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 $\mathbf{1} \rightleftarrows \mathbf{2}$. 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 $\mathbf{3} \rightleftarrows \mathbf{4}$ 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 $\mathbf{1} \rightleftarrows \mathbf{2}$ 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 $\mathbf{3} \rightleftarrows \mathbf{4}$ is possible; further decomposition

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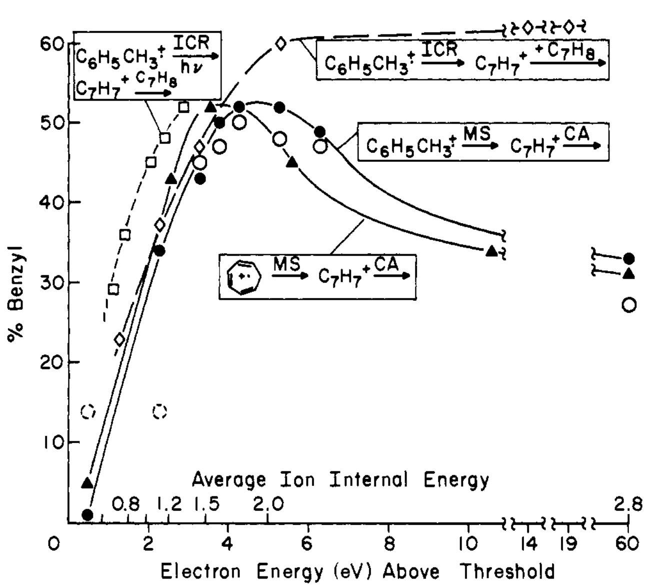
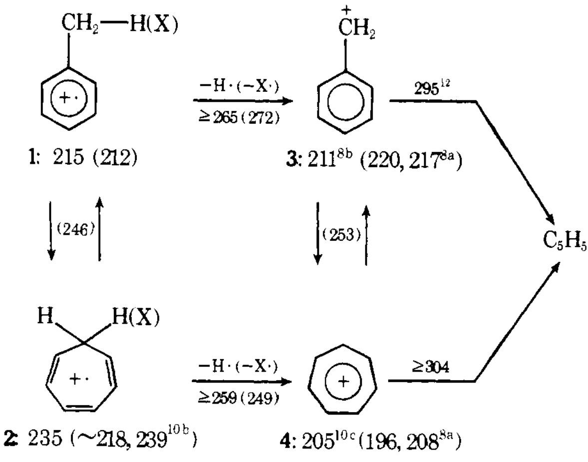


Figure 1. Benzyl and tropylium (**4**) ions formed from toluene (**1**) and cycloheptatriene (**2**) as a function of energy above the threshold for **4** formation (electron energy, lower scale). ● and ○: CA data for **1** from $[77^+]/[74^+]$ and $[91^{2+}]/[74^+]$, respectively; dashed open circles are data of high uncertainty (see text). ▲: CA data for **2** from $[77^+]/[74^+]$. ◇: ion-molecule reactivity data for **1** of Ausloos et al., ref 11. □: photodissociation data for **1** of Dunbar, ref 6, using average ion internal energies (upper scale) calculated as described in the text.

Scheme I



requires much more energy (~90 kcal/mol).[12,13] Such equilibration should favor the more stable **4**, consistent with our collisional activation (CA)[16] data showing for both **1** and **2** a *decrease* in [**3**] from 45-50 to 25% in increasing the ionizing electron energy from 13 to 70 eV.[5] The lower energy data are in agreement with those of Jackson, Lias, and Ausloos[11] from recent ion-molecule reaction studies on **1** utilizing ion cyclotron resonance (ICR) spectroscopy; however, they conclude that an even *higher* proportion of **3** ions is formed from **1** at higher energies (62% **3** using 30-eV electrons). The purity of the **3** and **4** reference ions used[5] could account for part of the discrepancy; our CA data indicated that only 45% of $C_7H_7^+$ ions formed from benzyl chloride (X = Cl) at 70 eV are **3**,[5] while other studies assume that mainly **3** ions are formed from this precursor.[8,11,12] To clarify these discrepancies we have now made detailed CA measurements on these systems using instrumentation of higher reproducibility, sensitivity, and resolution,[17] including the determination of CA spectral data on pure **3** and **4**[6] ions and on very low energy $C_7H_7^+$ ions formed by decomposition of metastable **1** and **2** ions.[18] Although our earlier results[5] are confirmed, at lowest energies the proportion of benzyl is dramatically reduced.

Experimental Section

Measurements were made with a reversed-geometry double-focusing mass spectrometer,[1,17] ion accelerating potential 7.8 kV and ion source temperature 150 °C. The magnetic field is set to select $C_7H_7^+$ precursor ions; ionic products of their metastable decompositions (the MI spectrum) occurring between the magnetic and electrostatic (ESA) analyzers are measured by computer-controlled multiple scans of the ESA. The pressure in a special collision chamber near the β-focal point is increased with helium until the precursor ion intensity is reduced to 25% of its original value, and CA product abundances are determined in a second set of ESA scans. The *m/e* 77, 76, 75, 74, and 45.5 (91^{2+}) CA peaks are the most characteristic; 20-30 scans of these were taken for the weakest precursor $C_7H_7^+$ signals. The plots of [**3**]/([**3**] + [**4**]) vs. electron energy (Figure 1) are based on $[91^{2+}]/[74^+]$ (for **1**) and $[77^+]/[74^+]$ values (derived from peak heights) using interpolation between the values from the reference CA spectra of **3** and **4** (see below) and sensitivities measured at the same precursor ion abundance and target gas pressure.[19] The results using $[91^{2+}]/[74^+]$ are of lower accuracy as noise is poorly distinguishable in the narrow *m/e* 45.5 peak. The width of this peak is near the limit of mass reproducibility in the repeated scans, leading to a larger variation in the relationship of height to area and poor results for low-abundance precursor ions. The *m/e* 91^{2+} results for $C_7H_7^+$ ions from **2** are qualitatively[19] consistent with those from $[77^+]/[74^+]$. For $C_7H_7^+$ ions formed in the first field-free region[18] the value of the electron energy above threshold is estimated[3] as 0.5 eV based on the 0.8-eV kinetic shift indicated by the appearance potential of 11.55 eV.[13]

Reference CA Spectrum of 3 Ions. The $C_7H_7^+$ ions formed by 11.5-eV electron ionization of 1,2-diphenylethane (**5**) should be ≥90% **3**, based on the $C_7H_5D_2^+$ ions produced by CA from **5**-*1,1,2,2-d*$_4$.[5] In recent studies[8,11,12] benzyl chloride has been assumed to give mainly **3** ions on electron ionization, but their CA spectra (Table I) show a maximum of 92% (12-eV electrons, 57% with 70 eV) **3**. Chemical ionization of benzyl acetate (isobutane reagent gas)[20] and of benzyl fluoride (CH_4 reagent),[21] which were thought to form pure **3**, show maxima of 90 and 64% **3**, respectively, under our conditions. However, the CA spectrum of $C_7H_7^+$ ions from the 12-eV electron ionization of benzyl fluoride was the same as that from **5** within experimental error (100 ± 3% **3**), so that these data were assumed to represent those of pure **3**.[22] Following Dunbar,[6] pure **4** ions were prepared from **1** by removing the **3** ions through reaction with toluene at high ion source pressure.

The ion photodissociation data[6] for **1** was compared with the electron ionization data from these CA experiments in terms of the average internal energy of the $C_7H_8^+$ ions available for $C_7H_7^+$ formation (Figure 1, as energy above the threshold for **4** formation, 1.9 eV).[10] For the photodissociation data the photon energy was added to the average thermal energy of **1** at room temperature (0.11 eV)[6] under the assumption that ion thermalization is complete. For the CA data the distribution of internal energy values of **1** ions formed with 70-eV electrons,[3] adjusted for 150 °C, was used to estimate the average energies of **1** ions formed at lower electron energies using a linear probability function.

Results

Our previous limited results[5] on the formation of **3** and **4** from **1** and **2** are reproduced, within experimental error, by the new CA data (Figure 1), but are still in contrast to the ICR results[11] at higher energies. The reliability of these CA determinations depends on our previous conclusions that the quantitative abundances of CA spectral peaks arising from higher energy processes (those not found for metastable ions) are characteristic of the precursor ion's structure, independent (~±2%) of its internal energy.[16] The latter assumption is obviously of key importance; note that no exceptions have yet been found experimentally in a large number of studies,[16] and that this assumption can be justified on theoretical grounds.[23] If the rearrangement **3** → **4** (or **4** → **3**) were competitive with the CA decompositions,[24] the extent of post-CA rearrangement

Table I. Isomeric Composition of $C_7H_7^+$ Ions from $C_6H_5CH_2X$ Compounds

	[benzyl$^+$]/[$C_7H_7^+$], %[a]				[m*] × 10^4 [b]	
compd	CI[c]	70 eV	12 eV	m* [d]	$M^{+\cdot} - X$	$M^{+\cdot} - H$
$C_6H_5CH_2F$	75[g]	51	100	*e*	<0.03	90
$C_6H_5CH_2Cl$	69[h]	57	92	*f*	3	0.3
$C_6H_5CH_2Br$	74	60	96[i]	~50	2	0.5
$(C_6H_5CH_2-)_2$		62	100[j]	~25[k]	30	
$C_6H_5CH_2OCOCH_3$	90[l]	54				

[a] Based on [77^+]/[74^+] in the CA spectrum of $C_7H_7^+$. [b] Abundance of the peak from metastable $M^{+\cdot}$ decomposition relative to [$M^{+\cdot}$] × 10^{-4}; value for toluene = 90. [c] $C_7H_7^+$ formed by isobutane chemical ionization. [d] $C_7H_7^+$ formed by metastable $M^{+\cdot}$ decomposition in the first field-free region.[16] [e,f] Measurement not possible because of insufficient $C_7H_7^+$ abundance[e] or interference.[f] [g] CI/CH_4, 64%. [h] CI/CH_4, 59%. [i] 10.5-eV electrons. [j] Used as reference CA spectrum of benzyl$^+$. [k] 24-eV electrons. [l] 55% at long ion source residence times (maximum + repeller).

Table II. Effect of Collision Gas Pressure on the Determination of Isomeric Composition

precursor ion abundance,[a] %	[benzyl$^+$]/[$C_7H_7^+$], %[b] toluene	1,2-diphenylethane
50	30.8	65.5
40	33.0	64.4
30	33.1	63.4
20	33.1	62.0
10	30.7	60.0

[a] He pressure increased to reduce [$C_7H_7^+$] to this proportion of original value; ~25% gives maximum sensitivity. [b] Footnote *a*, Table I.

(and the proportion of resulting products) should also be independent of precursor internal energy; thus the CA spectrum of a mixture of **3** and **4** should still represent a linear superposition of the individual spectra from the corresponding amounts of pure **3** and **4**, independent of their mode of formation.

Several observations here provide further support for these conclusions. For $C_7H_7^+$ ions from **1** the CA data for the higher energy formation of $C_7H_7^{2+}$, for which any competing rearrangement should be minimized, yields comparable **3** values (Figure 1). The Ausloos ICR data[11] are also in surprisingly close agreement at energies below the predicted[9] threshold for **3** → **4**; ΔH_f(transition state **3** $\rightleftarrows$ **4**) − ΔH_f(**4**) = 2.0 eV. Thus for these low-energy $C_7H_7^+$ ions no important error is caused by an initial collision raising the ion internal energy sufficiently to cause isomerization (without dissociation), followed by a second collision[24] leading to the fragmentation observed in the CA spectrum. To check this for higher energy ions, [**3**]/([**3**] + [**4**]) was measured by CA at He target gas pressures varying from that required to scatter 50% of the $C_7H_7^+$ ions to that required to scatter 90%; for the $C_7H_7^+$ ions undergoing high-energy CA decomposition this should change substantially the proportion involved in a prior collision which could produce isomerization. Low-energy **3** and **4** reference ions (vide supra) were used to determine the reference CA abundance and sensitivity values, and mixtures of high average energy **3** and **4** ions were generated from toluene and 1,2-diphenylethane using 70-eV electrons (for the latter the previous study[5] found 65% **3**). The data of Table II show that any effect of multiple collisions is not large; the values are the same within experimental error (which is substantially larger at 10 and 50% precursor ion abundances).[25] Separate experiments showed also that precursor ion intensity has a negligible effect on these values.

Discussion

The CA data (Figure 1) show that tropylium ions (**4**) are the dominant product from **1** and **2** at threshold energies, with the proportion of benzyl ions (**3**) increasing rapidly as the internal energy of the precursor $C_7H_8^+$ ions is increased immediately above threshold. This agrees quite well with the previous data for **1** decompositions,[5,9,10] even for the ICR experiments[6,11] involving much longer ion lifetimes. The ~0.4-eV energy difference of the nearly parallel photodissociation data of Dunbar[6] could result from incomplete thermalization prior to the photodissociation and/or inaccuracies in our calculation of average ion internal energies. The near identity of the CA data for low-energy **2** and **1** decompositions is consistent with the ready isomerization **1** $\rightleftarrows$ **2** depicted in Scheme I. This also indicates that **1** is heavily favored in the equilibrium, consistent with $\Delta H_f(\mathbf{1}) < \Delta H_f(\mathbf{2})$.[13]

The theoretical calculations[9] predict the threshold for **3** $\rightleftarrows$ **4** isomerization to be 2.0 eV above that for **4** formation. $C_7H_7^+$ ions of this internal energy should be formed from $C_7H_8^+$ of slightly more than 2 eV energy above threshold; this corresponds to the maximum [**3**] found by CA (Figure 1), consistent with the rapid isomerization of ions of >2 eV internal energy to an equilibrium mixture favoring heavily the more stable **4**.[26] The maximum in [**3**] from **2** occurs at ~0.3 eV lower energy than that from **1**; this could arise from **2** → **4** (and **1** → **3**) becoming competitive with **2** → **1** (and **1** → **2**) for $C_7H_8^{+\cdot}$ ions of nearly 2 eV internal energy above threshold, so that these **1** and **2** ions have a higher tendency to form **3** and **4**, respectively. Note that the rapid equilibration **3** $\rightleftarrows$ **4** for higher energy ions also explains the complete isotopic scrambling found in studies of labeled toluenes for metastable $(^{12}C,^{13}C)_7(H,D)_7^+$ ions undergoing loss of acetylene.[4,27]

The fast isomeric equilibration **3** $\rightleftarrows$ **4** also offers an explanation for the higher [**3**] values found by Ausloos and coworkers[11] (Figure 1) at higher electron energies. This study assumed (as found by Dunbar)[6] that **3**, but not **4**, ions react with compounds such as toluene. The reported[11] values represent **3** ions reacting within ~0.1 s; thus these ions include not only those originally formed as **3** but also those formed as **4** which have isomerized to **3**. The rapid equilibration **3** $\rightleftarrows$ **4** should make available for reaction a substantial proportion of the $C_7H_7^+$ ions formed with >2 eV internal energy which do not undergo thermalizing collisions. This would appear to account for the 62% **3** reported[11] as formed with 30-eV electrons vs. the ~35% found in this study. Note that the CA measurements of [**3**]/[**4**] should not remove either product preferentially, and thus should *not* displace the equilibrium **3** $\rightleftarrows$ **4** (Table II).[28]

Substituent Effects. The production of **3** and **4** ions from other benzylic compounds (X = F, Cl, Br, benzyl) is also consistent with the Scheme I mechanism. Again, the yield of **3** is lower using 70-eV ionizing electrons, consistent with the isomerization **3** → **4** for $C_7H_7^+$ ions formed with high internal energies. Using low electron energies >90% **3** ions are formed; the lower bond dissociation energy of the C–X bond, in comparison to that of the C–H bond, apparently leads to the production of a higher proportion of **3** ions with internal energies below the isomerization threshold.[5] For the $C_7H_7^+$ ions formed with the lowest internal energies (from metastable decomposition[18] of **1**-X ions of X = Br and benzyl, as well as H) the proportion of **3** again decreases, indicating for these **1**-X ions that the isomerization/decomposition pathway **1**-X → **2**-X → **4** requires less energy than **1**-X → **3**. Thus these benzylic precursors cannot lead to pure **3** ions at any ionizing electron energy.

Although the metastable decompositions of **1**-F from benzyl fluoride may also involve prior isomerization to **2**-F, these decompositions lead mainly to $C_7H_6F^+$, not $C_7H_7^+$, ions. (If the latter are formed at threshold,[22] our data indicate that this reaction channel is poorly competitive at only slightly higher energies.) Formation of $C_7H_7^+$ requires **1**-F ions of higher internal energy; for these the simple cleavage loss of F giving **3** should be much more favored than the isomerization to **2**-F, so that nearly pure benzyl ions are formed from benzyl fluoride at electron energies near threshold.

Acknowledgment. We are grateful to Drs. Pierre Ausloos, B. S. Freiser, and J. C. Traeger for communication of results prior to publication, to the National Institutes of Health (GM16609) for generous financial support, and to the Army Research Office, Durham, for funds for instrument improvements.

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(20) M. Meot-Ner, E. P. Hunter, and F. H. Field, *J. Am. Chem. Soc.*, **99**, 5576 (1977).

(21) A. G. Harrison and P.-H. Lin, *Can. J. Chem.*, **53**, 1314 (1975).

(22) Recent photoionization appearance potential measurements of benzyl fluoride by J. C. Traeger (private communication, June 1978) indicate that $\Delta H_f(C_7H_7^+) \sim 197$ kcal/mol; thus at lowest energies this precursor may also form **4** ions.

(23) M. S. Kim and F. W. McLafferty, *J. Am. Chem. Soc.*, **100**, 3279 (1978).

(24) In the apparatus used the average time between multiple collisions is $\sim 10^{-7}$ s; this should lower the importance of tight-complex rearrangement reactions in comparison to those occurring in the ion source (residence times of $\sim 10^{-6}$ s) and in the $\sim 10^{-5}$ s required to reach the collision chamber.

(25) As observed previously,[16a] the increased number of collisions per ion increased the proportion of higher energy CA fragmentations which are observed; increasing the He pressure to decrease the $C_7H_7^+$ intensity from 50% to 10% of its original value decreased $[77^+]/[74^+]$ by 17% for **3** and 35% for **4**.

(26) Ionization with 70-eV electrons should produce initial 1 ions of which ~37% will have internal energy values <2 eV above threshold.[3] Because the lowest energy ions of these will form **2**, little of the 33% **3** formed from 1 using 70-eV electrons can come from $C_7H_8^+$ with internal energy values >2 eV above threshold.

(27) A. Siegel, *J. Am. Chem. Soc.*, **96**, 1251 (1974).

(28) A referee has suggested the possibility that the stable $C_7H_7^+$ ions of high internal energy (>46 kcal/mol) have yet another structure, possibly ill defined, representing either **3** or **4** as limits. Although all our CA data (such as Table II) are consistent with the presence of only isomers **3** and **4**, the presence of another isomer with a similar CA spectrum cannot be ruled out. However, to be an important product in an equilibrium with **3** and **4**, or in competition with the formation of **3** or **4**, should require a comparable stability; apparently no experimental[2-7,10-13,15] or theoretical[8,9] studies to date have suggested the possibility of such a $C_7H_7^+$ isomer.

Loss of Allyl Cation Configuration in Cycloadditions to Electron-Rich Conjugated Dienes[1]

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Received August 28, 1978

Abstract: The cycloaddition of W-configurated 1,3-dimethyl-2-oxyallyl cations to electron-rich cyclic conjugated dienes is accompanied by configurational losses and leads to cycloadducts with α,β-configurated (equatorial, axial) methyl groups. For aromatic "dienes" such as benzene and *N*-alkylpyrroles, electrophilic substitution competes strongly with $[4 + 3 \rightarrow 7]$ cycloaddition which, nonetheless, can be accomplished by choice of an oxyallyl moiety with the proper blend of electrophilicity and nucleophilicity. It is suggested that formation of the seven-membered ring proceeds in two distinct stages, i.e., the stepwise pull-push mechanism involving formation of the first σ bond in an electrophilic step and the second σ bond in a nucleophilic step.

Introduction

The allyl cation route to seven-membered rings is a preparatively useful reaction which, as the increasing number of papers[3-15] shows, is meeting with general interest, not least because of the challenging synthetic and mechanistic problems which are involved. In the present paper we address ourselves mainly to a mechanistic question, i.e., the timing of bond changes on the way from reactants to products. Although the concerted $[4 + 3 \rightarrow 7]$ concept has been helpful in the past and

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