Structural Effects in Solvolytic Reactions. 25. Solvolysis of Aryl(2-norbornyl)methylcarbinyl *p*-Nitrobenzoates. Search for a Special Stereoelectronic Effect with the Tool of Increasing Electron Demand

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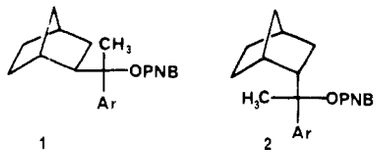
The relative electronic stabilization of a carbonium center by α *exo*- and *endo*-norbornyl groups was studied by synthesizing and solvolyzing representative aryl(2-norbornyl)methylcarbinyl *p*-nitrobenzoates in 80% aqueous acetone. The endo derivatives solvolyze four or five times faster than the exo derivatives, presumably attributable to enhanced steric strain facilitating the ionization of the endo isomer. The exo derivatives yield a value of ρ^+ of −4.44, almost identical with the value of ρ^+ of −4.47 observed for the endo derivatives. It is concluded that the application of the tool of increasing electron demand to these systems fails to reveal any significant electronic factor in the exo isomers facilitating their ionization, an electronic factor not present in the corresponding endo derivatives.

A number of proposals have appeared for the existence of special stereoelectronic factors operating in *exo*-norbornyl derivatives so as to favor their reactions as compared to the endo isomers.[2] The original proposal was that σ bridging favored the solvolysis of *exo*-norbornyl derivatives, but was stereoelectronically inoperative in the corresponding endo isomers.[3] Later, it was suggested that the stereoelectronic contribution need not involve σ bridging. Instead, it was proposed that the *exo*-norbornyl transition state could be stabilized by hyperconjugative interactions involving the 1,6-bonding pair.[4,5] This stereoelectronic interpretation differs from the older nonclassical ion proposal in that major distortion of the structure is not essential for the operation of the electronic contribution facilitating ionization of the exo isomer.[4,5]

More recently it has been suggested that such stereoelectronic contributions from the 2-norbornyl system also operate to stabilize developing electron deficiencies in the position α to the 2-norbornyl structure preferentially from the exo direction.[6-8]

We had earlier applied the tool of increasing electron demand[9] to test for enhanced electronic contributions from the *exo*-norbornyl system to stabilize a developing electron deficiency at the 2 position.[10] It appeared desirable, therefore, to apply the tool of increasing electronic demand to this newer proposal of a preferential stereoelectron contribution in *exo*-norbornyl derivatives which can stabilize a developing electron deficiency in the α position. Accordingly, we undertook to synthesize and to determine the rates of solvolysis of the aryl(2-norbornyl)methylcarbinyl *p*-nitrobenzoates (**1** and **2**).



1 **2**

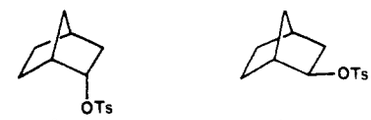
Results

Synthesis. The preparation of *exo*- and *endo*-2-acetylnorbornane was described earlier.[11] The addition of the appropriate Grignard reagents to the 2-acetylnorbornanes gave the tertiary alcohols. The *p*-nitrobenzoates of the tertiary alcohols were obtained by the *n*-butyllithium method.[12]

Solvolysis. The rates of solvolysis of the *p*-nitrobenzoates were determined in 80% aqueous acetone by the titrimetric procedure.[12] The rate constants for the highly reactive *p*-methoxy derivatives were obtained by multiplying the rate of the benzoate by a factor of 20.8.[13] The pertinent rate data and activation parameters are summarized in Table I.

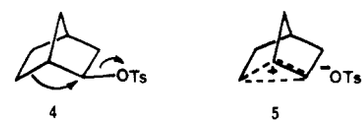
Discussion

The high exo/endo rate ratio exhibited in the acetolysis of the 2-norbornyl tosylates (**3** and **4**) has long intrigued chemists.[2] It was originally proposed that the faster rate of the exo isomer (**4**) was the result of σ participation by the 1,6-bonding pair, leading to a stabilized σ-bridged cation (**5**).[3,15] The endo isomer (**3**) is postulated to be stereoelectronically unfavorable for such participation.[16]



3 **4**

Rel rate (25°C)[14] 1.00 280



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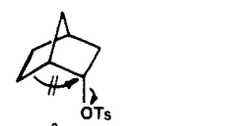
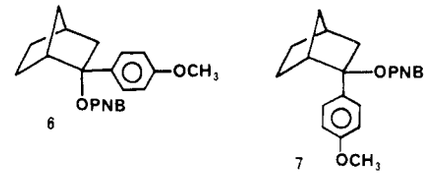


3

It is a well-established characteristic of such participation that it requires a cationic center with considerable electron demand—a highly stabilized cationic center should not involve such σ bridges.[2] Yet the solvolysis of the 2-*p*-anisyl-2-norbornyl *p*-nitrobenzoates (**6** and **7**) exhibits equally high exo/endo rate ratios.[17]



6 **7**

Rel rate (25°C) 1.00 284

Indeed, 2-*p*-anisyl-2-camphenilyl (**8** and **9**) exhibits a much higher exo/endo rate ratio.[17]

Merely by varying the steric requirements, it has proven possible to realize enormous changes in the exo/endo rate ratios (**10**, **11**, and **12**).[18]

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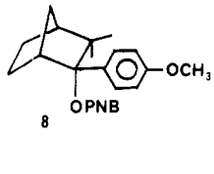
Table I. Rates of Solvolysis of Aryl(2-norbornyl)methylcarbinyl *p*-Nitrobenzoates

System	Substituent in aryl	$k_1 \times 10^{-6}$, s^{-1} T_1, °C	T_2, °C	25 °C	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	Rel rate 25 °C
1 (exo)	*p*-CH_3O			112[a]			0.16
	p-H	359 (100)	28.0 (75)	0.0472[b]	25.8	−5.7	0.33
	p-CF_3	503 (150)	47.0 (125)	6.73×10^{-5} [b]	31.2	−0.6	0.22
	3,5-$(CF_3)_2$	605 (175)	60.1 (150)	1.04×10^{-6} [b]	34.8	2.4	0.19
2 (endo)	*p*-CH_3O			708[a]			1.00
	p-H	776 (100)	66.8 (75)	0.144[b]	25.7	−8.6	1.00
	p-CF_3	102 (125)	8.02 (100)	3.02×10^{-4} [b]	29.4	−3.4	1.00
	3,5-$(CF_3)_2$	82.1 (150)	6.92 (125)	5.52×10^{-6} [b]	32.5	−0.9	1.00

[a] Calculated by multiplying the rate of benzoate by a factor of 20.8.[9] [b] Extrapolated from data at higher temperatures.



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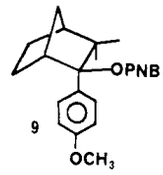
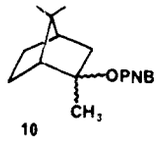


9

Rel rate (25°C) 1.00 44 000



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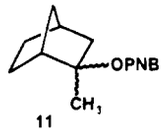

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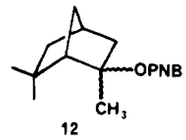


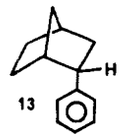
12

exo/endo (25°C) 6.1 885 3 630 000

These results have led to the alternative proposal that solvolysis is related to other reactions of the norbornyl system, with separation of the group being more favored from the exposed exo face than from the hindered U-shaped endo face.[2]

The newer proposal of a hyperconjugative interaction of the 1,6-bonding pair with the developing electron deficiency at the *exo*-2 position[4,5] appears to suffer from the same difficulty. Such hyperconjugative interactions would also be expected to decrease with decreasing electron demand by the developing cationic center at C-2. Yet such variation in the exo/endo rate ratio with increasing electron demand at C-2 is not observed.[10]

Let us now consider the more recent proposals for a significant stereoelectronic contribution operating preferentially from the exo direction of the norbornyl structure to stabilize a developing electron deficiency in the α position. Jensen and Smart observed that the benzoylation of 2-phenylnorbornanes is somewhat faster for the exo isomer (**14**) than for the endo (**13**).[6]



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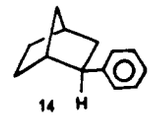


14

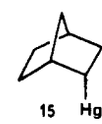
Rel rate (25°C) 1.00 1.57

They observed that 1-phenylnorbornane was even more reactive (relative rate (25 °C), 1.72) than *exo*-phenylnorbornane (1.57). They proposed that the strained σ bonds of the norbornane structure could stabilize the developing positive charge in the aromatic ring by enhanced hyperconjugative interactions.

The interpretation is similar to that later advanced by Traylor and co-workers.[5] According to this stereoelectronic interpretation, "vertical stabilization" or conjugation involving strained σ bonds can stabilize the developing cationic center. In **13** and **14** it is considered that the developing positive charge at the position of the phenyl ring where it is attached to the norbornane structure would be stabilized by hyperconjugative interactions with the strained 1,2 and 2,3 σ bonds.

Although Jensen and Smart did not discuss this question in their publication, in private communications to one of the present authors (H.C.B.) they attributed the difference in reactivities of the exo and endo isomers, **14** vs. **13**, to more favorable hyperconjugative contributions in the former.

The acetolyses of *exo*- and *endo*-2-norbornylmethylmercury (**15** and **16**) similarly show a small preference for the exo



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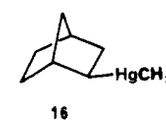


16

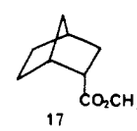
Rel rate (37.5°C) 1.00 1.3

isomer.[7] The reaction involves formation of methane by rupture of the Hg–CH_3 bond.

$$RHgCH_3 + CH_3CO_2H \rightarrow RHgO_2CCH_3 + CH_4$$

It is postulated to proceed through an intermediate or transition state with an electron deficiency on mercury, RHg^+.[19]

These differences between *exo*- and *endo*-norbornyl derivatives are very small. Experience teaches us the dangers in attempting to interpret such small differences in chemical reactivity. For example, the difference in the rates of alkaline hydrolysis of *endo*- and *exo*-norbornanecarboxylic acid esters is considerably larger[21] (**17** and **18**). Surely we cannot take this



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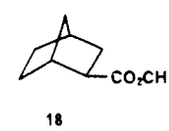


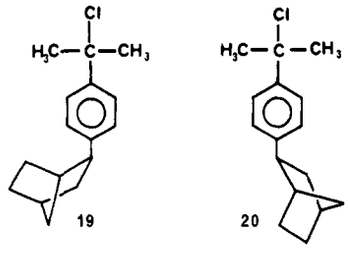
18

Rel rate (35°C) 1.00 12.0

difference as evidence for a significant difference in the electronic supply from the *exo*- and *endo*-norbornyl structures to the reaction center. The relative rates are more plausibly interpreted in terms of the large steric difference between *endo*- and *exo*-norbornyl derivatives.[2,11] A similar steric factor may also contribute to the small differences in the relative reactivities of **13** and **14**, and **15** and **16**.

Our preferred approach to test the relative abilities of various groups to contribute to electron-deficient centers has involved the *tert*-cumyl system.[22] Here also we observe a small difference in rates, 1.15, between *exo*- and *endo*-norbornyl (**19** and **20**).[22a]

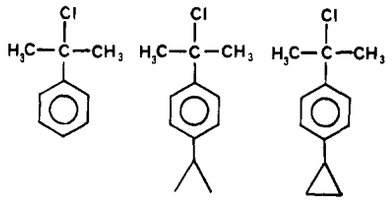
It should be pointed out that comparable variations in reactivity are realized for *p*-cyclobutyl (20.7), *p*-cyclopentyl (23.7), and *p*-cyclohexyl (19.6).[22b] Consequently, we concluded that such small variations could well arise from minor variations in conformations and in hyperconjugative contributions and could not be attributed with any confidence to a significant difference in stereoelectronic contributions of *exo*- and *endo*-norbornyl.[11,23]



	19	20
Rel rate (*p*-H = 1.00) (25°C)	21.8	25.2

These effects are all very small. It has been argued that the amount of positive charge delocalized to the para position of the *tert*-cumyl system is relatively small. Such a small deficiency can make but a small demand on the alkyl group for electronic contributions.

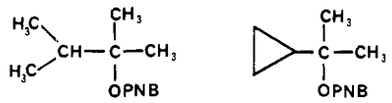
In the case of other groups, the observed effect is significant. Thus the cyclopropyl group in the *tert*-cumyl system (**23**) is



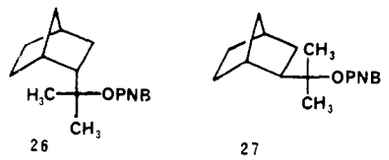
	21	22	23
Rel rate (25°C)	1.00	18.0	154

unambiguously better than a simple alkyl group in providing electronic stabilization.[24]

By placing the developing charge α to the group, the electronic demand and the observed effect should be much larger. For example, cyclopropyldimethylcarbinyl *p*-nitrobenzoate (**25**) solvolyzes enormously faster than the corresponding isopropyl derivative (**24**).[25] We tried to utilize this approach



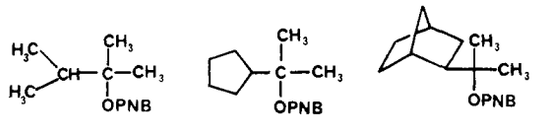
	24	25
Rel rate (25°C)	1.00	170 000



	26	27
Rel rate (25°C)	1.00	0.055

with 2-norbornyl (**26** and **27**).[11] However, it was the endo isomer, not the exo isomer, that exhibited the enhanced rate. Presumably, relief of steric strain in the more hindered endo derivative dominates the situation, swamping out any small differences in the electronic contributions of the *exo*- and *endo*-norbornyl groups.

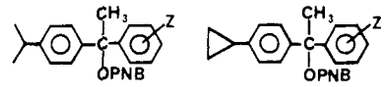
That the electronic contribution of the *exo*-norbornyl group cannot be very large compared to other aliphatic and alicyclic groups is indicated by the following comparison of isopropyl (**24**), cyclopentyl (**28**), and *exo*-norbornyl (**27**) derivatives.[9] Compare these values with **25/24.**



	24	28	27
Rel rate (25°C)	1.00	1.54	2.78

The tool of increasing electron demand appeared to offer a more objective means for comparing the electronic contributions of the *exo*- and *endo*-norbornyl groups. Here we vary the electron demand by introducing appropriate substituents in the meta and para positions of the aryl group. Consequently, within each series the steric effects are maintained constant as the electron demand is varied.

We have established that the tool of increasing electron demand is quite sensitive. By introducing a phenyl group between the isopropyl and cyclopropyl groups and the developing electron-deficient center we greatly damped out the effects of these groups. The parent compounds (X = *p*-H) exhibit a relative reactivity of only 2.8 (**29** and **30**).[26] Yet the



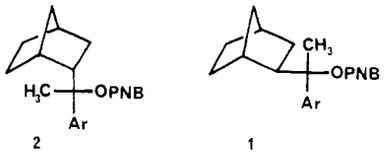
	29	30
Rel rate (Z = H) (25°C)	1.00	2.8
ρ^+	-2.91	-2.24

values of ρ^+ clearly establish a greater electron supply from the *p*-cyclopropyl substituent (ρ^+ −2.24) than the *p*-isopropyl substituent (ρ^+ −2.91) with $\Delta\rho^+$ −0.67.

Recently Peters has applied the tool of increasing electron demand to the cyclobutyl system.[27] Examination of the solvolysis of the usual substituted arylcyclobutylmethylcarbinyl *p*-nitrobenzoate yielded a value of ρ^+ of −3.94, as compared to a value of −4.65 for the related arylisopropylmethylcarbinyl derivatives. The author concluded that in these cyclobutyl derivatives the strained σ bonds do make a significant contribution to the stability of the developing cationic center.[28] Consequently, it appeared of special interest to establish what the tool of increasing electron demand would reveal about electronic contributions from the two isomeric groups—α-*exo*-norbornyl and α-*endo*-norbornyl.

Solvolysis of the aryl(2-norbornyl)methylcarbinyl *p*-nitrobenzoates revealed that here also the endo isomers exhibit the faster rates, as in the corresponding dimethyl derivative, **26.** However, the exo/endo rate ratios (**1/2**), ~4.8, are considerably smaller than the value (18.2) for the corresponding methyl derivatives (**27/26**). This suggests that the steric requirements of the phenyl group in **1** and **2** must be somewhat smaller than the steric requirements of the corresponding methyl groups in **26** and **27.**

However, more critical for the main objective of the present study is an examination of the sensitivity of the developing cationic center to electronic contributions from the substituents in the aromatic ring. The larger the electronic contributions from the norbornyl structure, the less demand there should be for electron supply from the aromatic ring, and the smaller should be ρ^+. However, no significant difference in ρ^+ is observed.



	2	1
ρ^+	-4.47	-4.44

We have now tested for differential electronic supply from *exo*-norbornyl, as compared to *endo*-norbornyl, in three ways. First, we placed the groups in the para position of the *tert*-cumyl system.[22] The small difference in relative rates, 1.00 vs. 1.15, comparable to the differences found for *p*-cyclobutyl, *p*-cyclopentyl, and *p*-cyclohexyl, does not support a significant stereoelectronic contribution from *exo*-norbornyl to the stabilization of the developing cation.

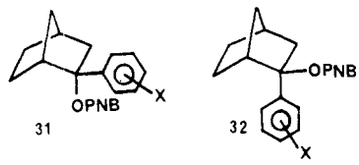
Then we have placed the two groups α to the developing

Table II. Properties of Aryl(2-norbornyl)methylcarbinyl *p*-Nitrobenzoates

System	Substituent in aryl	Yield, %	Mp, °C	Analyses
1 (exo)	*p*-H	68	141–142	C, H, N
	p-CF_3	61	146–147	C, H, N, F
	3,5-$(CF_3)_2$	65	100.5–101	C, H, N, F
2 (endo)	*p*-H	77	115–116 dec	C, H, N
	p-CF_3	81	155.5	C, H, N, F
	3,5-$(CF_3)_2$	71	127.5–128	C, H, N, F

electron-deficient center. The differences in ρ^+, −4.47 vs. −4.44, fail to reveal any evidence for greater electronic supply from the exo center.

Finally, we have placed the developing electron-deficient center on C-2 of the norbornyl structure (**31** and **32**).[10] Again,



ρ^+ -3.72 -3.82

ρ^+ fails to detect any significant difference in the stereoelectronic properties of *exo*- and *endo*-norbornyl. (The small difference, −3.72 vs. −3.82, is actually in the opposite order for a preferential stereoelectronic contribution in the exo isomer.)

Conclusion

We conclude from the present solvolytic study that the stabilization of the developing carbonium ion center by α *exo*- and *endo*-norbornyl groups is nearly the same, without significantly greater electron supply from exo as compared to endo. Finally, even when the developing electron deficiency is actually on the ring (C-2), no differential electron supply for the exo isomer, as compared with the endo isomer, is observed.

Experimental Section

Preparation of Tertiary Alcohols. The Grignard reagents prepared from *p*-bromoanisole, bromobenzene, *p*-bromobenzotrifluoride, and 3,5-bis(trifluoromethyl)bromobenzene were added to *exo*- and *endo*-2-acetylnorbornanes to afford the tertiary alcohols.

Preparation of *p*-Nitrobenzoates. These derivatives were synthesized by treating the tertiary alcohols with *n*-butyllithium and *p*-nitrobenzoyl chloride in THF.[12] Properties of the *p*-nitrobenzoates are listed in Table II.

Kinetic Measurements. The rates of solvolysis of the *p*-nitrobenzoates were determined in 80% aqueous acetone following the titrimetric procedure.[12] The rate data and activation parameters are listed in Table I. The rate constants are reproducible to within ±1%.

Registry No.—**1/2** (Ar = *p*-$CH_3OC_6H_4$), 65749-06-6; **1/2** (Ar = *p*-$CH_3OC_6H_4$) free alcohol, 65749-07-7; **1/2** (Ar = C_6H_5), 65749-08-8; **1/2** (Ar = C_6H_5) free alcohol, 65749-09-9; **1/2** (Ar = p-$CF_3C_6H_4$), 65749-10-2; **1/2** (Ar = p-$CF_3C_6H_4$) free alcohol, 65749-11-3; **1/2** (Ar = 3,5-$(CF_3)_2C_6H_4$), 65749-12-4; **1/2** (Ar = 3,5-$(CF_3)_2C_6H_4$) free alcohol, 65749-13-5; *p*-bromoanisole, 104-92-7; bromobenzene, 108-86-1; *p*-bromobenzotrifluoride, 402-43-7; 3,5-bis(trifluoromethyl)bromobenzene, 328-70-1; *exo*-2-acetylnorbornane, 824-59-9; *endo*-2-acetylnorbornane, 824-58-8; *p*-nitrobenzoyl chloride, 122-04-3.

References and Notes

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$$RHgMe \rightarrow RHgMe^+ + e$$

and therefore attribute both the greater ease of ionization and the faster rate of acetolysis of the exo isomer to the relative ease of electron release by *endo*- and *exo*-norbornyl groups to the electron deficiency. Difficulties with their interpretation of the vertical ionization potentials is discussed in a manuscript by W. L. Jorgensen and J. E. Munroe (ref 20) soon to appear. However, on a more pragmatic level, Kochi and his co-workers report that the rate of acetolysis of 2-propylmethylmercury is essentially identical with that for *exo*-norbornylmethylmercury. This is not consistent with the proposed enhanced electronic contribution from the *exo*-norbornyl group.

The authors attribute the slightly greater reactivity of the exo isomer (**16**) over the endo isomer (**15**) loosely to "σ participation." However, they must be referring to σ conjugation or hyperconjugation involving the electron deficiency on mercury and the strained 1,2 and 2,3 carbon–carbon bonds, as in the Jensen–Smart system (**13** and **14**).[6] See ref 2, pp 63–66, for a discussion of the difference between π and σ conjugation and participation.
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