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Structural Effects in Solvolytic Reactions. 31. High Exo:Endo Rate and Product Ratios in the Solvolyses of the 2-Methyl-, 2-Phenyl-, and 2-(5′-Coumaranyl)-*exo*-5,6-trimethylene-2-norbornyl *p*-Nitrobenzoates. Further Evidence for the Unimportance of σ-Participation as a Factor in the High Exo:Endo Rate and Product Ratios Realized in the Solvolysis of Tertiary 2-Norbornyl Derivatives[1]

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Abstract: Solvolyses of 2-methyl-, 2-phenyl-, and 2-(5′-coumaranyl)-*exo*-5,6-trimethylene-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone reveal high exo:endo rate ratios of 420, 118, and 286, respectively. The solvolyses of these derivatives in the presence of sodium acetate afford exclusively the exo-substituted alcohol. The secondary *exo*-5,6-trimethylene-2-norbornyl system, with its low exo:endo rate ratio, 11.2, has been proposed as a model norbornyl system which solvolyzes through the intermediacy of classical carbocations, constrained into the classical structure by the 5,6-trimethylene bridge. Consequently, these stabilized tertiary derivatives should also undergo solvolyses through the intermediacy of classical carbocations. Yet they exhibit high exo:endo rate and product ratios, at one time considered essential criteria supporting σ-participation with the formation of a σ-bridged intermediate in the solvolysis of the exo derivative. It is clear that steric effects must make major contributions to the high exo:endo rate and product ratios observed in the solvolyses of these stabilized tertiary derivatives.

Winstein and Trifan observed[4] that *exo*-norbornyl *p*-bromobenzenesulfonate (**1**) solvolyzes 350 times faster than its endo epimer (**2**). They suggested that the C_1–C_6 bonding pair assists in the ionization of *exo*-brosylate; however, the geometry of the *endo*-brosylate prevents such anchimeric assistance. The norbornyl cation was formulated as the σ-bridged structure (**3**). Since then, various approaches have been made by physical organic chemists to confirm the existence of such a σ-bridged species in solvolytic media. The question was, is the high exo:endo rate and product ratio observed in the solvolysis of 2-norbornyl brosylate due to the driving force associated with the formation of a stabilized σ-bridged species (**3**) in the transition state? Or is some other factor responsible? The observation that highly stabilized tertiary norbornyl derivatives, such as 2-(5′-coumaranyl)-,[5] 2-*p*-anisyl-2-norbornyl[6] (**4**, **5**), and 2-*p*-anisyl-2-camphenilyl[6] (**6**), are also capable of exhibiting such high exo:endo rate and product ratios failed to support the original conclusion. The high exo:endo rate ratios in these systems (**4**, **5**, **6**) were ascribed to the steric characteristics of the norbornyl system.[7]

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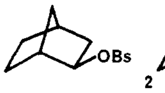

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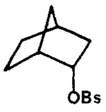

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RR(25°C) 350 1·00

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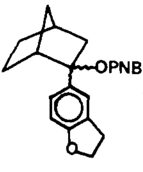

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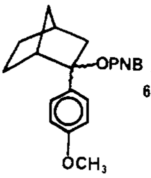

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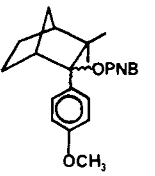

exo:endo 240 284 44,000

High exo:endo rate ratios were also observed in the case of destabilized norbornyl derivatives carrying electron-withdrawing substituents in the 7 position.[8] It was proposed that such substituents resist σ-bridging. Consequently, it would appear that σ-participation cannot be a factor in the high exo:endo rate ratios observed in these derivatives.

On the other hand, the low exo:endo rate ratio, 11.2, observed in the acetolysis of *exo*-5,6-trimethylene-2-norbornyl tosylates (**7**, **8**)[9] has been interpreted as indicating that σ-participation cannot be a major factor in this system. It is argued that the 5,6-trimethylene bridge prohibits σ-bridging

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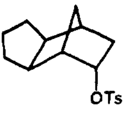
Table I. Rates of Solvolysis of Tertiary *exo*-5,6-Trimethylene-2-norbornyl *p*-Nitrobenzoates in 80% Aqueous Acetone

derivative	isomer	$k_1 \times 10^6\ s^{-1}$			$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	exo:endo
		t_1, °C	t_2, °C	25 °C			
2-(5′-coumaranyl)-	exo			53 000[a]			286
	endo	5.72 (0)		185	21.9	−2.1	
2-phenyl-	exo	109 (50)		4.24	24.2	−1.8	118
	endo	337 (100)	24.6 (75)	3.6×10^{-2}[b]	26.3	−4.5	
2-methyl-	exo	552 (125)	48.9 (100)	3.0×10^{-3}[b]	27.9	−4.2	420
	endo	49.8 (150)	4.69 (125)	7.14×10^{-6}[b]	30.8	−6.0	

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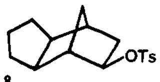

8

RR (25°C) 1.00 11.2

because of the steric difficulties involved in moving the trimethylene bridge to the position it would occupy in the σ-bridged cation.[10,11] On this basis this structure provides a norbornyl system where σ-participation should not be a significant factor in the solvolytic behavior of these compounds.

If the *exo*-5,6-trimethylene-2-norbornyl secondary system involves classical ions, the solvolysis of the stabilized tertiary derivatives in this system must surely proceed through classical ions.

Now we have an interesting situation on hand. How will the tertiary derivatives of the *exo*-5,6-trimethylene-2-norbornyl system behave regarding exo:endo rate ratios? Will they exhibit low exo:endo rate ratios, since they are classical, forced to be so by the trimethylene bridge? Or will they parallel the behavior of the tertiary esters in the 2-norbornyl system, with high exo:endo rate and product ratios, not because of σ-participation in the solvolysis of the exo derivative, but because of steric hindrance to ionization of the endo derivative?

In order to answer these questions, we synthesized the 2-methyl-, 2-phenyl-, and 2-(5′-coumaranyl)-*exo*-5,6-trimethylene-2-norbornyl *p*-nitrobenzoates and established their rates and products of solvolysis in 80% aqueous acetone.

Results

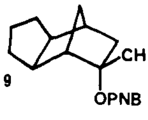
Synthesis. Addition of methylmagnesium iodide, phenylmagnesium bromide, and 5-coumaranyllithium to *exo*-5,6-trimethylene-2-norbornanone gave the tertiary endo alcohols. The alcohols were converted into the tertiary exo chlorides in the automatic hydrochlorinator.[12] Solvolysis of the chlorides in 60% aqueous acetone containing excess potassium bicarbonate yielded the corresponding exo alcohols. The endo alcohols were converted into the corresponding endo *p*-nitrobenzoates by treating the alcohol with *n*-butyllithium, followed by *p*-nitrobenzoyl chloride in THF. The 2-methyl- and the 2-phenyl-*exo-p*-nitrobenzoates were made in the same way. The 2-(5′-coumaranyl)-*exo-p*-nitrobenzoate was too unstable to be isolated and hence the benzoate was synthesized for solvolytic studies.

Rate Studies. The *p*-nitrobenzoates were solvolyzed in 80% aqueous acetone and their rates measured. The rate constant for the solvolysis of 2-(5′-coumaranyl)-*exo*-5,6-trimethylene-2-norbornyl *p*-nitrobenzoate was determined by multiplying the rate of the benzoate by the usual factor, 20.8.[6] The rate data and the thermodynamic parameters are listed in Table I.

Solvolytic Product. The *p*-nitrobenzoates were solvolyzed in 80% aqueous acetone in the presence of 10% molar excess of sodium acetate for 10 half-lives. After the usual workup, the product was analyzed by ^{1}H NMR.

Discussion

Exo:Endo Rate Ratios in 2-Methyl- and 2-Phenyl-*exo*-5,6-trimethylene-2-norbornyl. The low exo:endo rate ratio of 11.2 observed in the acetolysis of *exo*-5,6-trimethylene-2-norbornyl tosylates (**7, 8**) becomes 420 for the tertiary 2-methyl (**9, 10**).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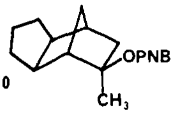
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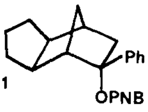
RR(25°C) 1.00 420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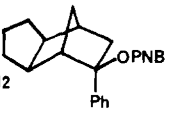
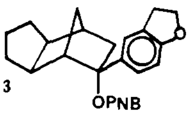

12

RR(25°C) 1.00 118

In the case of the tertiary 2-phenyl (**11, 12**), the exo:endo rate ratio is 118. The exo:endo rate ratios observed in these tertiary derivatives are similar to the data for the corresponding 2-norbornyl tertiary esters (885 in the case of 2-methyl[13] and 127 for 2-phenyl[14]), leading one to conclude that similar reaction intermediates are involved.

Exo:Endo Rate Ratio in 2-(5′-Coumaranyl)-*exo*-5,6-trimethylene-2-norbornyl. The σ^+ constant for the 5-coumaranyl substituent has a high negative value of −0.984,[15] considerably more negative than that for *p*-anisyl, σ^+ −0.778. As has been pointed out above, in the *exo*-5,6-trimethylene-2-norbornyl system, if the secondary and the tertiaries, 2-methyl and 2-phenyl cations, are classical, there surely cannot be any argument about the exceptionally highly stabilized 2-(5′-coumaranyl) derivative. The 2-(5′-coumaranyl)-*exo*-5,6-trimethylene-2-norbornyl cation ought to be classical. What will be the exo:endo rate ratio in this system?

The rate data indicate that the 2-(5′-coumaranyl) derivatives (**13, 14**) show a high exo:endo rate ratio of 286. Yet these derivatives must solvolyze with the formation of classical cations.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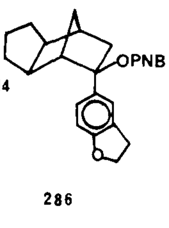

14

RR (25°C) 1.00 286

Exo:Endo Product Ratios. The acetolyses of *exo*- and *endo*-norbornyl brosylates (**1, 2**) yield the exo-substituted product in amounts greater than 99%.[16] This was considered to provide major support for σ-bridging. Consequently, it was of interest to examine the products of solvolyses of these highly stabilized derivatives purported to involve the intermediacy of classical cations, even in the secondary system.

The solvolyses of 2-methyl-, 2-phenyl-, and 2-(5′-coumar-

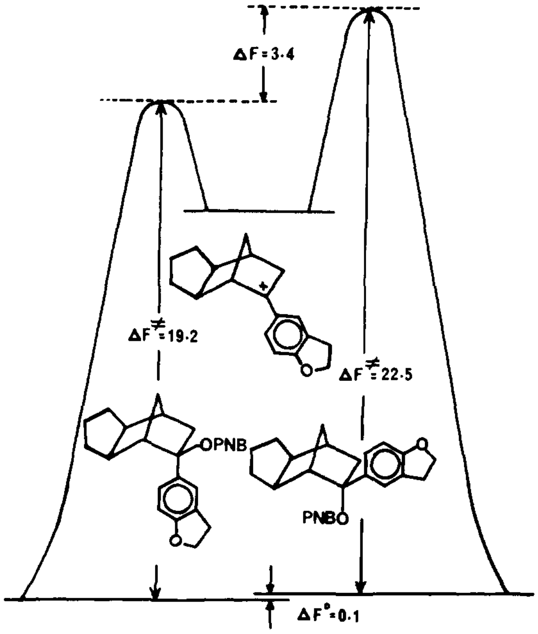
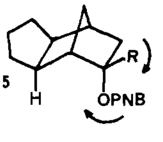


Figure 1. Free-energy diagram for the solvolysis of the 2-(5′-coumaranyl)-*exo*-5,6-trimethylene-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25 °C.

anyl)-*exo*-5,6-trimethylene-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone in the presence of sodium acetate yields the corresponding exo alcohols in amounts greater than 99%. Therefore, even these highly stabilized derivatives undergoing solvolyses through classical cations exhibit predominant substitution from the exo side.

Goering-Schewene Diagram. Treatment of the rate data in the manner developed by Goering and Schewene[16,17] reveals differences in energy of the two transition states of 3.6, 2.9, and 3.4 kcal/mol for the 2-methyl, 2-phenyl, and 2-(5′-coumaranyl) derivatives, respectively. Here we present the Goering-Schewene diagram for the 2-(5′-coumaranyl) derivative only (Figure 1). If σ-participation is absent in the secondary *exo*-5,6-trimethylene-2-norbornyl derivative, it surely cannot be significant in these highly stabilized tertiary derivatives. It appears possible to account for this phenomenon only in terms of the changes in steric strain in approaching the respective transition states (**15**, **16**).[7]



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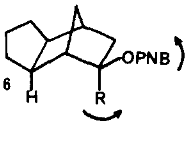

16

The "Tool of Increasing Electron Demand". ^{13}C Nuclear Magnetic Resonance as a Probe. Farnum and his co-workers[18] examined the ^{13}C NMR behavior of the 2-aryl-*exo*-5,6-trimethylene-2-norbornyl cations under stable ion conditions. The aryl group was varied in electron demand from *p*-anisyl to 3,5-bis(trifluoromethyl)phenyl. They conclude that the cations where the aryl group is phenyl or more electron-supplying than phenyl are classical. But they observed certain changes in the NMR spectra with less electron-supplying substituents (p-CF_3 and m,m'-$(CF_3)_2$). This led them to the conclusion that they might be observing the inception of σ-bridging in these cations.

As discussed in previous publications[5,19] from this laboratory, extreme caution should be exercised in trying to correlate ^{13}C chemical shifts in superacids and charge densities. Our attempts to treat the ^{13}C NMR shifts of Olah[20] and Farnum[18] with σ^+ constants have revealed very poor correlations. As pointed out by Farnum himself,[21] such ^{13}C chemical shifts are affected by many factors. Clearly, judgment should be reserved as to the meaning of such ^{13}C shifts until the theoretical background is better understood.

Conclusion

On the basis of the accepted argument that the trimethylene structure resists bridging, even in the secondary cation, it follows that the solvolysis of the 2-methyl-, 2-phenyl- and 2-(5′-coumaranyl)-*exo*-5,6-trimethylene-2-norbornyl *p*-nitrobenzoates must proceed through classical cations without such σ bridges. Yet these derivatives yield high exo:endo rate as well as high exo:endo product ratios. Clearly, it is necessary to reconsider the proposal that high exo:endo rate and product ratios are essential criteria supporting the formation of stabilized σ-bridged species.

Experimental Section

2-Methyl-*exo*-5,6-trimethylene-2-*endo*-norbornanol was prepared by the addition of methylmagnesium iodide [made from magnesium (6.4 g, 0.266 g-atom) and methyl iodide (34 g, 0.266 mol)] in ether to *exo*-5,6-trimethylene-2-norbornanone (20 g, 0.133 mol). The endo alcohol was recrystallized from pentane to get 12.7 g (58%) of the pure material, mp 81.5-82 °C.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.81; H, 11.01.

2-Methyl-*exo*-5,6-trimethylene-2-*endo*-norbornyl *p*-nitrobenzoate (**9**) was prepared following the reported method.[22] The *p*-nitrobenzoate was obtained in 69% yield after recrystallization from hexane, mp 130-130.5 °C.

Anal. Calcd for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.42; H, 6.73; N, 4.60.

2-Methyl-*exo*-5,6-trimethylene-2-*exo*-norbornanol. The endo alcohol was converted into the exo chloride by treating with dry HCl gas in methylene chloride at 0 °C in an automatic hydrochlorinator.[10] Solvent was pumped off and the chloride was hydrolyzed in 60% aqueous acetone at room temperature in the presence of 100% excess sodium bicarbonate. After the usual workup, the exo alcohol was obtained as a colorless solid, recrystallized from pentane, mp 77.2-77.8 °C. Analysis by vapor phase chromatography (Perkin-Elmer 226 unit using 150 ft × 0.01 in. i.d. Carbowax 20M Golay column) showed that the product was free from isomeric impurities.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.41; H, 10.80.

2-Methyl-*exo*-5,6-trimethylene-2-*exo*-norbornyl-*p*-nitrobenzoate (**10**) was prepared from the exo alcohol following the reported method.[22] The yield of the *p*-nitrobenzoate was 59%, mp 114.5-115 °C (hexane).

Anal. Calcd for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.82; H, 6.80; N, 4,47.

2-Phenyl-*exo*-5,6-trimethylene-2-*endo*-norbornanol was prepared by the addition of phenylmagnesium bromide [made from magnesium (3 g, 0.125 g-atom) and bromobenzene (19.6 g, 0.125 mol)] in ether to *exo*-5,6-trimethylene-2-norbornanone (10 g, 0.0667 mol). The endo alcohol was recrystallized from pentane to yield 10.5 g (69%) of the pure alcohol, mp 73.4-74.6 °C.

Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.30; H, 8.85.

2-Phenyl-*exo*-5,6-trimethylene-2-*endo*-norbornyl *p*-nitrobenzoate (**11**) was prepared following the reported procedure.[22] The *p*-nitrobenzoate was obtained in 18% yield, mp 153-154 °C dec.

Anal. Calcd for $C_{23}H_{23}NO_4$: C, 73.19; H, 6.14; N, 3.71. Found: C, 72.94; H, 5.97; N, 3.94.

2-Phenyl-*exo*-5,6-trimethylene-2-*exo*-norbornanol was prepared from the corresponding endo alcohol following the procedure described under the preparation of 2-methyl-*exo*-5,6-trimethylene-2-*exo*-norbornanol. The exo alcohol was recrystallized from pentane to get the pure alcohol, mp 94.5-95.2 °C.

Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.33; H, 8.86.

2-Phenyl-*exo*-5,6-trimethylene-2-*exo*-norbornyl *p*-nitrobenzoate (**12**) was made from the corresponding exo alcohol according to the method previously described.[22] The *p*-nitrobenzoate was recrystallized from hexane to get the pure ester in 41% yield, mp 127 °C dec.

Anal. Calcd for $C_{23}H_{23}NO_4$: C, 73.19; H, 6.14; N, 3.71. Found:

C, 72.94; H, 5.79; N, 3.94.

2-(5'-Coumaranyl)-*exo*-5,6-trimethylene-2-*endo*-norbornanol was made by the addition of 5-coumaranyllithium[5] [made from 5-bromocoumaran (16 g, 0.08 mol) and *n*-butyllithium (1.9 M, 42 mL, 0.08 mol)] in ether to *exo*-5,6-trimethylene-2-norbornanone (10.5 g, 0.07 mol) in ether at 0 °C. The endo alcohol was recrystallized from hexane-chloroform (70:30) to get the pure alcohol in 69% yield, mp 119-120 °C.

Anal. Calcd for $C_{18}H_{22}O_2$: C, 80.0; H, 8.15. Found: C, 80.16; H, 8.00.

2-(5'-Coumaranyl)-*exo*-5,6-trimethylene-2-*endo*-norbornyl *p*-nitrobenzoate (13) was made from the corresponding endo alcohol following the method described previously.[22] The *p*-nitrobenzoate was recrystallized from hexane to get the pure ester in 56% yield, mp 136-137 °C.

Anal. Calcd for $C_{25}H_{25}NO_5$: C, 71.59; H, 5.97; N, 3.34. Found: C, 71.46; H, 5.90; N, 3.56.

2-(5'-Coumaranyl)-*exo*-5,6-trimethylene-2-*exo*-norbornanol was made from the endo alcohol following the procedure described under the preparation of 2-methyl-*exo*-5,6-trimethylene-2-*exo*-norbornanol. The exo alcohol so obtained was recrystallized from hexane-chloroform (70:30) to get the pure alcohol, mp 131-132 °C.

Anal. Calcd for $C_{18}H_{22}O_2$: C, 80.0; H, 8.15. Found: C, 79.95; H, 8.39.

2-(5'-Courmaranyl)-*exo*-5,6-trimethylene-2-*exo*-norbornyl benzoate was made from the corresponding exo alcohol by the addition of *n*-butyllithium followed by benzoyl chloride in THF following the reported method.[22] The benzoate obtained was found to be over 95% pure by ^{1}H NMR and was used for the solvolytic study without further purification.

Kinetic Measurements. The method used for determining the rate constants of the *p*-nitrobenzoates and benzoates is essentially the same as described earlier.[22] The rates and thermodynamic parameters are listed in Table I.

Solvolysis Products. The *p*-nitrobenzoates were solvolyzed in 80% aqueous acetone containing a 10% molar excess of sodium acetate at temperatures of 125 °C for the 2-methyl, 75 °C for the 2-phenyl, and 25 °C for the 2-(5'-coumaranyl) derivatives. After 10 half-lives, the reaction mixtures were worked up and analyzed by ^{1}H NMR. In all of the cases, the solvolysis products were almost exclusively the tertiary exo alcohols.

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Formation of Benzyl and Tropylium Ions from Gaseous Toluene and Cycloheptatriene Cations[1]

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Abstract: A detailed study utilizing collisional activation (CA) mass spectra shows that decomposition of toluene (**1**) and cycloheptatriene (**2**) ions gives very similar proportions of benzyl (**3**) and tropylium (**4**) ions as a function of energy. Only the more stable **4** is formed at threshold decomposition energies through the prior equilibration **1** $\rightleftarrows$ **2**. In this **1** is favored; with increasing electron energy [**3**] increases to a maximum of 52%, falling to 33% for C_7H_8 ionization with 70-eV electrons because higher energy $C_7H_7^+$ ions undergo the equilibration **3** $\rightleftarrows$ **4** favoring **4**. The much higher [**3**] values from **1** measured using ion-molecule reactions of **3** apparently arose from the displacement of this equilibrium. Essentially pure benzyl ions are formed from benzyl fluoride at low ionizing energies.

The decompositions of gaseous toluene (**1**) and cycloheptatriene (**2**) cations are among the most thoroughly studied of unimolecular ion reactions.[2-12] However, for the dominant $C_7H_7^+$ product a major point of controversy apparently still exists concerning the relative proportion of benzyl (**3**) and tropylium (**4**) ions (Scheme I). Heat of formation values (ΔH_f, kcal/mol) for ions[13] and transition states (values from theoretical calculations in parentheses)[9] indicate that the unimolecular ion isomerization **1** $\rightleftarrows$ **2** requires less energy than hydrogen loss, and at threshold energies for the latter the more stable tropylium ions **4** should be formed, as observed.[6,11] At slightly higher energies direct formation of benzyl ions **3** should become competitive,[14] which also has been confirmed experimentally.[3,5,6,11,12] However, for **3** and **4** formed with substantial internal energy (>40 and 46 kcal/mol, respectively) the isomerization **3** $\rightleftarrows$ **4** is possible; further decomposition

0002-7863/79/1501-1783$01.00/0