Structural Effects in Solvolytic Reactions. XI. Rates and Products of Solvolysis of 2-Aryl- and 2-Methyl-2-norbornenyl *p*-Nitrobenzoates. Exo:Endo Rate Ratio as a Function of Increasing Electron Demand[1]

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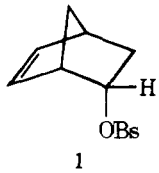
Abstract: Representative 2-aryl-2-norbornenyl *p*-nitrobenzoates with selected substituents in the aryl ring (*p*-CH_3O, *p*-H, *p*-CF_3, and 3,5-$(CF_3)_2$) were synthesized and their rates of solvolysis in 80% aqueous acetone determined in order to apply the tool of increasing electron demand as a test for the importance of π participation in this system. The study was extended to the corresponding 2-methyl-2-norbornenyl derivatives. The exo:endo rate ratios for the various *p*-nitrobenzoates are 312 for *p*-CH_3O, 202 for *p*-H, 283 for *p*-CF_3, and 447 for 3,5-$(CF_3)_2$. The exo:endo rate ratio in the solvolysis of the 2-methyl-2-norbornenyl *p*-nitrobenzoates (895) shows no significant increase over the corresponding saturated derivatives. On the other hand, the exo:endo rate ratio of the parent secondary 2-norbornenyl derivatives (7000) does reveal an appreciable increase over the saturated compound indicating that π participation is not important under the high electron demand of the tertiary methyl cationic center, but becomes significant under the even higher electron demand of the secondary system. The $\rho^+\sigma^+$ treatment reveals linear correlations for the *endo*-2-aryl-2-norbornenyl derivatives, but, in the case of exo compounds, a modest break appears following *p*-CF_3. The ρ^+ values are −4.21 for the exo isomers, omitting 3,5-$(CF_3)_2$, and −4.17 for the endo derivatives. The solvolysis of 2-*p*-anisyl- and 2-phenyl-*endo*-norbornenyl *p*-nitrobenzoates proceeds at rates 5 and 8.8 times slower than those for the saturated derivatives. Very similar modest rate retardations are also observed in the corresponding exo derivatives indicating the absence of significant π participation. Both *exo*- and *endo*-2-methyl-2-norbornenyl *p*-nitrobenzoates solvolyze at rates 21.3 and 21.5 times slower than the saturated analogs and this can be attributed to the rate retarding effect of the double bond with little π-participation. The solvolysis products confirm this conclusion. In the case of *p*-CH_3O, *p*-H, and *p*-CF_3 compounds, the predominant products of solvolysis are the corresponding 2-aryl-*exo*-norbornenols, but in the case of the 3,5-$(CF_3)_2$ exo isomer, the rearranged structure, 1-[3,5-bis(trifluoromethyl)phenyl]-3-nortricyclanol, constitutes the main product. These results are interpreted in terms of the essential absence of π participation in the solvolysis of the *p*-CH_3O, *p*-H, and *p*-CF_3 derivatives and the modest involvement of π electrons in the solvolysis of the 3,5-$(CF_3)_2$ derivative.

In estimating neighboring group effects, it is customary to compare the rate with a related rate not involving participation.[3,4] For the assessment of π participation in homoallylic systems, it is often useful to compare the rate of solvolysis of the homoallylic compound with the rate of solvolysis of its saturated analog.[5-7] However, this procedure is not always followed. For example, in the 2-norbornenyl system (**1**, **2**), the observed exo:endo ratio of 7000 for the brosylates was attributed to π participation in the exo isomer.[8] However, steric effects may also make major contributions to high exo:endo rate ratios.[9] Thus the original conclusion as to the magnitude of π participation in this system, based solely upon high exo:endo rate ratio, would appear to be questionable.



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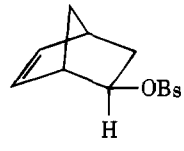
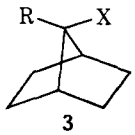


2

rel rate (25°): 1.00 7000

Gassman and coworkers[7] demonstrated that a *p*-anisyl group essentially "levels" the enormous stabilization afforded by the double bond in the solvolysis of *anti*-7-norbornenyl derivatives (**3**, **4**). Indeed, the 7-*p*-anisyl derivative **4b** solvolyzes at essentially the same rate as the corresponding saturated derivative **3b**. If the *p*-anisyl group can cause the rate difference of 10^{11} observed in *anti*-7-norbornenyl (**4a**/**3a**) to vanish, then the much smaller factor of 7000 observed for *exo*-norbornenyl brosylate (**2**) should also vanish *if this factor is solely due to π participation.* With alternations in the substituents in the meta and para positions of the 2-aryl group, electron demand at the 2-aryl position can be increased without altering the steric situation. Incursion of π participation should then be reflected in an increase in the exo:endo rate ratio over that observed for the 2-*p*-anisyl derivative.



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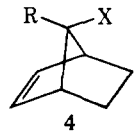


4

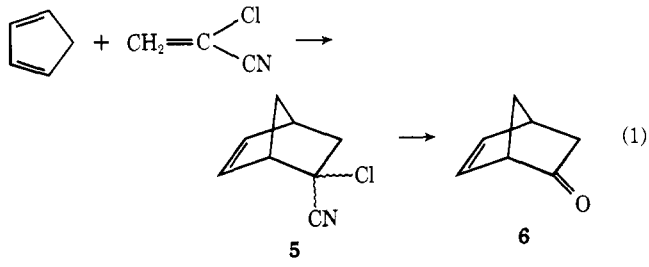
a R = H	1.0	10^{11}
b R = *p*-anisyl	1.0	3.4

Accordingly, we undertook to synthesize 2-aryl- and 2-methyl-2-norbornenyl derivatives and to study their rates and products of solvolysis. The electron demand of the 2-methyl cationic center is relatively high, considerably greater than that of the *p*-trifluoromethylphenyl substituent.[10,11] The application of the tool of increasing electron demand has established that it is capable of detecting even small electronic contributions[12] and the present study aims at providing a definite answer for the presence or absence of π participation in these systems.

Results

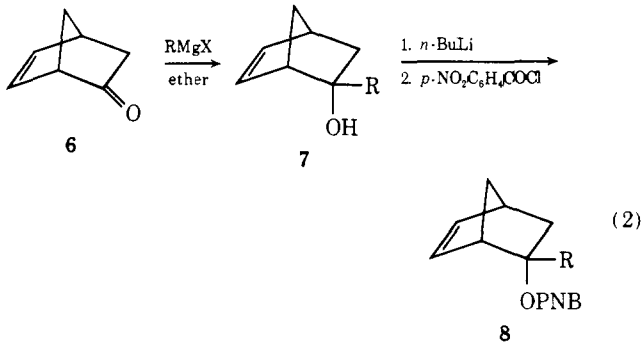
Synthesis. 5-Norbornen-2-one (**6**) was prepared according to Freeman's modification[13] of Krieger's procedure.[14] 2-Chloro-2-cyano-5-norbornene (**5**) obtained from the Diels–Alder reaction of α-chloroacrylonitrile and cyclopentadiene was converted to **6** upon treatment with potassium hydroxide in dimethyl sulfoxide at room temperature (eq 1).

The conversion of **6** into the 2-aryl-*endo*-norbornenols



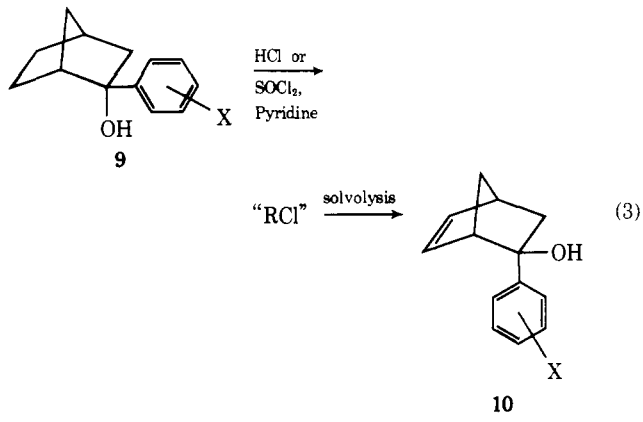
(1)

(7) and the subsequent preparation of the *p*-nitrobenzoates (**8**) are indicated in eq 2.



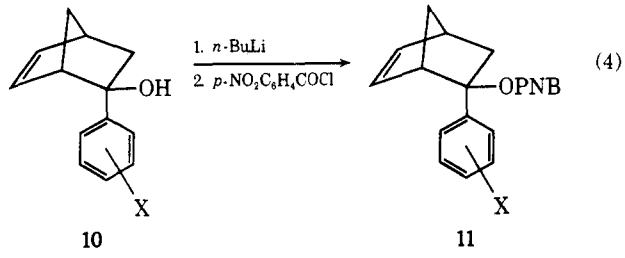
(2)

For preparing the exo derivatives, the endo alcohols (**9**) were converted to the chloride and then solvolyzed in buffered aqueous acetone (eq 3). Pure exo alcohols (**10**) were



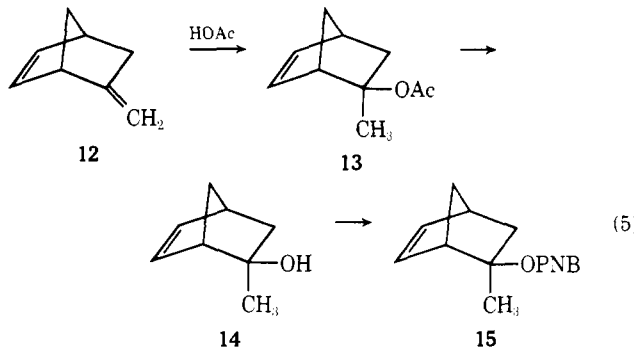
(3)

obtained from the resulting alcohol mixture by fractional crystallization. (In the case of the *p*-anisyl compound, solvolysis gave exclusively the desired exo alcohol; in all the other cases, the product was a mixture of the exo alcohol and the corresponding 1-aryl-3-nortricyclanol.) The *p*-nitrobenzoates were obtained in the usual manner by the lithium alkoxide method[15] (eq 4).



(4)

2-Methyl-*exo*-norbornenyl acetate (**13**) was prepared by Mälkonen and Toivonen in less than 3% yield by the Diels–Alder reaction of isopropenyl acetate with cyclopentadiene.[16] Because of the very poor yield of **13** realized, this method seemed undesirable and a better method was devised. Addition of hydrogen chloride and acetic acid to bicyclic olefins has been shown to proceed with exo stereochemistry and with little rearrangement.[17] Therefore, the addition of acetic acid to a 2.4-fold excess of 5-methylenenorbornene (**12**) was tried and resulted in a fair yield of 2-methyl-*exo*-norbornenyl acetate (**13**). After hydrolysis, 2-methyl-*exo*-norbornenol (**14**) was obtained (eq 5).



(5)

Addition of methylmagnesium iodide to **6** afforded a mixture of 2-methyl-*endo*-norbornenol (**7**, R = CH_3, 97%) and the exo isomer **14** (3%). The pure endo isomer was obtained by preparative GLC. The syntheses of 1-methylcyclopentyl,[18] 1-methylcyclopent-3-enyl,[19] and 2-methyl-*exo*- and -*endo*-norbornyl *p*-nitrobenzoates[20] have been reported.

Rate Studies. The rate constants and thermodynamic parameters for the solvolysis of 2-aryl- and 2-methyl-2-norbornenyl *p*-nitrobenzoates in 80% aqueous acetone are listed in Table I. 2-*p*-Anisyl-*exo*-norbornenyl *p*-nitrobenzoate was too unstable to be isolated and hence the rate constant for this derivative was estimated by multiplying the rate constant for the benzoate by the factor 20.8.[21] The rate constant for 2-[3,5-bis(trifluoromethyl)phenyl]-*endo*-norbornenyl *p*-nitrobenzoate was obtained from the log k–σ^+ plot for the other derivatives. The rate of solvolysis of 2-methyl-*endo*-norbornenyl *p*-nitrobenzoate proved to be difficult to measure in 80% acetone because of its exceedingly slow reactivity. Consequently, its rate of solvolysis was determined in 50 and 60% acetone (v/v) from which the rate constant in 80% acetone was calculated by the method of Grunwald and Winstein.[22]

Product Studies. The products of solvolysis of the 2-aryl-2-norbornenyl *p*-nitrobenzoates were determined in 80% aqueous acetone containing 10 mol % excess sodium acetate and analyzed by NMR. In the case of 2-methyl derivatives, the products were determined in 50% aqueous acetone and analyzed by GLC. The results are tabulated in Table II.

Discussion

The data now available for the 2-norbornenyl permit an analysis for the presence or absence of π participation through a number of different approaches. For example, we can examine the exo:endo rate ratio in a 2-aryl-2-norbornenyl derivative where the cationic center is highly stabilized to see if the exo:endo rate ratio essentially diminishes to unity. Secondly, we can apply the tool of increasing electron demand and ascertain if the exo:endo rate ratio exhibits increases with increasing electron demand. Then it is possible to ascertain the effect of the double bond in the endo isomer, where π participation cannot be significant, and ascertain if the effect of the double bond is altered in the exo isomer, reflecting the incursion of π participation. Finally, we can examine the products to ascertain whether they undergo the changes anticipated for π participation.

Exo:Endo Rate Ratio in the Highly Stabilized 2-*p*-Anisyl-2-norbornenyl System. As was pointed out earlier, Gassman and Fentiman observed that the introduction of a *p*-anisyl group into the 7-*anti*-norbornenyl structure causes the 10^{11}

Table I. Rates of Solvolysis of 2-Aryl- and 2-Methyl-2-norbornenyl *p*-Nitrobenzoates and Related Derivatives in 80% Aqueous Acetone

p-Nitrobenzoate	$k_1 \times 10^6$, sec^{-1} (T_2, °C)	$k_1 \times 10^6$, sec^{-1} (T_1, °C)	$k_1 \times 10^6$, sec^{-1} 25°	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	Exo:endo
2-*p*-Anisyl-*exo*-norbornenyl			2520[a]			312
2-*p*-Anisyl-*endo*-norbornenyl	170 (50°)		8.08	22.7	−5.6	
2-Phenyl-*exo*-norbornenyl	570 (75°)	33.7 (50°)	1.24[b]	24.7	−2.5	202
2-Phenyl-*endo*-norbornenyl	55.5 (100°)	4.10 (75°)	6.03×10^{-3}[b]	26.3	−7.9	
2-*p*-Trifluoromethylphenyl-*exo*-norbornenyl	38.6 (100°)	2.73 (75°)	3.60×10^{-3}[b]	26.8	−7.4	283
2-*p*-Trifluoromethylphenyl-*endo*-norbornenyl	63.8 (150°)	6.33 (125°)	1.27×10^{-5}[b]	30.4	−6.6	
2-[3,5-Bis(trifluoromethyl)-phenyl]-*exo*-norbornenyl	138 (150°)	17.2 (125°)	1.26×10^{-4}[b]	27.3	−12.3	447
2-[3,5-Bis(trifluoromethyl)-phenyl]-*endo*-norbornenyl			2.82×10^{-7}[c]			
1-Methylcyclopentyl[d]			2.11×10^{-3}[b]			
1-Methylcyclopent-3-enyl[e]	232 (150°)	27.2 (125°)	1.41×10^{-4}[b]	28.1	−9.3	
2-Methyl-*exo*-norbornyl[f]	94.6 (100°)	6.94 (75°)	1.00×10^{-2}[b]	26.3	−7.0	885
2-Methyl-*endo*-norbornyl[f]	5.41 (125°)	0.395 (100°)	1.13×10^{-5}[b]	30.2	−7.5	
2-Methyl-*exo*-norbornenyl	95.3 (125°)	8.24 (100°)	4.70×10^{-4}[b]	28.2	−6.8	895
2-Methyl-*endo*-norbornenyl			5.27×10^{-7}[g]			

[a] Rate constant was estimated by multiplying the rate constant for the benzoate by the factor 20.8.[21] [b] Calculated from data at higher temperatures. [c] Estimated by extrapolation of the log $k-\sigma^+$ plot for other derivatives. [d] Reference 18. [e] Mp 103–104.5°; ref 19. [f] Reference 20. [g] Calculated from data in other solvents (ref 22). In 50% acetone: $k_1^{25} = 1.90 \times 10^{-11}$; [b] $\Delta H^{\ddagger} = 29.8$ kcal/mol; $\Delta S^{\ddagger} = -7.6$ eu. In 60% acetone: $k_1^{25} = 6.62 \times 10^{-12}$; [b] $\Delta H^{\ddagger} = 30.6$ kcal/mol; $\Delta S^{\ddagger} = -7.1$ eu.

Table II. Products of Solvolysis of 2-Aryl- and 2-Methyl-2-norbornenyl *p*-Nitrobenzoates in 80% Aqueous Acetone at 100°[a]

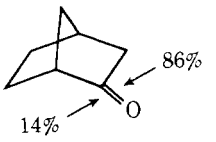
2-Substituent	Isomer	Products,[b] % Exo-OH	Endo-OH	3-Nortricyclanol
p-Anisyl	Exo[c]	>99	–	–
	Endo	>99	–	–
Phenyl	Exo	95	–	5
	Endo	95	–	5
p-Trifluoromethylphenyl	Exo	88	–	12
	Endo[d]	88	–	12
3,5-Bis(trifluoromethyl)phenyl	Exo[d,e]	23	–	77
Methyl	Exo[d-f]	67.7	–	15.6
	Endo[d-f]	68.1	<0.5	16.4

[a] Carried out in 10 mol % excess sodium acetate. [b] Determined by NMR spectroscopy. [c] Benzoate ester was used. [d] Products were determined in 50% aqueous acetone. [e] Products were determined at 125°. [f] Determined by GLC after 20% completion.

rate acceleration of the parent system essentially to vanish (**3, 4**).[23] This is attributed to the greater stabilization of the cationic center by the *p*-anisyl substituent, essentially canceling π participation by the double bond.

If an anisyl group can cause π participation of 10^{11} magnitude to vanish in the *anti*-7-norbornenyl system, surely it should cause the 10^3 to 10^4 factor in 2-norbornenyl to vanish. However, 2-*p*-anisyl-2-norbornenyl exhibits an exo:endo rate ratio of 312. Consequently, π participation cannot be significant in this exo:endo rate ratio and the observed value of 312 must be due to some factor other than π participation. Steric hindrance to ionization of the endo isomer, such as has been proposed to account for the behavior of 2-arylnorbornyl compounds,[9,21] has been advanced as an explanation. If this interpretation is valid, it would mean that the π cloud of the double bond in the rigid bicyclic system resists the departure of the anion in the same manner as the endo-6-hydrogen in the saturated derivative.[9,24,25]

That this explanation is not unreasonable is indicated by the stereoselectivity observed in a number of reactions of norbornyl and norbornenyl derivatives. For example, the stereoselectivity of the reduction of dehydronorcamphor (**17**) by sodium borohydride is even greater than that of norcamphor[26] (**16**).



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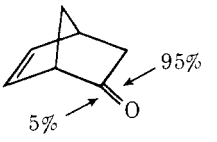

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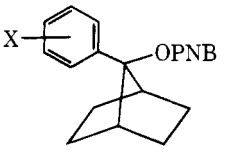
The results on the reduction of bicyclo[2.2.2]octanone and bicyclo[2.2.2]octenone also support the proposal.[24] Indeed, a number of norbornene derivatives undergo reactions with predominant exo attack of the reagent. Among these may be mentioned hydroboration,[27] carbenation of norbornadiene,[28] the reaction of methylmagnesium iodide and dimethylsulfonium methylide with dehydronorcamphor,[29] deuterium exchange in dehydronorcamphor,[30] and the addition of acetic acid to norbornadiene.[31]

Effect of Increasing Electron Demand. As has been pointed out, the more stable a cationic center, the less demand that center will make on neighboring groups for additional stabilization through participation. Conversely, as the cationic center is made more electron demanding, participation should increase and become readily observable. For example, Gassman and Fentiman have shown that the ability of π electrons to stabilize the electron deficient center in 7-aryl-*anti*-norbornenyl *p*-nitrobenzoates (**19**) increases as a function of the electron demand of that center.[23]



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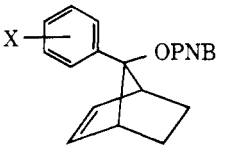

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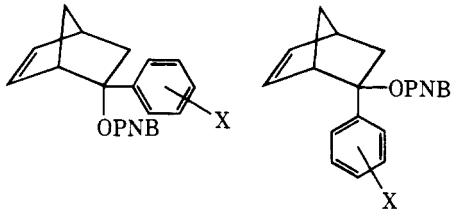
X	rel rate (25°)	
p-CH_3O	1.0	3.4
p-H	1.0	41.5
p-CF_3	1.0	34500
3,5-$(CF_3)_2$	1.0	255000

In the 2-aryl-2-norbornenyl system (**8, 11**) the exo:endo rate ratio remains essentially constant when the substituent is varied from *p*-CH_3O to *p*-CF_3. If π participation is a significant factor in the exo:endo rate ratio, then one should observe increasing neighboring double bond participation,



8 11

X	rel rate (25°)	
p-CH_3O	1.0	312
p-H	1.0	202
p-CF_3	1.0	283
3,5-$(CF_3)_2$	1.0	447

accompanied by increasing exo:endo rate ratios as the electron demand of the carbonium ion center is increased. However, with the more deactivating 3,5-$(CF_3)_2$ the exo:endo rate ratio exhibits a modest increase to 447. Thus it appears that as the electron demand of the cationic center is further increased in the 3,5-$(CF_3)_2$ derivatives, π participation finally becomes a contributing factor in the rate determining step.

An alternative means of examining the effect of increasing electron demand is the change in ρ^+ for the reaction. For example, the 7-aryl-7-norbornyl derivatives exhibit a ρ^+ of -5.27. On the other hand, the 7-aryl-*anti*-norbornenyl derivatives exhibit a ρ^+ value of -2.30. The difference in the ρ^+ values measures the effect of the π participation.[15]

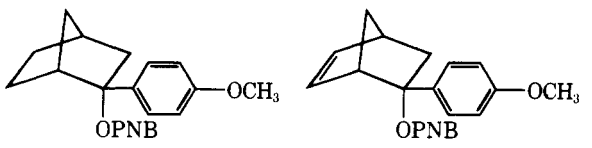
The 2-aryl-*endo*-norbornenyl derivatives (Table I) exhibit a ρ^+ value of -4.17 (correlation coefficient 1.000). For the exo isomers a break in the $\rho^+\sigma^+$ plot occurs between p-trifluoromethyl and 3,5-bis(trifluoromethyl)phenyl substituted compounds. This break in the $\rho^+\sigma^+$ plot indicates a change in the mechanistic aspects of solvolysis of the exo isomers. Thus as the cationic center is made more electron demanding by substituents less capable of stabilizing a positive charge than a p-trifluoromethylphenyl group, participation by the π-electrons of the 5,6-double bond becomes significant. For substituents such as p-anisyl, phenyl, p-trifluoromethylphenyl which are more effective than the 3,5-$(CF_3)_2$ derivative in stabilizing the carbonium ion center participation by the π electrons is not needed and hence does not occur. Indeed, these substituents yield a ρ^+ value of -4.21 (correlation coefficient 1.000) which is comparable with the ρ^+ value exhibited by the endo isomers.

The exo:endo rate ratio in 2-methyl-2-norbornenyl is 895. Unfortunately it is not possible to compare this value with the ratios observed for the 2-aryl derivatives since the steric effects of a methyl and an aryl substituent may differ significantly.

One way of extrapolating the results to the 2-methyl derivative is to take the rate of the endo isomer as a measure of the electron demand (Figure 1). (For the 2-aryl derivatives, this is equivalent to a plot against σ^+).

Extending the treatment to the parent 2-norbornenyl derivative reveals a definite upturn in the line (Figure 1) corresponding to an increase in the exo:endo rate ratio with increasing electron demand.

Effect of a Homoallylic Double Bond. 2-p-Anisyl-*endo*-norbornenyl p-nitrobenzoate (**21**) solvolyzes at a rate five



20 **21**

rel rate (25°) 1.0 1/5.0

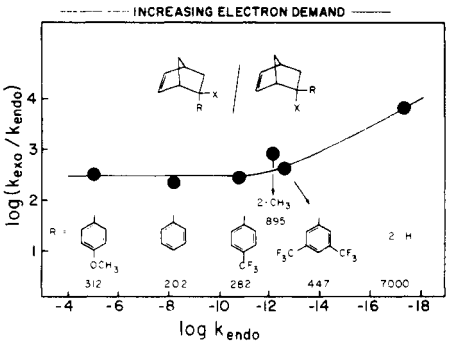
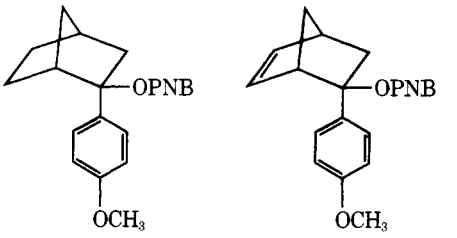


Figure 1. Exo:endo rate ratio as a function of increasing electron demand in 2-norbornenyl derivatives.

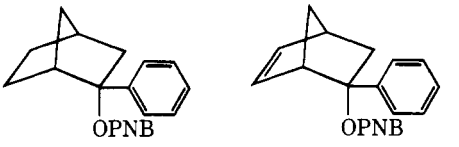
times slower than the saturated derivative (**20**). The corresponding exo compound (**23**) solvolyzes 4.5 times slower than the saturated compound (**22**). In the case of phenyl de-



22 **23**

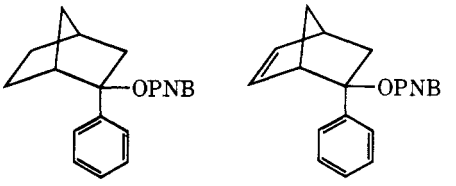
rel rate (25°): 1.0 1.0/4.5

rivatives, the introduction of the homoallylic bond decreases the reactivity of the endo (**24, 25**) and exo (**26, 27**) isomers by similar factors.



24 **25**

rel rate (25°): 1.0 1/8.8

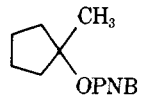


26 **27**

rel rate (25°): 1.0 1/6.2

These results show that the effect of the double bond on the exo isomer is almost identical with the effect of the double bond in the endo isomer. π participation has never been considered to be a factor in the solvolysis of *endo*-norbornenyl derivatives. Consequently, the modest rate retardations (**21/20, 25/24**) are presumably the result of the inductive influence of the double bond.[32] Rate retardations of comparable magnitude by the homoallylic double bond are also observed in the solvolysis of 1-phenylcyclopent-3-enyl p-nitrobenzoate[33] and 4-bromocyclopentene.[34] Clearly π participation is not significant in the solvolysis of 2-p-anisyl (**23**) and 2-phenyl-*exo*-norbornenyl p-nitrobenzoates (**27**).

The homoallylic double bond in 1-methylcyclopent-3-enyl p-nitrobenzoate (**29**) retards the rate of the saturated derivative (**28**) by a factor of 15.



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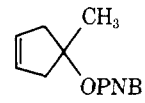
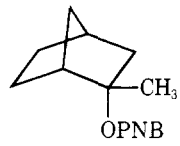


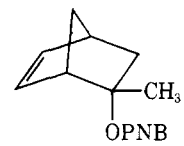
29

rel rate (25°): 1.0 1.0/15.0

2-Methyl-*endo*-norbornenyl *p*-nitrobenzoate (**31**) undergoes solvolysis at a rate 21.5 times slower than that of the saturated derivative (**30**). The magnitude of the effect is



30

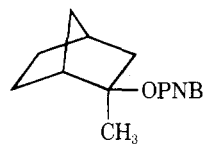


31

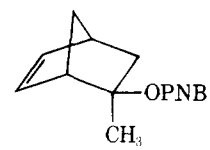
rel rate (25°): 1.0 1.0/21.5

comparable (slightly larger) with that observed in the corresponding cyclopentyl derivatives (**28, 29**).

The exo isomer (**15**) where participation might be significant also reacts slower than the saturated analog (**32**) by an almost identical factor.



32



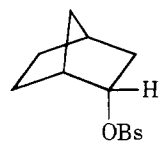
15

rel rate (25°): 1.0 1.0/21.3

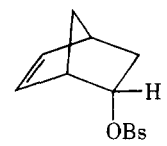
Hence it can be concluded that in the absence of π participation, a homoallylic double bond has a significant rate retarding effect.[35]

It is of course possible to argue that σ participation in **32** is identical in magnitude with the π participation in **15** so that there is a fortuitous cancellation of the participation contributions. However, there is now a huge mass of experimental evidence to establish that σ participation is not important in the solvolysis of such tertiary derivatives.[36] Therefore, it is reasonable to conclude that the homoallylic double bond provides no significant anchimeric assistance in the solvolysis of 2-methyl-*exo*-norbornenyl *p*-nitrobenzoate (**15**).

2-*endo*-Norbornenyl brosylate (**1**) solvolyzes 44 times slower than the saturated compound (**33**). This indicates



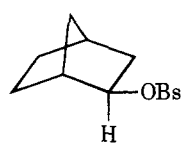
33



1

rel rate (25°): 1.0 1.0/44.0

that the rate retarding effect of the double bond in the secondary derivative (**1**) is even larger than in the tertiary derivatives.[35] However, the rate retarding effect essentially vanishes in the exo derivative (**34, 2**). Clearly, this marked



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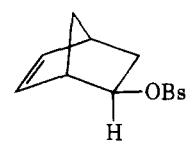
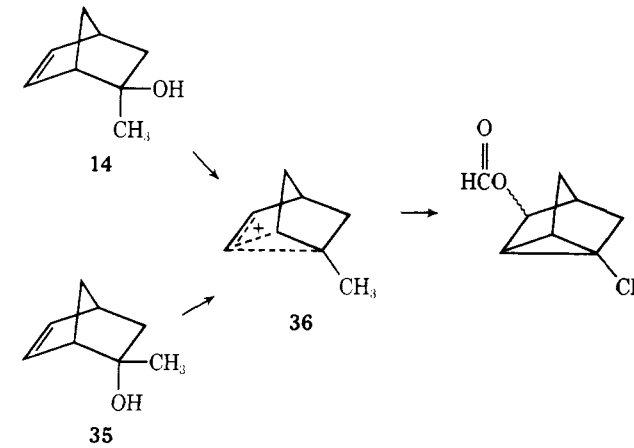


2

rel rate (25°): 1.0 1.0/1.96

change in the effect of the double bond must reflect the incursion of π participation which counters and almost overcomes the rate retarding inductive effect of the double bond.

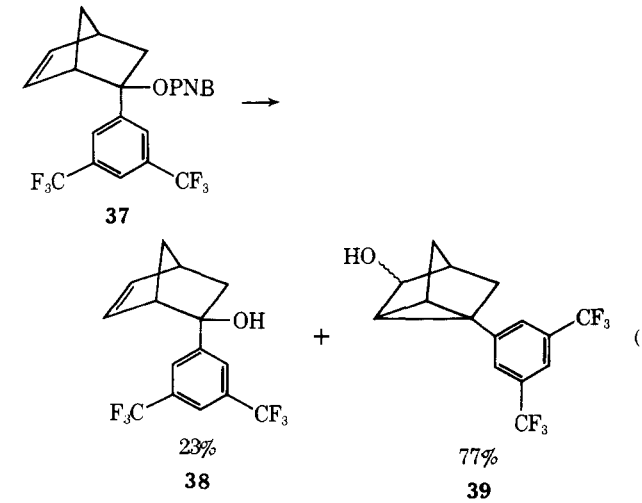
Formolysis of the 2-Methyl-2-norbornenols. The utility of this approach is indicated by an examination of the data for the reaction of the 2-methyl-2-norbornenols with formic acid.[37] The reaction exhibits an exo:endo rate ratio of 183 (as compared to 5800 for the saturated derivatives) and has been interpreted to proceed through the formation of a homoallylic carbonium ion[37] (**36**).



14 36 35

2-Methyl-*endo*-norbornenol (**35**) reacts four times slower than the saturated derivative.[38] Since anchimeric assistance is unlikely in the endo isomer, the slower rate of formolysis can be attributed to the inductive effect of the double bond. If anchimeric assistance is significant in the exo compound, then **14** should react faster than the saturated compound, 2-methyl-*exo*-norbornanol. However, it was observed that **14** actually reacts 131 times slower than the saturated compound. Hence the original argument based on the formation of a stabilized homoallylic carbonium **36** seems questionable.

Products of Solvolysis as a Criterion for π Participation. The predominant solvolysis product of 2-aryl-2-norbornenyl derivatives with *p*-CH_3O, *p*-H, and *p*-CF_3 substituents is the corresponding 2-aryl-*exo*-norbornenol (Table II). This is in accord with the indicated absence of significant interaction of the double bond in the ionization step. On the other hand, in the case of the 3,5-$(CF_3)_2$ derivative (**37**), the predominant product is that arising from a rearrangement involving the 5,6 π electrons, 1-[3,5-bis(trifluoromethyl)phenyl]-3-nortricyclanol (**39**) (eq 6). This result is in



37 38 39 (6)

agreement with the rate data. Thus the involvement of the π electrons of the double bond becomes more important as

Table III. Preparation of 2-Aryl-*endo*-norbornenols

Aryl group	% yield	Mp or bp, °C	Molecular formula	Analyses
p-Anisyl	73	110.5 (0.15 mm)	$C_{14}H_{16}O_2$	C, H
Phenyl[a]	86	95 (5.0 mm)	$C_{13}H_{14}O$	C, H
p-Trifluoromethylphenyl	80	58–59	$C_{14}H_{13}F_3O$	C, H, F
3,5-Bis(trifluoromethyl phenyl)	85	63–65	$C_{15}H_{12}F_6O$	C, H, F

[a] Bp 99° (0.10 mm). C.J. Collins and B.M. Benjamin, *J. Am. Chem. Soc.*, 89, 1652 (1967).

the electron demand of the incipient carbonium ion is increased by the 3,5-bis(trifluoromethyl)phenyl group.

The initial products of solvolysis of *exo*- and *endo*-2-methyl-2-norbornenyl *p*-nitrobenzoates were determined in buffered 50% aqueous acetone at 125° because some of the products proved to be unstable over the longer periods of time required for the less aqueous solvents. Both exo and endo isomers underwent solvolysis to give the same product distribution: 16% of 5-methylenenorbornene (**12**) and 2-methyl-*exo*-norbornenol (**14**) and 1-methyl-3-nortricyclanol in approximately 80:20 ratio (Table II). The observed product distribution does not indicate significant involvement of the double bond in the solvolysis of the exo isomer.

Conclusion

In the tertiary 2-norbornenyl derivatives exo:endo rate ratios of 200 to 900 are observed. The various approaches discussed above make it clear that π participation is not important in the high exo:endo rate ratios observed in these derivatives. Only with the more electron demanding 3,5-[bis(trifluoromethyl)phenyl] derivative is there observed a modest increase in the exo:endo rate ratio attributable to the initiation of π participation in this derivative. Consequently, some other factor such as steric hindrance to ionization must be responsible for the high exo:endo rate ratios.[9] If we assume that the exo:endo rate ratio in these tertiary derivatives of approximately 350, attributed to steric factor can be carried over to the parent norbornenyl, we are left with a factor of 20 attributable to π participation.

One can argue that the steric factor of approximately 350, observed for the tertiary derivatives, should not be carried over to the secondary. Possibly, some new, smaller factor should be used. Unfortunately, it is not now possible to estimate that factor.

An alternative approach permits one to circumvent this argument. The inductive effect of the double bond in the endo isomer **1** is 44. In the absence of π participation one would expect the same rate retarding effect of the double bond in the exo isomer **2**. However, the observed effect is 1.96. Therefore, π participation must be increasing the rate of the exo isomer by a factor of approximately 22. Consequently, this approach yields the same conclusion: the exo:endo rate factor in 2-norbornenyl must be made up of a factor of approximately 20 due to π participation and a factor of 350 attributable to steric hindrance to ionization.

Experimental Section

Melting points and boiling points are uncorrected. Ir spectra were recorded on a Perkin-Elmer Model 137 or 700 spectrometer. NMR spectra were taken on a Varian T-60 spectrometer.

2-Chloro-2-cyano-5-norbornene was prepared from cyclopentadiene and α-chloroacrylonitrile according to the method of Krieger:[14] yield 89%, mp 48.8–49.3° (lit.[14] mp 45–47°).

5-Norbornen-2-one. 2-Chloro-2-cyano-5-norbornene was hydrolyzed according to the method of Freeman et al.:[11] yield 77.5%, mp 22–23° (lit.[13] mp 22–23°), n^{20}D 1.4872 (lit.[39] n^{25}D 1.4857). The ir spectrum was in agreement with that reported for 5-norbornen-2-one.[40]

General Procedure for the Preparation of 2-Aryl-*endo*-norbornenols. The Grignard reagents of *p*-bromoanisole, bromobenzene, *p*-bromobenzotrifluoride, and 3,5-bis(trifluoromethyl)bromobenzene were prepared by the reaction of the respective bromides with magnesium in anhydrous ether. A solution of 5-norbornen-2-one in ether was added to a stirred solution of the Grignard reagent under N_2 at 0–5°. After hydrolysis of the reaction mixture with saturated ammonium chloride solution, the organic layer was separated and the aqueous layer extracted twice with ether. The combined ether extracts were dried over anhydrous magnesium sulfate and solvent evaporated. The alcohols were purified by distillation or crystallization. Properties of 2-aryl-*endo*-norbornenols are listed in Table III.

2-*p*-Anisyl-*exo*-norbornenol. The endo alcohol (30 mmol) was converted into the chloride with hydrogen chloride gas in a hydrochlorinator.[41] Without further purification, the chloride was solvolyzed in 450 ml of 70% acetone containing sodium acetate (35 mmol) for 10 days at 40°. The acetone was removed on a rotoevaporator and the residue extracted with ether. The ether extracts were dried over anhydrous magnesium sulfate and solvent evaporated. The crude product was found to contain more than 98% exo alcohol by NMR. It was purified by recrystallizing twice from hexane, mp 65.4–66.5°. Anal. ($C_{14}H_{16}O_2$) C, H.

2-Phenyl-*exo*-norbornenol. To the endo alcohol (58.38 mmol) was added pyridine (4.79 ml, 59.39 mmol) and ether (40 ml) in an atmosphere of nitrogen. The mixture was cooled in an ice bath and 4.31 ml (60 mmol) of thionyl chloride was added dropwise. After the addition, the reaction mixture was refluxed for 1 hr. The ether was decanted from the pyridine hydrochloride and evaporated to yield a mixture of 1-phenyl-3-nortricyclyl chloride and 2-phenyl-2-*exo*-norbornenyl chloride. This mixture of chlorides was hydrolyzed in a solution of 200 ml of water, 200 ml of acetone, and sodium bicarbonate (12 g). Acetone was evaporated and the product was isolated from the aqueous residue by extraction with ether. The ether extract was dried over anhydrous magnesium sulfate and solvent evaporated. The crude reaction mixture was found to consist of 2-phenyl-2-*exo*-norborneol (60%) and 1-phenyl-3-nortricyclanol (40%). The exo alcohol was purified by fractional crystallization from hexane, mp 66.3–67°. Anal. ($C_{13}H_{14}O$) C, H.

2-*p*-Trifluoromethylphenyl-*exo*-norbornenol. Following the procedure for the preparation of 2-phenyl-*exo*-norbornenol, the endo

Table IV. Preparation of 2-Aryl- and 2-Methyl-2-norbornenyl *p*-Nitrobenzoates

2-Substituent	Isomer	% yield	Mp, °C	Molecular formula	Analyses
p-Anisyl	Exo[a]	72	100.7–101.9	$C_{21}H_{20}O_3$	C, H
	Endo	62	106.5 dec	$C_{21}H_{19}NO_5$	C, H, N
Phenyl	Exo	93	99–101.5	$C_{20}H_{17}NO_4$	C, H, N
	Endo	75	114.4–115.1		
p-Trifluoromethylphenyl	Exo	90	130.4–131.2	$C_{21}H_{16}F_3NO_4$	C, H, N, F
	Endo	74	115.1–116.4	$C_{21}H_{16}F_3NO_4$	C, H, N, F
3,5-Bis(trifluoromethyl)-phenyl	Exo	92	118–119	$C_{22}H_{15}F_6NO_4$	C, H, N, F
Methyl	Exo	85	121.5–122.2	$C_{15}H_{15}NO_4$	C, H, N
	Endo[b]	73	128.6–129.8	$C_{15}H_{15}NO_4$	C, H, N

[a] Benzoate. [b] Mp 117–118.5°, ref 43.

alcohol (60 mmol) was converted into the chloride with thionyl chloride. The chloride mixture was hydrolyzed and worked up to give a mixture of 1-*p*-trifluoromethylphenyl-3-nortricyclanol (73%) and 2-*p*-trifluoromethyl-2-*exo*-norborneol (27%). The exo alcohol was purified by fractional crystallization from hexane, mp 98.5–99.4°. Anal. ($C_{14}H_{13}F_3O$) C, H, F.

2-[3,5-Bis(trifluoromethyl)phenyl]-*exo*-norbornenol. The procedure employed is the same as that of 2-phenyl-*exo*-norbornenol. The tertiary chloride mixture obtained from the endo alcohol (59.38 mmol) and thionyl chloride (4.31 ml, 60 mmol) was solvolyzed and the crude alcohol was isolated. Analysis by NMR showed a mixture of mostly tricyclic alcohol and about 18% exo alcohol. Several crystallizations from pentane at −78° removed most of the nortricyclanol which crystallized out. The remaining tricyclic alcohol was removed by column chromatography over neutral alumina. The small amount of exo-alcohol was further purified by bulb-to-bulb distillation at 0.1 mm (oven temperature, 85–90°). ^{1}H NMR δ 2.88 (m, 4-bridgehead), 3.03 (m, 1-bridgehead), 5.71 (m, 1 H, 6-olefinic), 6.32 (m, 1 H, 5-olefinic), and 7.77 (3 H, aromatic). Anal. ($C_{15}H_{12}F_6O$) C, H, F.

2-Methyl-*exo*-norbornenyl Acetate. 5-Methylenenorbornene (**12**) (146 g, 1.375 mol) and glacial acetic acid (35 g, 0.582 mol) were refluxed for 180 hr. The brownish yellow reaction mixture was cooled (no acetic acid was detectable by GLC in the reaction mixture). The excess methylenenorbornene was removed by distillation (bp 40° (45 mm)). Distillation of the residue through a 12-cm column yielded 35 g (36%) of the desired acetate, bp 60° (10 mm). Redistillation through a 30 cm Vigreaux column produced 25 g of acetate which was 92% pure by GLC (5% DEGS, 6 ft × ⅛ in., 90°): bp 58.8° (7 mm) (lit.[16] bp 76–79° (14 mm)) ^{1}H NMR (CCl_4) δ 6.10 (2 H, olefinic), 2.98 (1 H, 1-bridgehead H), 2.78 (1 H, 4-bridgehead H), 1.2–2.0 (10 H, remaining protons).

2-Methyl-*exo*-norbornenol. The exo acetate (**13**) (24 g), potassium hydroxide (13.7 g), water (14 ml), and methanol (40 ml) were heated under reflux for 5 hr. Most of the methanol and water were removed on a roto-evaporator. The residue was shaken up with hexane and the insoluble material removed by filtration. The hexane solution was dried and the solvent evaporated. The residue was purified by vacuum sublimation. White crystals (14.48 g, 80%) were obtained. The material was found to be more than 92% pure by GLC. After further purification by preparative gas chromatography (15% Carbowax on Chromosorb W 60/80), GLC analysis showed more than 99% purity: mp 58.8–60.0° (lit.[16] mp 54.8–55.8°). The ^{1}H NMR[42] and ir[16] of this compound were similar to that reported in the literature.

2-Methyl-*endo*-norbornenol was prepared by the addition of methyl Grignard to 2-norbornenone. Yield, 90%, bp 77° (26 mm) (lit.[43] 30–32° (2.5 mm)). The product was further purified by preparative gas chromatography (15% Carbowax 20M on Chromosorb W at 108°) to remove the exo isomer (3%). GLC showed greater than 99% purity: mp 11° (lit.[44] mp 11°). The ^{1}H NMR spectrum was identical with that reported for **35**.[42]

Preparation of *p*-Nitrobenzoates. The *p*-nitrobenzoates of both exo and endo alcohols were prepared from the lithium alkoxide and *p*-nitrobenzoyl chloride as described by Brown and Peters.[15] The benzoate of 2-*p*-anisyl-*exo*-norbornenol was obtained in a similar manner. The properties of these derivatives are listed in Table IV.

Kinetic Procedure. The procedure employed for determining the rate constants is described in the literature.[15,45]

Product Analysis. Products of solvolysis of 2-aryl- and 2-methyl-2-norbornenyl *p*-nitrobenzoates were determined in buffered aqueous acetone and analyzed by NMR. The results are tabulated in Table II.

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