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(27) (a) This material was contaminated with small amounts of the 8-acetyl regioisomer. (b) The extra ^{13}C NMR resonances are due to the 8-acetyl isomer.

Structural Effects in Solvolytic Reactions. 30. Solvolysis of 2-(5'-Coumaranyl)-2-norbornyl *p*-Nitrobenzoates. Evidence for the Unimportance of σ Participation as a Factor in the High Exo/Endo Rate and Product Ratios Realized in the Solvolysis of Exceptionally Highly Stabilized Tertiary 2-Norbornyl Derivatives

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Received August 14, 1978

The 5-coumaranyl group, σ^+ −0.984, possesses electron-releasing properties considerably greater than those of *p*-anisyl, σ^+ −0.778. The solvolyses of *exo*- and *endo*-2-(5'-coumaranyl)-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone reveal a high exo/endo rate ratio of 240. The solvolysis of 2-(5'-coumaranyl)-*endo*-norbornyl *p*-nitrobenzoate in the presence of sodium acetate affords the exo-substituted alcohol in amounts greater than 99%. These highly stabilized norbornyl derivatives show high exo/endo rate ratios and high exo/endo product ratios, at one time considered essential criteria required for σ participation with formation of a σ-bridged intermediate. But σ participation cannot be a factor in the solvolysis of such highly stabilized tertiary norbornyl derivatives. These results must be accounted for alternatively in terms of steric effects.

The high exo/endo rate ratio and predominant exo substitution observed in the acetolysis of *exo*- (**2**) and *endo*-norbornyl (**1**) brosylates led to the postulation of σ participation of the 1,6 bonding pair in the exo isomer **3** facilitating ionization.[2,3] It is a generally accepted postulate that the importance of neighboring group participation should diminish as the incipient carbonium ion center is stabilized by substitution.[4,5]

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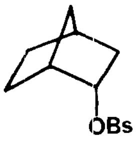

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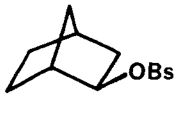


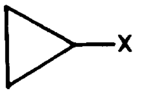
RR(25°C) **1.00** **350**

3

However, solvolysis of 2-aryl-2-norbornyl derivatives containing the substituents *p*-OCH_3, *p*-H, *p*-CF_3, and *m,m'*-$(CF_3)_2$ on the aromatic ring revealed essentially constant exo/endo ratios of 284, 127, 187, and 176, respectively. It is noteworthy that even the *p*-anisyl derivatives exhibit a high exo/endo rate ratio.[6,7]

In a previous paper we established the σ^+ constant for the 5-coumaranyl substituent.[8] It possesses a high negative value of −0.984, considerably more negative than that for *p*-anisyl, σ^+ −0.778. We also established that the 5-coumaranyl substituent (**5**) is capable of completely nullifying the rate enhancement of approximately 10^{12} observed in the solvolysis of secondary cyclopropyl derivatives[9] (**4**).

We decided to investigate whether the 5-coumaranyl substituent was also capable of completely nullifying the oft postulated σ participation in norbornyl derivatives. If the 5-coumaranyl group can cause the truly enormous π–σ participation (×10^{12}) observed in cyclopropyl derivatives to vanish, it should surely cause the much smaller σ participation (×350) proposed for *exo*-norbornyl to vanish.



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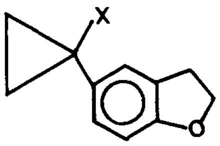

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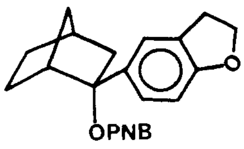
Results

Synthesis. Addition of 5-coumaranyllithium to 2-norbornanone yielded 2-(5'-coumaranyl)-*endo*-norbornanol. Treatment with hydrogen chloride gave the exo chloride. Hydrolysis then yielded the 2-(5'-coumaranyl)-*exo*-norbornanol. The endo alcohol was converted into the *p*-nitrobenzoate by treating with *n*-butyllithium, followed by *p*-nitrobenzoyl chloride. The *exo*-*p*-nitrobenzoate was too unstable to be isolated, and hence the benzoate was synthesized for solvolytic studies.

Rate Studies. The rates of solvolysis of 2-(5'-coumaranyl)-2-norbornyl derivatives were measured in 80% aqueous acetone. The rate constant for the solvolysis of 2-(5'-coumaranyl)-*exo*-norbornyl *p*-nitrobenzoate (**7**) was determined

6



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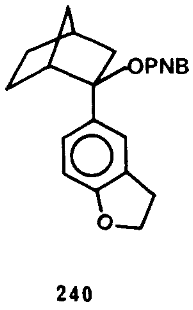


RR(25°C) **1.00** **240**

0022-3263/79/1944-0133$01.00/0

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

substituent on the aryl	isomer	registry no.	$k_1 \times 10^6\ s^{-1}$ T_1, °C	T_2, °C	25 °C	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	exo/endo
p-OCH_2CH_2-*m*	exo	68150-98-1			66 600[a]			240
	endo	68150-99-2	9.04 (0)		278	21.6	−2.4	
p-OCH_3	exo	20550-37-2			11 400[a]			284
	endo	20547-61-9	1.17 (0)		40.2	22.3	−3.8	
p-H	exo	20550-35-0	179 (50)		7.56	23.6	−2.7	127
	endo	21845-81-8	364 (100)	30.2 (75)	0.059[b]	25.1	−7.4	
p-CF_3	exo	20530-02-3	400 (100)	29.4 (75)	0.0427[b]	26.4	−3.8	187
	endo	20530-03-4	70.1 (125)	5.62 (100)	2.27×10^{-4} [b]	29.2	−4.7	
m,m′-$(CF_3)_2$	exo	56068-58-7	363 (125)	29.3 (100)	1.2×10^{-3} [b]	29.2	−1.5	176
	endo	56068-59-8	49.2 (150)	4.63 (125)	6.88×10^{-6} [b]	31.1	−5.4	

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

by multiplying the rate of the benzoate by the usual factor 20.8. The rate data and thermodynamic parameters are listed in Table I.

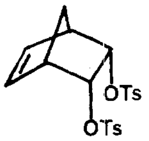
Solvolytic Product. 2-(5′-coumaranyl)-*endo*-norbornyl *p*-nitrobenzoate (**6**) was solvolyzed in 80% aqueous acetone at 25 °C in the presence of 10% molar excess of sodium acetate for 10 half-lives. After the usual workup, the product was analyzed by ^1H NMR.

Discussion

Exo/Endo Rate Ratio in 2-(5′-Coumaranyl)-2-norbornyl. Solvolysis of the 2-(5′-coumaranyl) derivatives in 80% aqueous acetone reveals an exo/endo rate ratio of 240. This compares with a value of 350 for the parent 2-norbornyl brosylate, 280 for the corresponding tosylates,[10] and 284, 127, 187, and 176 for the corresponding 2-aryl-2-norbornyl derivatives *p*-OCH_3, *p*-H, *p*-CF_3, and *m,m′*-$(CF_3)_2$.[6,7] Consequently, we do not observe a significant decrease in the exo/endo rate ratio in spite of the high stability of the cationic center, which should make σ bridging insignificant.

It should be pointed out that the opposite approach to test for σ participation has also failed.[11] Lambert and Mark achieved inductively enhanced electronic demand in both secondary 2-norbornenyl and 2-norbornyl by introducing −I substituents into the 3 position. They observed a major increase in the exo/endo rate ratio for the 2-norbornenyl system (**8**, **9**). However, they failed to observe any increase in the exo/endo rate ratio in the 2-norbornyl system (**10**, **11**), which would be expected to accompany enhanced σ participation, were that a significant factor.

8



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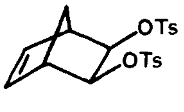
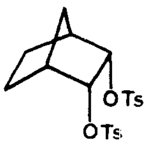


RR(25°C) 1.00 1.4×10^5

10



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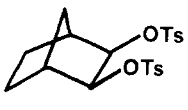


RR(25°C) 1.00 50

Both ^1H and ^{13}C NMR studies of the 2-phenyl-2-norbornyl cation indicate it to be classical.[12,13] If the 2-phenyl and the 2-anisyl derivatives are classical, there surely cannot be any argument about the far more stable 2-(5′-coumaranyl) derivative. Clearly the high exo/endo rate ratios in the 2-norbornyl system cannot be the result of σ participation in the exo. Steric hindrance to ionization in the endo is offered as an alternative explanation.[14]

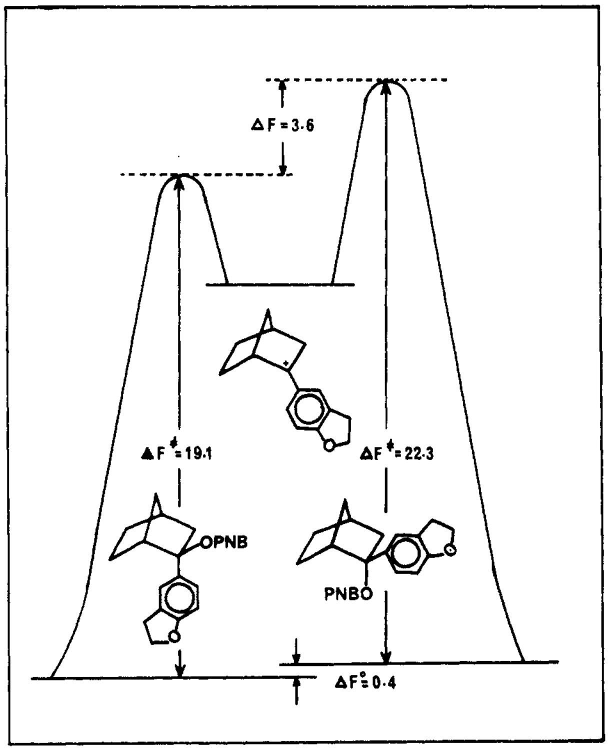


Figure 1. Free-energy diagram for the solvolysis of the 2-(5′-coumaranyl)-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25 °C.

Exo/Endo Product Ratios. The predominant exo substitution (>99%) observed in the acetolysis of 2-norbornyl brosylate has been considered to provide major support for σ bridging. Consequently, it was of interest to examine the products of solvolysis of these highly stabilized norbornyl derivatives. It was established in a previous publication from this laboratory that the solvolysis of 2-*p*-anisyl-2-norbornyl chlorides yields the exo product in over 98% yield.[6]

The solvolysis of 2-(5′-coumaranyl)-*endo*-norbornyl *p*-nitrobenzoate in 80% aqueous acetone in the presence of sodium acetate yields the 2-(5′-coumaranyl)-*exo*-norbornanol in amounts greater than 99%. Therefore, even these highly stabilized derivatives exhibit predominant substitution from the exo side.

Goering–Schewene Diagram. Treatment of the data in the manner developed by Goering and Schewene[3,15,16] reveals a typical such diagram, with a difference in the energies of the two transition states of 3.6 kcal mol^{-1} (Figure 1). A major

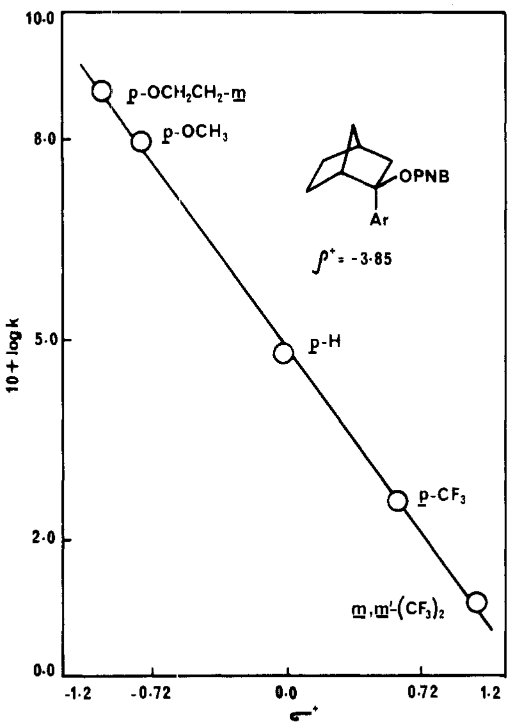


Figure 2. Log k–σ^+ plot for the solvolysis of the 2-aryl-*exo*-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25 °C.

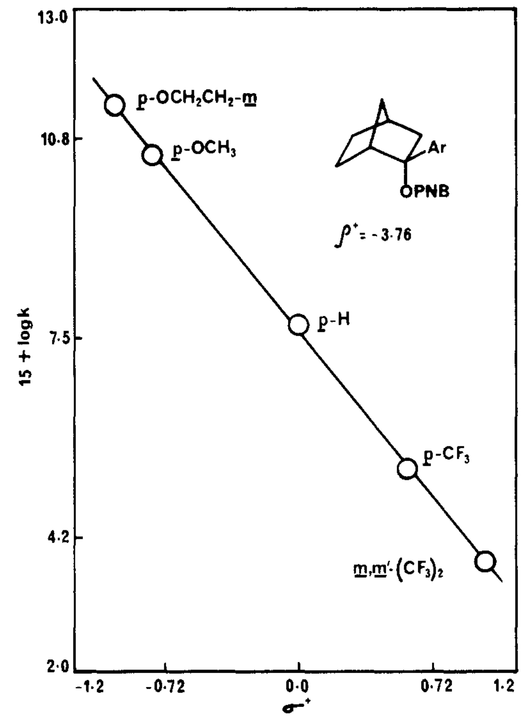
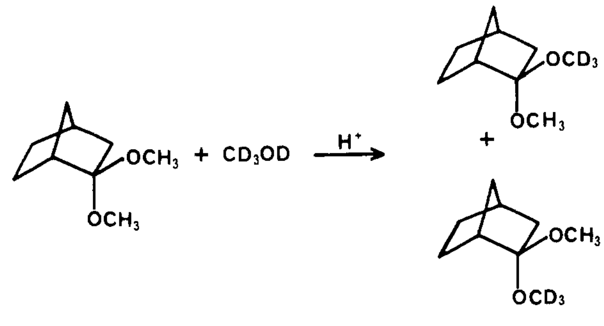


Figure 3. Log k–σ^+ plot for the solvolysis of the 2-aryl-*endo*-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25 °C.

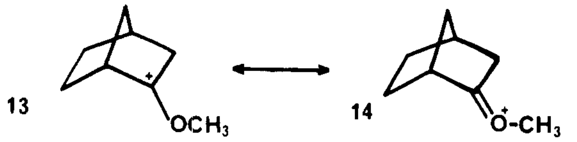
point of our argument urging a reexamination of σ bridging as a factor in the high exo/endo rate ratios of 2-norbornyl derivatives is the marked similarity in the Goering–Schewene diagrams for stabilized tertiary 2-norbornyl derivatives and the less stabilized secondary 2-norbornyl derivatives. If highly stabilized 2-norbornyl derivatives, such as the 2-(5′-coumaranyl)-2-norbornyl, which cannot possibly involve σ bridging, give Goering–Schewene diagrams essentially identical with such diagrams for the parent system, it appears implausible to attribute the latter diagram to entirely different physical origins.[16]

Contrary Arguments. The methanolysis of norcamphor dimethyl ketal (12) reveals an exo/endo rate ratio of 16.[17] The

12



authors conclude that this must be the true exo/endo rate ratio for a classical 2-norbornyl system, so that higher values, such as that observed in the present study, must be the result of σ bridging. However, the ionic intermediate (13 ↔ 14) from the



ketal carries its positive charge largely on oxygen. The analogy with a true carbonium ion is questionable. Moreover, the protonolysis of ketals is a reaction of low selectivity. Such reactions are not sensitive to structure and are therefore not ideal for studying structural effects.[18]

Recently, both Olah[19] and Farnum[13] examined the ^{13}C NMR behavior of the 2-aryl-2-norbornyl cations under stable ion conditions. They confirm the earlier conclusion that the 2-phenyl-2-norbornyl cation and 2-aryl-2-norbornyl cations, where the aryl group is phenyl, or more electron-supplying than phenyl, are classical. However, they observed certain changes in the NMR spectra with less electron-supplying substituents which led them to conclude that they were observing the inception of nonclassical electronic interactions.

It is difficult to know how pertinent these results are to the solvolytic phenomena we have been studying. Farnum himself has pointed out that results in superacid do not always parallel results under solvolytic conditions.[20] We have realized excellent agreement of our solvolytic rate data against the σ^+ constants[21] (Figures 2 and 3). Attempts to treat the ^{13}C NMR shifts reported by Olah[19] and Farnum[13] reveal very poor correlations,[22] in contradiction to earlier claims that satisfactory correlations exist for the *tert*-cumyl cations.[23] Such ^{13}C shifts are affected by many factors.[24] Accordingly, it appears best at this time to reserve judgement as to the meaning of these results until the theoretical background is better understood.

ρ^+–σ^+ Plot. A log k–σ^+ plot of the rates of solvolysis of 2-(5′-coumaranyl)-2-norbornyl derivatives with the values of the previously reported rates of solvolysis of 2-aryl-2-norbornyl derivatives yields excellent linear plots with ρ^+ values of −3.85 for the exo and −3.76 for the endo derivatives (see Figures 2 and 3). It should be noted that the small difference in the values of ρ^+ is actually in the opposite direction to that anticipated for σ participation in the exo and its absence in the endo.

Conclusion

The solvolysis of the 2-(5′-coumaranyl)-2-norbornyl *p*-nitrobenzoates must proceed through classical cations without σ bridges. Yet this system reveals both high exo/endo rate and high product ratios comparable to those in the parent secondary norbornyl itself. These and other results can be rationalized in terms of steric interactions with a high order of consistency.

Experimental Section

5-Coumaranyllithium was prepared by the addition of *n*-BuLi (1.9 M, 21 mL, 40 mmol) in hexane to bromocoumaran (8 g, 40 mmol) in ether at 0 °C. The mixture was stirred at 0 °C for 1 h.

2-(5′-Coumaranyl)-*endo*-norbornanol was prepared by the addition of 5-coumaranyllithium, prepared as described earlier, to norbornanone (3.85 g, 35 mmol) in ether at 0 °C. The reaction mixture was left overnight at room temperature. After the usual workup and removal of solvent, 2-(5′-coumaranyl)-*endo*-norbornanol was obtained as a colorless solid. It was recrystallized from hexane to give a colorless crystalline solid, mp 75–76 °C.

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.26; H, 7.83. Found: C, 78.01; H, 7.62.

2-(5′-Coumaranyl)-*endo*-norbornyl *p*-nitrobenzoate was prepared by treating the endo alcohol with *n*-BuLi and then with *p*-nitrobenzoyl chloride in the usual manner,[25] mp 115–116 °C dec.

Anal. Calcd for $C_{22}H_{21}O_5N$: C, 69.66; H, 5.54; N, 3.69. Found: C, 69.56; H, 5.50; N, 3.52.

2-(5′-Coumaranyl)-*exo*-norbornanol. The endo alcohol was converted into the chloride by treating with dry HCl gas in methylene chloride at 0 °C in an automatic hydrochlorinator.[26] Solvent was pumped off, and the chloride was hydrolyzed in 60% aqueous acetone at 0 °C in the presence of 100% excess bicarbonate. After the usual workup and removal of solvent, the exo alcohol was obtained as colorless solid. Following recrystallization from hexane, the melting point was 85–86 °C.

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.26; H, 7.83. Found: C, 78.10; H, 7.57.

2-(5′-Coumaranyl)-*exo*-norbornyl benzoate was prepared by treating the alcohol with *n*-butyllithium followed by benzoyl chloride in THF. After the usual workup, the benzoate was used for the solvolytic work without further purification.

Kinetic Measurements. The method used for determining the rate constants of the *p*-nitrobenzoates and benzoates is essentially the same as that described earlier.[25] The rates and thermodynamic parameters are listed in Table I.

Solvolysis Product. 2-(5′-Coumaranyl)-*endo*-norbornyl *p*-nitrobenzoate (1 mmol) was solvolyzed in 80% aqueous acetone containing a 10% molar excess of sodium acetate at 25 °C. After 10 half-lives, the reaction mixture was worked up in the usual way and the product was analyzed by ^1H NMR.

Registry No.—5-Coumaranyllithium, 68151-00-8; 2-(5′-coumaranyl)-*endo*-norbornanol, 68151-01-9; 2-(5′-coumaranyl)-*exo*-norbornanol, 68151-02-0; norbornanone, 497-38-1; 2-(5′-coumaranyl)-*exo*-norbornyl benzoate, 68151-03-1; 5-bromocoumarin, 38169-99-2.

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Substituent Effects in Micellar Catalysis

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Micellar catalysis with sodium 1-dodecanesulfonate has been demonstrated for the acidic hydrolysis of a series of substituted phenylacetohydroxamic acids. The substrate–micelle association constants for the series of compounds correlates well with the empirical lipophilicity substituent constants, π.

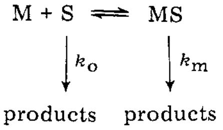
Micellar catalysis of many reactions is well documented.[1] Recently we reported micellar catalysis in hydroxamic acid hydrolysis.[2] Previously the only apparent example of micellar effects on amide-like hydrolyses was the very small effect observed in some acetanilide hydrolyses.[3]

The micellar effects on the hydroxamic acid hydrolysis corresponded to the mechanism[4] of Scheme I, where M and S are micelle and substrate, respectively, and k_o and k_m are the rate constants for product formation outside and within the micelle, respectively. This model leads to the relationship[4]

$$\frac{1}{k_o - k_1} = \frac{1}{k_o - k_m} + \left(\frac{1}{k_o - k_m}\right)\left(\frac{N}{K(C_D - \mathrm{cmc})}\right) \tag{1}$$

in which k_1 is the observed pseudo-first-order rate constant,

Scheme I



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