Structural Effects in Solvolytic Reactions. XII. Solvolysis of 2-Aryl-5-methyl- and 2,5-Dimethyl-2-norbornenyl *p*-Nitrobenzoates. Evidence for Major π Participation Revealed by the Tool of Increasing Electron Demand[1]

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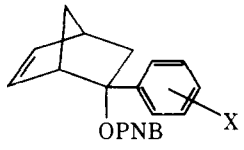
Abstract: The exo:endo rate ratio in the solvolysis of 2-aryl-5-methyl-2-norbornenyl *p*-nitrobenzoates increases markedly as the electron demand by the 2-aryl substituent is increased: 354 for *p*-OCH_3, 1260 for *p*-H, 6700 for *p*-CF_3. An exo:endo rate ratio of 112000 is realized in the solvolysis of the 2,5-dimethyl-2-norbornenyl *p*-nitrobenzoates. This increase in the value of the exo:endo rate ratio over that observed in the solvolysis of the corresponding 2-phenyl-5-methyl-2-norbornenyl derivatives, 1260, is attributed to the higher electron demand of the tertiary methyl cationic center, as contrasted to the much less demanding tertiary 2-phenyl cationic center. In addition, the reaction products reveal increasing involvement of the double bond with increasing demand at the cationic center. It is concluded that the double bond activated by the 5-methyl substituent is strongly involved in the solvolysis of these derivatives, in contrast to the behavior of the parent system where such activation is not present.

The tool of increasing electron demand has been applied as a probe to test for σ or π contribution in a number of systems. The available data confirm the presence of such contributions in 7-aryl-*anti*-norbornenyl,[4] arylcyclopropylcarbinyl,[5] and 3-aryl-3-nortricyclyl.[6] However, the data also indicate the essential absence of participation in the solvolysis of 2-aryl-2-norbornenyl (**1**, **2**)[7] and 2-aryl-2-norbornyl (**3**, **4**).[8,9]



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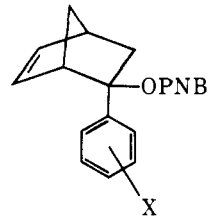

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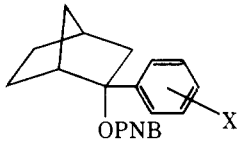

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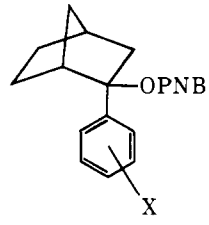

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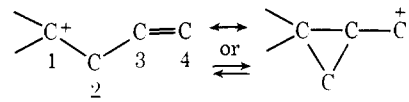
The solvolysis of the 2-aryl-2-norbornenyl derivatives fails to reveal any significant increase in the exo:endo rate ratio with increasing electron demand over the usual range of substituents (*p*-CH_3O, *p*-H, *p*-CF_3). Only with the

X	1	2
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

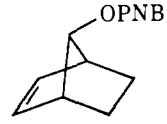
major increase in electron demand provided by the 2-[3,5-bis(trifluoromethyl)phenyl] substituent is there observed a modest increase in the exo:endo ratio attributable to the initiation of modest π participation in this derivative.[10] Consequently, it was concluded that π participation cannot be a significant factor in the high exo:endo rate ratio observed in the 2-aryl-2-norbornenyl derivatives (*p*-CH_3O through *p*-CF_3).[7]

In a homoallylic cation the electron deficiency should reside on C_1 as well as C_4 (eq 1). Groups on C_4 with the abili-



(1)

ty to stabilize carbonium ions should facilitate the delocalization of positive charge into the homoallylic double bond. Thus the introduction of a methyl group into C_4 greatly increases the ability of the double bond to participate by appreciable factors. Indeed, in 1958, Sneen demonstrated that a methyl group at C_6 in cholesteryl tosylate increases the rate of solvolysis by a factor of 75.[11] In 1969 Gassman and Patton showed that methyl groups attached to the double bond in 7-norbornenyl *p*-nitrobenzoate (**5**) enhances the rate of solvolysis of **6** and **7**.[12] In 1965 Bartlett and Sargent



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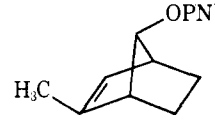

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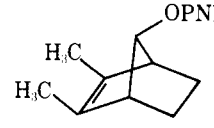
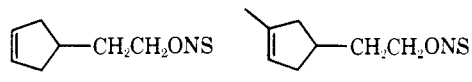
rel rate (25°): 1.0 13.3



7

rel rate (25°): 148

established that the introduction of a methyl group into the 3-position of 2(Δ^3-cyclopentenyl)ethyl *p*-nitrobenzenesulfonate (**8**) accelerates the rate of acetolysis by a factor of 7.[13]



8 **9**

Rel rate (25°): 1.0 7.0

Consequently, the introduction of one or more methyl groups in a participating double bond brings about signifi-

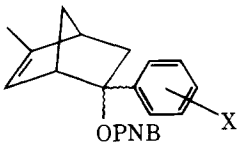
Table I. Solvolysis of 2-Aryl-5-methyl- and 2,5-Dimethyl-2-norbornenyl *p*-Nitrobenzoates in 80% Aqueous Acetone

Substituent in 2-position	Isomer	$k_1 \times 10^6$, sec^{-1} (T_2, °C)	(T_1, °C)	25°	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	k_1 5-Me/ k_1 5-H[a]	Exo:endo
p-Anisyl	Exo[b]			3000[c]			1.19	354
	Endo			8.48			1.05	
Phenyl	Exo			9.18			7.4	1260
	Endo	69.3 (100°)	5.07 (75°)	7.28×10^{-3}[d]	26.4	−7.2	1.21	
p-Trifluoromethylphenyl	Exo			7.94×10^{-7}[e]			26.0	6700
	Endo	62.5 (150°)	6.16 (125°)	1.19×10^{-5}[d]	30.4	−6.4	0.93	
Methyl	Exo	269 (100°)	24.1 (75°)	5.75×10^{-7}[d]	24.3	−10.1	122.0	112000
	Endo			5.13×10^{-7}[f]			0.98	

[a] Values of k_1 5-H for 1 and 2 are from ref 7 and for 2-Me (**24**) from ref 22. [b] Benzoate, $k_1^{25} = 1.44 \times 10^{-4}$ sec^{-1}. [c] Rate constant for the *p*-nitrobenzoate estimated by multiplying the rate constant for the benzoate by the factor 20.8.[8] [d] Calculated from data at higher temperatures. [e] Rate constant calculated from values for *p*-OCH_3 and *p*-H using the equation log $(k/k_H) = \rho^+\sigma^+$.[18] [f] Calculated from data in other solvents using Grunwald–Winstein relationship.[19] In 50% acetone $k_1^{25} = 3.59 \times 10^{-11}$,[d] $\Delta H^{\ddagger} = 29.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = -7.6$ eu. In 60% acetone $k_1^{25} = 1.07 \times 10^{-11}$,[d] $\Delta H^{\ddagger} = 30.8$ kcal mol^{-1}, $\Delta S^{\ddagger} = -5.3$ eu.

cant rate acceleration. Therefore we undertook to activate the double bond of **1** and **2** moderately by introducing a methyl substituent at the 5-position in order to test whether with such activation the tool of increasing electron demand could detect π participation. It has been suggested that tertiary benzylic cations are so stable that participation could be detected only in systems where such participation is of very large magnitude,[14] such as those observed in the 7-*anti*-norbornenyl[5] and the cyclopropyl carbinyl systems.[6]

Accordingly, we undertook to synthesize 2-aryl-5-methyl- (**10**) and 2,5-dimethyl-2-norbornenyl *p*-nitrobenzoates (**11**). We are also seeking to increase the electron demand



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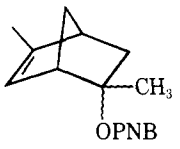


11

at the cationic center of **1** and **2** in the hope of facilitating the incursion of π participation by such means.

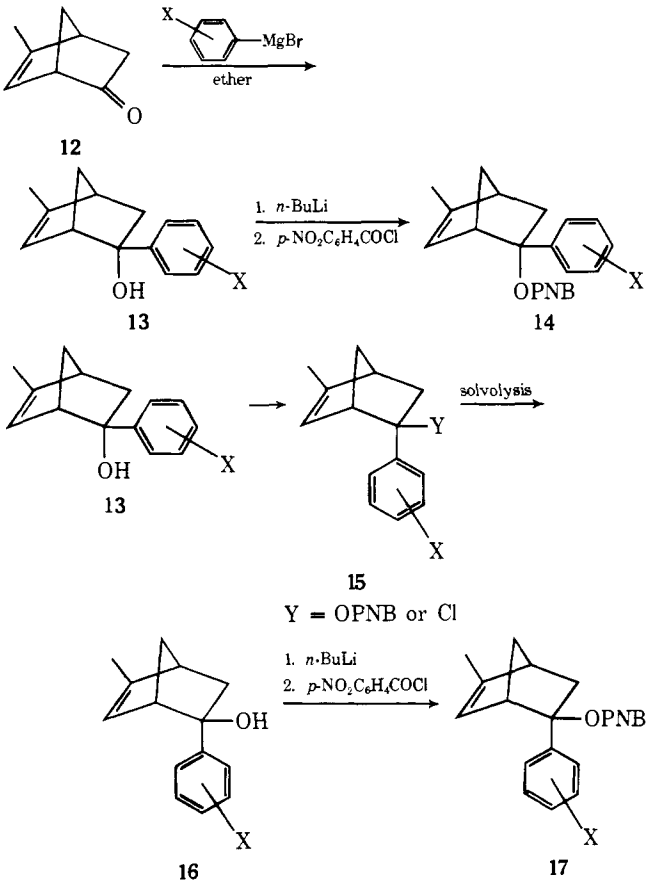
Results

Synthesis. 5-Methyl-2-norbornenone (**12**) was synthesized from methylcyclopentadiene and vinyl acetate following literature procedures.[15,16] The ketone (**12**) was treated with various Grignard reagents prepared from *p*-bromoanisole, bromobenzene, and *p*-bromobenzotrifluoride and magnesium to yield the respective tertiary endo alcohols (**13**). The exo alcohols with the *p*-CH_3O and *p*-H substituents were prepared by the solvolysis of the appropriate derivatives. Unfortunately, the exo alcohol corresponding to *p*-CF_3 (**16** *p*-CF_3) could not be realized by this procedure. The exo and endo alcohols were converted into the *p*-nitrobenzoates (**14** and **17**) by the lithium alkoxide method.[6] The synthetic scheme is outlined in Scheme I.

2,5-Dimethyl-2-*endo*-norbornenol was obtained by the addition of methylmagnesium chloride to **12**. The exo isomer could not be made by the usual method of solvolysis because the major solvolysis product was found to be the rearranged isomer, 1,3-dimethyl-3-nortricyclanol. Consequently, the exo isomer was synthesized by treating dimethylsulfonium methylide with **12** to give the unsaturated exo epoxide (**20**).[17] The epoxide (**20**) was reduced with lithium aluminum hydride in THF to furnish the exo alcohol.[17] The alcohols were converted into the *p*-nitrobenzoates in the usual manner (Scheme II).[6]

Kinetic Studies. The rate constants for the solvolysis in

Scheme I. Synthesis of *exo*- and *endo*-2-Aryl-2-norbornenyl *p*-Nitrobenzoates



80% aqueous acetone of *exo*- and *endo*-2-aryl-5-methyl- and 2,5-dimethyl-2-norbornenyl *p*-nitrobenzoates (**10** and **11**) are listed in Table I. 2-*p*-Anisyl-5-methyl-2-norbornenyl *p*-nitrobenzoate was too unstable to be isolated and hence the rate constant for the *p*-nitrobenzoate was obtained by multiplying the rate constant for the benzoate by the factor of 20.8.[8] The rate constant for **17** *p*-CF_3 was calculated from the log k–σ^+ plot, assuming the applicability of the relationship log $(k/k_H) = \rho^+\sigma^+$.[18] Since the rate of solvolysis for 2,5-dimethyl-*endo*-norbornenyl *p*-nitrobenzoate (**19**) was difficult to measure in 80% acetone, the rate of solvolysis for **19** was determined in 50 and 60% aqueous acetone from which the rate constant in 80% acetone was calculated by the method of Grunwald and Winstein.[19]

Scheme II. Synthesis of *exo*- and *endo*-2,5-Dimethyl-2-norbornenyl *p*-Nitrobenzoates

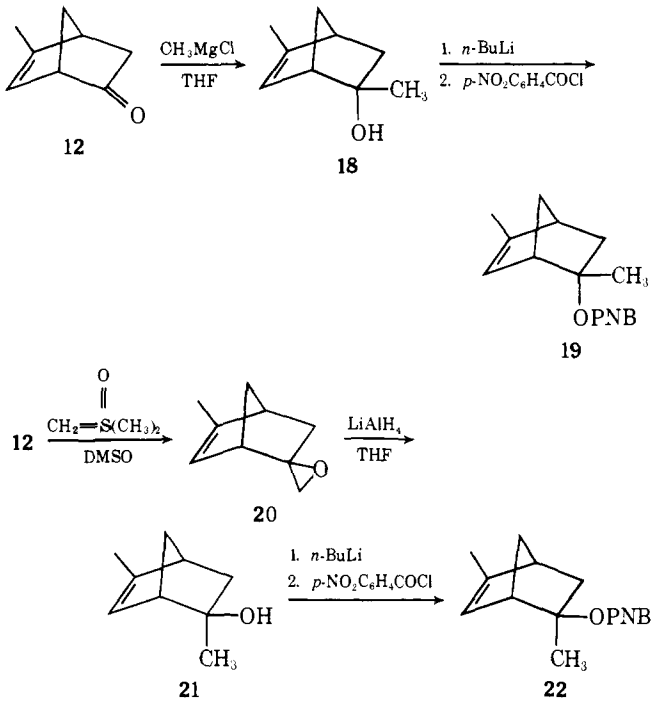


Table II. Products of Solvolysis of 2-Aryl-5-methyl- and 2,5-Dimethyl-2-norbornenyl *p*-Nitrobenzoates in Aqueous Acetone[a]

	Products[b]	
Compound solvolyzed	Exo alcohol	3-Methyl-3-nortricyclanol
17 *p*-OCH_3 or 14 *p*-OCH_3[c]	75 ± 3	25 ± 3
17-H or 14-H[d]	18 ± 3	82 ± 3
17 *p*-CF_3[e]	<2	>98
22[e]	<2	>98

[a] 10 mol % excess sodium acetate was used. [b] Determined by NMR. [c] Products were estimated at 25°. [d] Estimated at 75°. [e] Estimated at 100°.

Product Studies. The products of solvolysis were determined in buffered aqueous acetone and analyzed by ^1H NMR. The results are summarized in Table II.

Discussion

The exo:endo rate ratio has long been the standard criterion to estimate participation in norbornyl systems.[20,21] The summary of the rate ratio in Table I clearly reveals that in the 2-aryl-5-methyl-2-norbornenyl system there is increasing participation with increasing electron demand at the cationic center. Thus the exo:endo rate ratio increases from 354 for *p*-OCH_3 to 6700 for *p*-CF_3. The study could not be extended to aryl derivatives affording increased electron demand because of difficulties involved in the synthesis of exo isomers. Consequently π participation is becoming an important factor in the exo:endo rate ratio of these systems.

An exo:endo rate ratio of 112000 has been realized for the 2,5-dimethyl-2-norbornenyl system. On the other hand, the exo:endo rate ratio in the solvolysis of the 2-methyl-2-norbornenyl *p*-nitrobenzoates (**24**)[10] reveals no appreciable increase over the corresponding saturated derivatives (**23**).[22] Clearly the 5-methyl substituent activates the double bond, making π participation a significant factor in the observed exo:endo rate ratio. The increase in the value of the exo:endo rate ratio over that realized in the solvolysis of the corresponding 2-phenyl-5-methyl-2-norbornenyl derivatives (1260) is consistent with the much higher electron demand of the tertiary 2-methyl cationic center as contrasted to the less demanding tertiary 2-phenyl cationic center.[23]

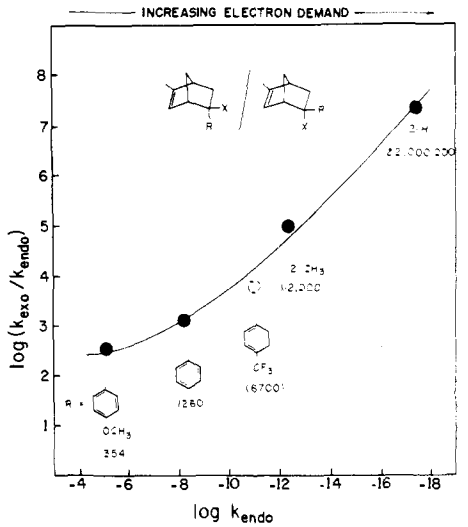
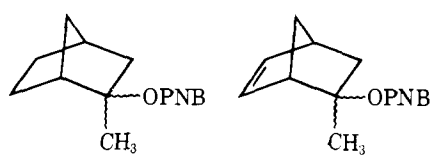
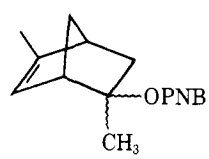


Figure 1. Effect of increasing electron demand on exo:endo rate ratio in 5-methyl-2-norbornenyl derivatives.



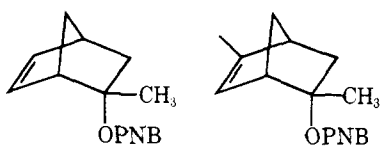
exo:endo 885 895



exo:endo 112000

If we take the rate of the endo isomer as a measure of the electron demand at the 2-position, then the increase in the exo:endo rate ratio with increasing electron demand is revealed in Figure 1. (This diagram should be compared with Figure 1 of the previous paper.[10])

The 5-methyl substituent has practically no effect upon the rates of the 2-aryl-5-methyl-*endo*-norbornenyl *p*-nitrobenzoates (**14**). Thus k_1 **14**/k_1 **1** is 1.05 for *p*-CH_3O, 1.21 for *p*-H, and 0.93 for *p*-CF_3. On the other hand, the 5-methyl substituent enhances the rate of the exo isomers (**17**): k_1 **17**/k_1 **2** is 1.19 for *p*-CH_3O, 7.4 for *p*-H, and 26 for *p*-CF_3. The effect of 5-methyl substituent is more marked in the solvolysis of 2,5-dimethyl-2-norbornenyl *p*-nitrobenzoates (**11**). The 5-methyl group has almost no effect on the rate of the endo derivatives. However, the 5-methyl group has a pronounced effect on the rate of the exo derivative.[24] Consequently the rate enhancement achieved by the 5-methyl substituent is in accordance with the increasing electron demand of the tertiary cationic center. The selective effect in the exo isomer is in agreement with π

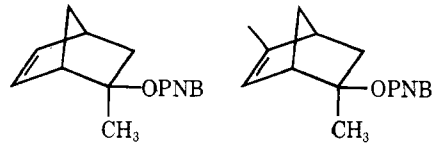


rel rate (25°): 1.00 0.98

Table III. Exo:Endo Rate Ratio as a Function of Increasing Electron Demand

2-Substituent	Exo:endo rate ratio k_t 2/k_t 1	k_t 17/k_t 14
p-Anisyl	312	354
Phenyl	202	1260
p-Trifluoromethylphenyl	283	6700
3,5-Bis(trifluoromethyl)phenyl	447	–
2-Methyl	895	112000
2-Hydrogen	7000	22000000[a]

[a] Private communication from C. F. Wilcox (ref 24).



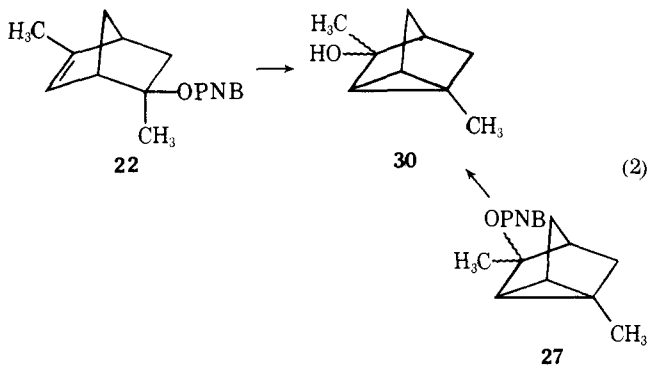
26 **22**

rel rate (25°): 1.00 122.0

participation in the exo and its absence in the endo derivative.

The effect of the 5-methyl substituent is also indicated by the ρ^+ values. The 2-aryl-5-methyl-*endo*-norbornenyl *p*-nitrobenzoates yield a ρ^+ value of −4.19 and the exo isomers yield one of −3.28. The ρ^+ values for the 2-aryl-*exo*- and -*endo*-norbornenyl derivatives are −4.21 and −4.17, respectively.[7] The change in the ρ^+ value ($\Delta\rho^+$ = 0.93) for the exo isomers is in the direction anticipated for π participation. The essential absence of any effect on ρ^+ in the endo isomer is again consistent with the proposed interpretation.

The products produced in the solvolysis of **10** and **11** also correspond to the effect anticipated for increasing participation of the double bond with increasing electron demand of the 2-substituent. In the case of the 2-aryl-2-norbornenyl *p*-nitrobenzoates (**1** and **2**), the predominant solvolysis product is the corresponding 2-aryl-*exo*-norbornenol.[7] (For the 3,5-$(CF_3)_2$ derivative, 1-aryl-3-nortricyclanol is the main product.[10]) This contrasts with the behavior of the 5-methyl derivatives (Table II). Here only the *p*-CH_3O compound yields the exo alcohol as the predominant product. The other derivatives involving greater electron demand yield chiefly the rearranged product, 1-aryl-3-methyl-3-nororicyclanol, resulting from a homoallylic rearrangement. In the secondary norbornenyl system where the involvement of π electrons is important, the products are predominantly the 3-nortricyclyl derivatives.[21] In the present investigation, the solvolysis of both 2,5-dimethyl-*exo*-norbornenyl (**22**) and 1,3-dimethyl-3-nortricyclyl *p*-nitrobenzoates (**27**) gave only 1,3-dimethyl-3-nortricyclanol (**30**) (eq 2).



(2)

Thus the 5-methyl group in the 2,5-dimethyl-2-norbornenyl system has a dramatic effect both on the rates and products of solvolysis. The high exo:endo rate ratio observed in this system is a consequence of π participation (×120) in the exo isomer and steric hindrance to ionization (×890) in the endo isomer.

Conclusion

The present two papers describe our results on the investigation of the presence or absence of π participation in the tertiary 2-norbornenyl system by the application of the tool of increasing electron demand. The exo:endo rate ratio as a function of increasing electron demand is tabulated in Table III. In the 2-norbornenyl system, a significant increase in the exo:endo rate ratio reflecting π participation is observed only with the secondary derivative (only with the more electron demanding 2-[3,5-bis(trifluoromethyl)phenyl] derivative do the exo:endo rate ratio and solvolysis products seem to indicate significant involvement of the double bond[10]). In the 5-methyl-2-norbornenyl system, such increase in the exo:endo rate ratio is observed with much smaller electron demand, following the 2-*p*-anisyl derivative.

Experimental Section

For general remarks, see Part XI of this series.[10]

1,4,5- and 6-Methylnorborn-5-en-2-yl Acetate. In a 500-ml autoclave was placed freshly distilled methylcyclopentadiene (121 g, dimer from Aldrich Chemical Co.), vinyl acetate (150 g), and a pinch of hydroquinone. The autoclave was heated at 180° for 18 hr. The pale yellow liquid obtained on distillation gave a mixture of acetates (150 g, 60% yield), bp 72–77° (10 mm) (lit.[16] bp 74–78° (13 mm)).

1,4,5- and 6-Methylnorborn-5-en-2-ol. The mixture of acetates (300 g) was hydrolyzed with potassium hydroxide (120 g) in methanol (400 ml) for 6 hr. After removing methanol, the residue was dissolved in ether and washed with water (3 × 100 ml). The ethereal layer was dried over anhydrous magnesium sulfate. Removal of solvent and distillation gave a mixture of alcohols (200 g, 90% yield), bp 65–85° (9 mm) (lit.[15] bp 63–77° (13 mm)).

1,4,5- and 6-Methyl-2-norbornenone. The mixture of alcohols was oxidized following the convenient two-phase oxidation developed by Brown et al.[25] Distillation of the resulting ketone through a 30-cm Vigreaux column gave four fractions: bp 61, 65, 67, and 67–70° (9 mm). The overall yield was 40%. Fractions distilled at 65 and 67° were found to contain mostly 5-methyl- and 6-methyl-2-norbornenone.

5-Methyl-2-norbornenone (12). This ketone was isolated from fractions distilled at 65 and 67° by preparative GLC (15% Carbowax 1540, 75°), ^{1}H NMR δ 5.55 (1 H, olefinic), 1.86 (3 H, methyl), 2.84 (1 H, 1-bridgehead), and 2.84 (1 H, 4-bridgehead).

2-*p*-Anisyl-5-methyl-*endo*-norbornenol. This alcohol was prepared by the addition of **12** to *p*-methoxyphenylmagnesium bromide in 89% yield: bp 108–110° (0.02 mm), ^{1}H NMR ($CDCl_3$) δ 1.71 (3 H, 5-methyl), 2.64 (m, 1 H, 4-bridgehead), 3.04 (m, 1 H, 1-bridgehead), 3.78 (s, 3 H, methoxy), 5.79 (m, 1 H, olefinic), and 6.83–7.48 (4 H, aromatic). Anal. ($C_{15}H_{18}O_2$) C, H.

2-Phenyl-5-methyl-*endo*-norbornenol. Addition of **12** to phenylmagnesium bromide gave the tertiary alcohol in 85% yield: bp 82° (0.12 mm); ^{1}H NMR (CCl_4) δ 1.87 (5-methyl), 2.57 (m, 1 H, 4-bridgehead), 2.92 (m, 1 H, 1-bridgehead), 5.69 (m, 1 H, olefinic), and 7.2 (m, 5 H, aromatic). Anal. ($C_{14}H_{16}O$) C, H.

2-*p*-Trifluoromethylphenyl-5-methyl-*endo*-norbornenol. This alcohol was obtained by the addition of **12** to *p*-trifluoromethylphenylmagnesium bromide followed by work-up in the usual manner in 73% yield: bp 103° (0.15 mm); ^{1}H NMR δ 1.92 (5-methyl), 2.70 (m, 1 H, 4-bridgehead), 3.00 (m, 1 H, 1-bridgehead), 5.80 (m, 1 H, olefinic), and 7.64 (s, 5 H, aromatic). Anal. ($C_{15}H_{15}F_3O$) C, H, F.

2-*p*-Anisyl-5-methyl-*exo*-norbornenol. This alcohol was prepared by the solvolysis of the corresponding endo *p*-nitrobenzoate in 60% acetone containing 10 mol % excess sodium acetate. After removal of most of the acetone, the aqueous residue was extracted with ether, the ether extract was dried over anhydrous magnesium sulfate. The ether was evaporated and the residue crystallized from pentane to constant melting point: mp 68–69°; ^{1}H NMR, δ 1.67 (5-methyl), 2.54 (m, 1 H, 4-bridgehead), 2.74 (m, 1-bridgehead).

Table IV. Preparation of 2-Aryl-5-methyl- and 2,5-Dimethyl-2-norbornenyl *p*-Nitrobenzoates

p-Nitrobenzoate 2-substituent	Isomer	% yield	Mp, °C	Molecular formula	Analyses
p-CH_3O-C_6H_4	Endo	88	112–113°	$C_{22}H_{21}NO_5$	C, H, N
C_6H_5	Exo	82	116–118°	$C_{21}H_{19}NO_4$	C, H, N
C_6H_5	Endo	93	109–110°	$C_{21}H_{19}NO_4$	C, H, N
p-CF_3-C_6H_4	Endo	68	155°	$C_{22}H_{18}F_3NO_4$	C, H, N, F
CH_3	Exo	72	133.2–133.8°	$C_{16}H_{17}NO_4$	C, H, N
CH_3	Endo	86	99.8–100.5°	$C_{16}H_{17}NO_4$	C, H, N

3.64 (s, 3 H, methoxy), 5.13 (m, 1 H, olefinic), and 6.63–7.10 (4 H, aromatic). Anal. ($C_{15}H_{18}O_2$) C, H.

2-Phenyl-5-methyl-*exo*-norbornenol. Treatment of the endo alcohol with thionyl chloride and pyridine in molar ratio, followed by solvolysis of the tertiary chloride gave a mixture consisting mostly of 1-phenyl-3-methyl-3-nortricyclanol and 1-phenyl-3-methylenenortricyclane. The 1-phenyl-3-methylenenortricyclane was removed by distillation (bp 80° at 0.03 mm). The tricyclic alcohol was removed from the small amount of exo alcohol by crystallization. The remaining oily material had a ^1H NMR expected for the desired exo alcohol. It was further purified by distillation: bp 90° (0.03 mm); ^1H NMR (CCl_4) δ 1.72 (5-methyl), 2.53 (m, 1 H, 4-bridgehead), 2.80 (m, 1 H, 1-bridgehead), 5.23 (m, 1 H, olefinic), and 7.15 (5 H, aromatic). Anal. ($C_{14}H_{16}O$) C, H.

2,5-Dimethyl-*endo*-norbornenol. This alcohol was obtained by treating **12** with methylmagnesium chloride in THF in 79% yield: bp 66–68° (6 mm); ^1H NMR (CCl_4) δ 1.43 (2-methyl), 1.85 (5-methyl), 2.50 (1- and 4-bridgehead protons), and 5.68 (olefinic).

2,5-Dimethyl-*exo*-norbornenol. In a dry 250-ml flask with side arm under nitrogen was placed 1.20 g (50 mmol) of sodium hydride (Ventron Corporation 50% oil dispersion), dimethyl sulfoxide (40 ml), and trimethylsulfoxonium iodide (11 g, 51 mmol). After the hydrogen evolution, 6.1 g (50 mmol) of 5-methyl-2-norbornenone (**12**) in 20 ml of dimethyl sulfoxide was added dropwise over a period of 20 min with cooling. The reaction mixture was stirred for 2 hr at room temperature and then for 1 hr at 55°. It was then cooled and poured into 100 ml of water and extracted with pentane. The pentane extract was washed with water and dried over anhydrous magnesium sulfate. Removal of solvent yielded the unsaturated epoxide (**20**), 4.75 g (70%). It was then reduced with excess lithium aluminum hydride in ether for 5 hr. The cooled reaction mixture was then hydrolyzed with 15% aqueous sodium hydroxide. The precipitated salts were removed by filtration. The ether extracts were dried and solvent evaporated. The oily material (^1H NMR indicated about 65% exo alcohol and 35% endo alcohol) was crystallized from pentane at −78°C. It was then sublimed and recrystallized twice from pentane: mp 65–66°; ^1H NMR (CCl_4) δ 1.15 (2-methyl), 1.68 (5-methyl), 2.30 and 2.47 (bridgehead protons), and 5.51 (olefinic). Anal. ($C_9H_{14}O$) C, H.

Preparation of *p*-Nitrobenzoates. The *p*-nitrobenzoates were prepared in the usual manner from the lithium alkoxide and *p*-nitrobenzoyl chloride.[6] The physical constants and analytical data are summarized in Table IV.

Kinetic Procedure. The rates of solvolysis of *p*-nitrobenzoates were determined according to literature procedures[6,26] and listed in Table I.

References and Notes

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