem. Soc.*, **90**, 2693, 5270 (1968); H. C. Brown and K. Takeuchi, *ibid.*, **90**, 5268 (1968); H. C. Brown, M. Ravindranathan, K. Takeuchi, and E. N. Peters, *ibid.*, **97**, 2899 (1975).
(2) Graduate research assistant on grants (G 19878 and GP 6492X) from the National Science Foundation.
(3) Postdoctoral research associate on grants provided by the Exxon Research and Engineering Co.
(4) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1147, 1154 (1952).
(5) H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, preceding paper in this issue.
(6) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952).
(7) P. G. Gassman and A. F. Fentiman, Jr., *J. Am. Chem. Soc.*, **92**, 2549 (1970).
(8) H. C. Brown, "The Nonclassical Ion Problem", Plenum Press, New York, N.Y., 1977, Chapter 10.
(9) H. C. Brown, E. N. Peters, and M. Ravindranathan, *J. Am. Chem. Soc.*, **99**, 505 (1977).
(10) H. C. Brown, E. N. Peters, and M. Ravindranathan, *J. Am. Chem. Soc.*, **97**, 7449 (1975).
(11) H. C. Brown and M.-H. Rei, *J. Org. Chem.*, **31**, 1090 (1966).
(12) H. C. Brown and E. N. Peters, *J. Am. Chem. Soc.*, **97**, 1927 (1975).
(13) H. M. Bell and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 1473 (1966).
(14) H. C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1972, Chapter 11. See also H. C. Brown, *Acc. Chem. Res.*, **6**, 377 (1973); *Tetrahedron*, **32**, 179 (1975).
(15) M.-H. Rei and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 5335 (1966).
(16) H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, **90**, 2691 (1968).
(17) H. C. Brown and Y. Okamoto, *J. Org. Chem.*, **22**, 485 (1957).
(18) Small changes in ρ^+ from the previously published values are the result of the inclusion of additional data.
(19) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **97**, 7454 (1975).
(20) H. C. Brown, M. Ravindranathan, and M. M. Rho, *J. Am. Chem. Soc.*, **98**, 4216 (1976).
(21) A. Battiste and R. A. Fiato, *Tetrahedron Lett.*, 1255 (1975).
(22) D. G. Farnum and G. Mehta, *J. Am. Chem. Soc.*, **91**, 3256 (1969).
(23) D. G. Farnum and A. D. Wolf, *J. Am. Chem. Soc.*, **96**, 5166 (1974).
(24) A study of this question in the 2-aryl-2-norbornenyl derivatives has recently been made. D. G. Farnum and R. E. Botto, *Tetrahedron Lett.*, 4013 (1975).
(25) G. D. Sargent, "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1972, Chapter 24.
(26) E. N. Peters, *J. Am. Chem. Soc.*, **98**, 5627 (1976).
(27) J. B. Lambert and H. W. Mark, *Tetrahedron Lett.*, 1765 (1976).
(28) H. C. Brown and E. N. Peters, *J. Am. Chem. Soc.*, **97**, 7442 (1975).
(29) K. Takeuchi, Ph.D. Thesis, Purdue University, 1969.
(30) H. C. Brown and C. J. Kim, *J. Am. Chem. Soc.*, **93**, 5765 (1971).

Synthesis of Tricyclo[3.1.1.$0^{3,6}$]heptan-6-yl Derivatives[1a]

Stephen A. Monti* and James M. Harless[1b]

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712.

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Abstract: Semibenzylic acid ring contraction of 6-halotricyclo[3.2.1.$0^{3,6}$]octan-7-one (**6**) furnished tricyclo[3.1.1.$0^{3,6}$]heptane-6-carboxylic acid (**1**), a novel, new ring system characterized by three cyclobutane rings fused to a common carbon atom. Tricyclic halo ketone **6** was prepared by base-catalyzed intramolecular cyclization of *exo,exo*-7-halobicyclo[3.2.1]octan-6-on-3-yl mesylate (**7**) which was derived from bicyclo[3.2.1]oct-6-en-3-one by reduction with sodium in ethanol, mesylation, and then oxidative chlorination with chromyl chloride or from the ketal of bicyclo[3.2.1]oct-2-(and -3-) en-6-one by regio- and stereoselective hydroboration/oxidation, mesylation, hydrolysis, and bromination. Curtius acid rearrangement of acid **1** produced the 6-acetamide derivative **2**. The ^1H and ^{13}C NMR spectra of this novel ring system are reported.

Tricyclo[3.1.1.$0^{3,6}$]heptane (**1**, R = H) represents a novel carbon skeleton characterized structurally by a chair cyclohexane ring in which the three alternate axial bonds are connected to a single bridging carbon atom. Herein we wish to describe the full details[2] of the synthesis and characterization of the first known examples[3] of this ring system, tricyclo[3.1.1.$0^{3,6}$]heptane-6-carboxylic acid (**1**) and the 6-acetamide derivative **2**. This symmetrical tricycloheptane skeleton[4] is the smallest isolated member of the general family of molecules characterized by the symmetrical spanning of a ring perimeter by a single bridging carbon atom. Other members of this class include the elusive tetrahedrane (**3**)[6] and the well-documented