

Quantum chemical characterization of cycloaddition reactions between 1,3-butadiene and oxyallyl cations of varying electrophilicity†

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ABSTRACT: Hydroxyallyl cation and lithium and sodium oxyallyl cations are predicted to react with 1,3-butadiene both in a stepwise fashion and via concerted [4 + 3] cycloaddition with so-called extended stereochemistry. With hydroxyallyl cation, the stepwise process is preferred and subsequent second bond closures generate products equivalent to those that would arise from concerted [4 + 3] or [3 + 2] cycloadditions. For lithium and sodium oxyallyl cations, concerted, asynchronous processes are predicted to be preferred over stepwise processes, with [3 + 2] cycloaddition to generate a 3*H*-dihydrofuran followed by Claisen rearrangement of that intermediate being the lowest energy pathway for formation of a seven-membered ring. In the case of uncharged 2-oxyallyl, only transition state structures for concerted cycloadditions appear to exist. We infer that for [4 + 3] cycloadditions, concerted pathways are preferred over stepwise pathways provided that the separation between the electrophilicity of the allyl component and the electrofugacity of the 4π component is not too large. The Hammond postulate is shown to rationalize variations in free energies of activation for different processes as a function of allyl electrophilicity. Factors influencing the stereochemical outcome of different cycloadditions are discussed. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: cycloaddition; [4 + 3]; [3 + 2]; allyl cation; seven-membered ring; oxyallyl; Claisen rearrangement

INTRODUCTION

The preparation of seven-membered carbocycles remains an important goal in many synthetic endeavors, and [4 + 3] cycloaddition reactions constitute one powerful technique for their construction.^{1–6} In a previous paper, we examined computationally the mechanistic details of seven-membered ring-forming reactions between the 2-hydroxyallyl cation and a series of dienes—in particular 1,3-butadiene, cyclopentadiene, furan and pyrrole—that were chosen to span a broad range of electrofugacity.⁷ We found that the highly electrophilic hydroxyallyl cation tends to react with dienes in a stepwise fashion so as to generate either [4 + 3] or [3 + 2] cycloadducts (Scheme 1). The relative barrier heights associated with ring closure steps (i.e., the second step after initial bond formation) are controlled by the distribution of positive charge in the substituted allyl cation that is generated by the first C—C bond formation.

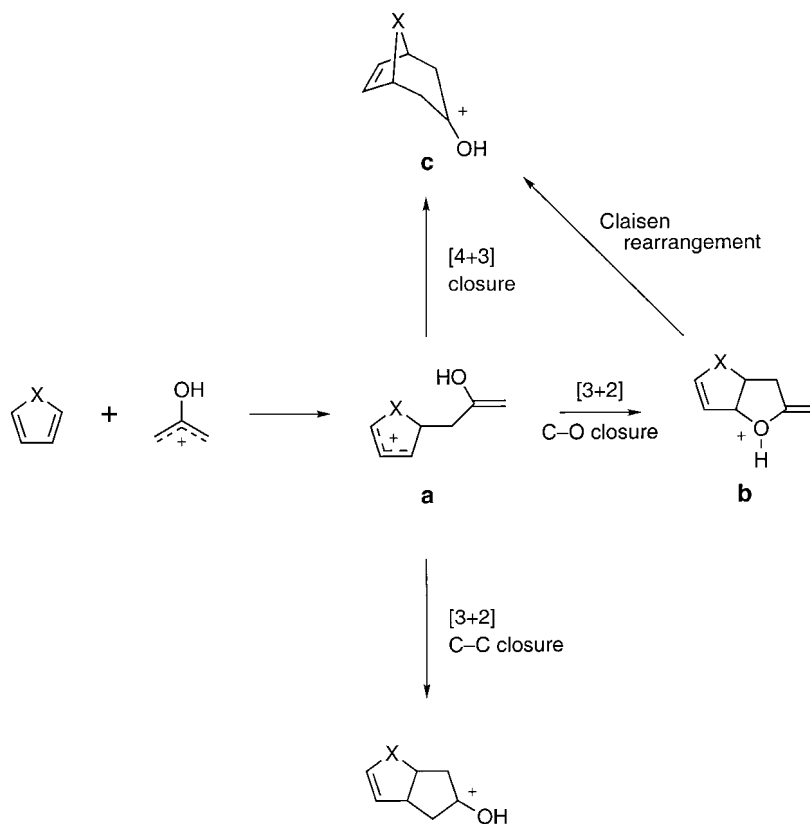
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For the intermediate **a** generated from initial attack on 1,3-butadiene (X = H,H in Scheme 1), subsequent steps completing [3 + 2] cycloaddition reactions are favored, but, when closure forms a C—O bond, the resulting intermediate **b** can undergo a low-energy Claisen rearrangement to form a seven-membered ring product **c** identical with that expected from so-called ‘compact’ [4 + 3] cycloaddition (‘compact’ [4 + 3] transition states place the 2-position of the allyl cation *endo* to the diene whereas ‘extended’ [4 + 3] transition states place that position *exo*). For cyclopentadiene as a substrate (X = CH₂ in Scheme 1) this preference is diminished, and [3 + 2] ring-closure barriers in this system are similar to [4 + 3] ring-closure barriers. The intermediate cation **a** generated from attack on furan has substantial oxonium ion character and charge localization favors direct [4 + 3] bond closure to **c** (X = O in Scheme 1). When pyrrole is the diene component (X = N in Scheme 1), the 1-azabutadienyl cation **a** created after initial C—C bond formation is so stable that *no* bond closure steps are energetically favorable, and theory predicts that only electrophilic substitution products will be observed. Thus, over a range of electrofugacity, changes in diene reactivity can be rationalized as deriving from differences in the charge distributions



Scheme 1.

found for the first intermediates formed along the cycloaddition pathways. These computational predictions proved consistent with results obtained from many different experimental studies.

The purpose of this paper is to focus on the mechanistic effects of variation in the electrophilicity of the *other* component of the cycloaddition, i.e. the oxyallyl component, with diene electrofugacity held constant. To that end, we computationally characterize the reactions of *s-cis*-1,3-butadiene (**1**) with 2-hydroxyallyl cation (**2**), lithium 2-oxyallyl cation (**3**), sodium 2-oxyallyl cation (**4**) and uncharged 2-oxyallyl (**5**). Compounds **2–5** are numbered, then, in order of decreasing electrophilicity.

COMPUTATIONAL METHODS

Molecular geometries for all species were optimized at the Hartree–Fock (HF) and second-order perturbation (MP2) levels of theory using the 6–31G* basis set.^{8–11} Local minima and transition state structures were verified by calculations of analytical force constants at the HF level, and at the MP2 level when warranted by large changes in geometry upon reoptimization. Transition states were further characterized by calculation of intrinsic reaction coordinates¹² (IRC) to identify the minima on either side of the saddle point; such

calculations were typically at the HF/3–21G level. The HF/6–31G* frequencies were used to compute zero-point vibrational energies (ZPVE) and 298 K thermal contributions ($H_{298}-H_0$ and S_{298}°) for all species. Composite G_{298}° is defined to be the sum of the gas-phase electronic energies calculated at the MP2/6–31G* level and thermal free energy contributions from the HF/6–31G* level.

DFT calculations were also carried out for the reactions of **1** with **2**, **3** and **5**; these employed a mixture of exact exchange with the gradient-corrected exchange functional of Becke¹³ and the gradient-corrected correlation functional of Lee *et al.*¹⁴ according to the adiabatic connection scheme first proposed by Becke¹⁵ and as implemented in Gaussian 94¹⁶ (B3LYP). Reaction coordinates at the MP2 and B3LYP levels were found to be qualitatively similar in each case. As noted previously,⁷ we have reason to consider the MP2 results to be of higher quality, so in the interests of brevity the B3LYP results are not reported. Since MP2 results are also expected to be superior to HF predictions, only the former level of theory is discussed below.

In our previous work,⁷ we also considered the effect of solvation on the reaction of **1** with **2** using the aqueous Solvation Model 2¹⁷ (SM2). As qualitative features of the gas-phase reaction potential energy surface after initial bond formation were unchanged by solvation, we did not carry out such calculations here.

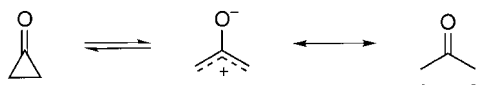


Figure 1. Resonance structures for oxyallyl

RESULTS AND DISCUSSION

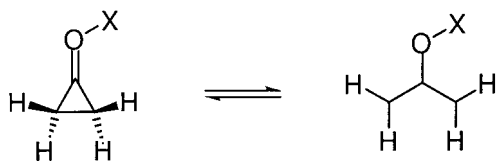
Oxyallyl vs cyclopropanone geometries

The valence tautomerism between oxyallyls and cyclopropanones (Fig. 1) has been the subject of considerable discussion, in part owing to proposals that oxyallyls are reactive intermediates in cyclopropanone/allene oxide tautomerizations,^{18,19} Favorskii rearrangements^{20,21} and [4 + 3] cycloaddition reactions.^{22,23} Oxyallyls are typically considerably less stable than their cyclopropanone (or allene oxide) valence tautomers.²⁴ Table 1 presents computed differences in energy between the cyclopropanone and oxyallyl tautomers of **2–5**.

As noted previously,⁷ the two tautomers are only slightly different in energy when protonated, although solvation would be expected to favor the greater charge localization found in the cyclopropanone. As the atom coordinated to oxygen becomes increasingly electropositive, the preference for the cyclopropanone tautomer increases substantially. When there is no coordination of a positively charged atom to oxygen, as is the case for **5**, the computed energy difference becomes very large indeed.

This large energy difference for **5** partly reflects the poor ability of the MP2 level of theory to describe accurately the electronic structure of neutral, planar oxyallyl. As illustrated in Fig. 1, oxyallyl may be alternatively envisioned as having either zwitterionic or diradical character. Experimental observations of relatively small solvent effects on reactions involving putative oxyallyl intermediates²⁵ have been interpreted to indicate that the diradical description of oxyallyl is to

Table 1. Relative energies (kcal mol⁻¹) of cyclopropanone and oxyallyl valence tautomers at the MP2/6–31G* level.



Compound	Cyclopropanone ^a	Oxyallyl
2 (X = H ⁺)	0.0	3.3
3 (X = Li ⁺)	0.0	21.6
4 (X = Na ⁺)	0.0	28.1
5 (X = lone pair)	0.0	46.4

Absolute energies (E_h), -191.282 80, -198.587 16, -352.992 04, -191.579 90.

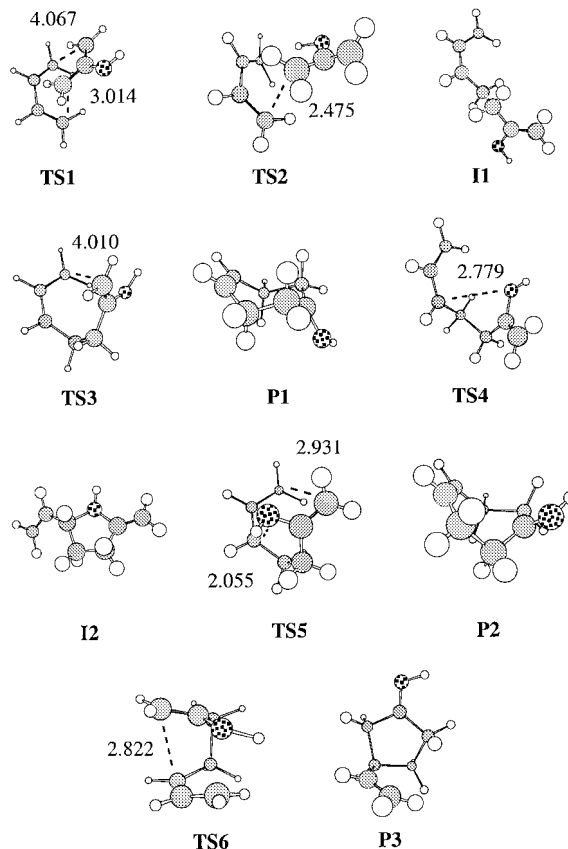


Figure 2. MP2/6–31G* optimized structures of stationary points on the potential energy surface for the reaction of 1,3-butadiene with hydroxyallyl cation. Forming and breaking heavy atom bond lengths are shown in Ångstroms

be preferred.²⁶ Theoretical studies of **5** similarly indicate the diradical description to be more accurate.^{26–29} The oxyallyl diradical, which is isoelectronic with the non-Kekulé hydrocarbon trimethylenemethane,^{27,30,31} has substantial multireference character and as such is found to be unrealistically high in energy at the MP2 level. A more accurate estimate of the energy difference between the cyclopropanone and oxyallyl tautomers of **5** has been provided by Lim *et al.*,²⁶ who computed the difference to be 32.4 kcal mol⁻¹ (1 kcal = 4.184 kJ) at the multireference CASPT2N/6–31G**/CASSCF/6–31G* level using a four-electron in four-orbital active space.

In this paper, we are not interested in isolated oxyallyl *per se*, but rather in qualitative trends in reactivity as a function of oxyallyl electrophilicity. Moreover, coordination of oxygen by cations (as in **2–4**) and/or the presence of alkyl groups or halogen atoms as substituents at the allylic termini (as is typical for substrates used in experimental [4 + 3] reactions), strongly increases the degree to which the zwitterionic mesomer contributes to the oxyallyl wavefunction. As the zwitterionic mesomer is well described by a single configuration, and thus well suited for treatment at the MP2 level of theory, the

Table 2. Relative energies (kcal mol⁻¹) of stationary points for the reaction of **1** and **2**

Reactants, initial C—C TS structures, and intermediate common to all stepwise pathways	Reactants			
	Reactants	TS1 (concerted [4 + 3])	TS2 (stepwise)	I1
MP2/6-31G*	90.7	79.1	72.3	41.7
Composite G ^o ₂₉₈	102.3	69.0	61.3	35.7
<i>Subsequent [4 + 3] closure to extended cycloadduct:</i>				
	TS3	P1		
MP2/6-31G*	46.2	-2.4		
Composite G ^o ₂₉₈	43.9	-1.3		
<i>Subsequent [3 + 2] cycloaddition/Claisen rearrangement:</i>				
	TS4	I2	TS5	P2 ^a
MP2/6-31G*	41.1	25.5	36.8	0.0
Composite G ^o ₂₉₈	36.9	23.6	31.2	0.0
<i>Subsequent all-carbon [3 + 2] cycloaddition:</i>				
	TS6	P3		
MP2/6-31G*	38.7	3.9		
Composite G ^o ₂₉₈	37.7	2.7		

^a Absolute energies (E_h), -347.137 57, -346.807 40.

multireference character of the parent diradical **5** is not expected to adversely affect the remaining calculations described here.

Hydroxyallyl cation + *s-cis*-1,3-butadiene (**1** + **2**)

As this reaction has already been summarized in some detail in a prior publication,⁷ we recapitulate here only those aspects most critical for comparison to the reactions of **1** with **3**, **4** and **5**. Figure 2 depicts 11 key stationary points found on the reaction potential energy surface. Relative energies and 298 K composite free energies associated with these structures are provided in Table 2.

In the gas phase, the separated reactants are at very high energy (although solvation effects, which are not detailed here, reduce the energy of the reactants to be well below bond-forming TS structures⁷). An exhaustive search for transition state (TS) structures provided two unique geometries involving C—C bond formation. Structure **TS1** is the saddle point for a concerted but highly asynchronous [4 + 3] process that leads in the forward direction to extended product **P1**. Structure **TS2**, which is about 8 kcal mol⁻¹ lower in free energy, is the saddle point for a single C—C bond formation that leads to flexible intermediate **I1** (intermediate **a** in Scheme 1 for X = H,H).

As described above, intermediate **I1** can follow any of three different pathways. Immediate C—C closure to form **P1** in a stepwise sense (as opposed to the concerted pathway associated with **TS1**) proceeds through **TS3**. Closure in a [3 + 2] sense can also take place, forming either a C—O bond to create *O*-protonated 3*H*-dihydrofuran intermediate **I2** via **TS4** or a C—C bond to create

O-protonated 3-vinylcyclopentanone product **P3** via **TS6**. Relative to common starting intermediate **I1**, the gas-phase free energies of activation for these processes are 8.2, 1.2, and 2.0 kcal mol⁻¹, respectively. Intermediate **I2** is an allyl vinyl ether and Claisen rearrangement to produce **P2** (the same product expected from direct [4 + 3] cycloaddition in a compact sense) proceeds with an activation free energy of about 7.6 kcal mol⁻¹ through **TS5**. Repeated attempts to characterize transition states for *concerted* [3 + 2] processes of any kind were unsuccessful.

Lithium oxyallyl cation + *s-cis*-1,3-butadiene (**1** + **3**)

Figure 3 illustrates the critical stationary points associated with the potential energy surface for reactions of **1** and **3**. Relative energies and 298 K composite free energies associated with these structures are given in Table 3.

Substitution of lithium for hydrogen in the electrophile has a large effect on the relative energies associated with stepwise vs concerted processes. The lowest energy structure located for formation of a single C—C bond, **TS7**, remains higher in energy than transition state structures associated with concerted [4 + 3] closure (**TS8**) and concerted [3 + 2] closure (**TS9**), where the latter pathway produces a lithiated 3*H*-dihydrofuran as an intermediate (**I3**). Structure **TS9** is the lowest energy transition state structure, with **TS8** and **TS7** lying, respectively, 2.8 and 5.6 kcal mol⁻¹ higher in free energy at 298 K.

As **TS7** corresponds to the least favorable reaction pathway between **1** and **3**, further characterization of

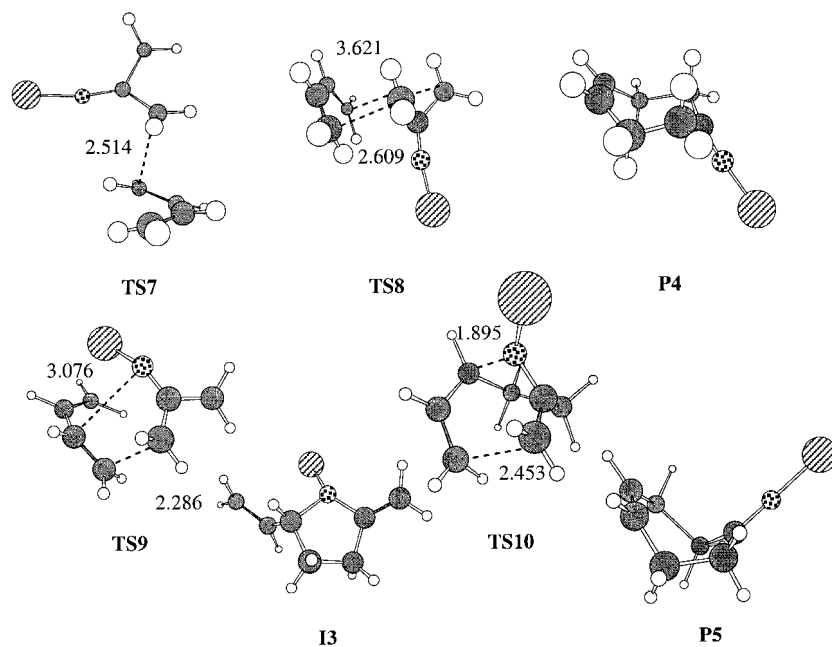


Figure 3. MP2/6-31G* optimized structures of stationary points on the potential energy surface for the reaction of 1,3-butadiene with lithium oxyallyl cation. Forming and breaking heavy atom bond lengths are shown in ångströms

stepwise processes was not undertaken. Concerted, but very asynchronous, [4 + 3] reaction through **TS8** leads directly to extended product **P4**, which represents the global minimum of the structures considered. As was found for the reaction of **1** and **2**, the 3*H*-dihydrofuran intermediate can undergo exergonic Claisen rearrangement to produce in this case the same lithium cycloheptenone cation, **P5**, that would be expected from compact [4 + 3] cycloaddition. The 298 K free-energy of activation for this process, 24.5 kcal mol⁻¹ via structure **TS10**, is considerably higher than was found for the analogous reaction with a proton in place of lithium, but is not so high that Claisen rearrangement might be expected to become the rate determining step for this

pathway. With lithium coordination to the carbonyl, stereoisomer **P5** is slightly disfavored relative to **P4**, in contrast to the weak preference for the opposite ordering with a proton for **P2** vs **P1**. The intrinsic reaction coordinate for the [3 + 2]/Claisen process, which is the lowest energy path for seven-membered ring construction in this system, is illustrated in Fig. 4.

Sodium oxyallyl cation + *s-cis*-1,3-butadiene (**1** + **4**)

Figure 5 illustrates the critical stationary points associated with the potential energy surface for reactions of **1** and **4**. Relative energies and 298 K composite free

Table 3. Relative energies (kcal mol⁻¹) of stationary points for the reaction of **1** and **3**

Reactants and TS for stepwise C—C bond formation:		Reactants	TS7		
MP2/6-31G*		78.6	88.0		
Composite G_{298}°		59.3	79.2		
Concerted [4 + 3] reaction path in extended sense:		TS8	P4 ^a		
MP2/6-31G*		85.6	0.0		
Composite G_{298}°		76.4	0.0		
Concerted [3 + 2] cycloaddition/Claisen rearrangement:		TS9	I3	TS10	P5
MP2/6-31G*		81.0	19.2	45.5	0.7
Composite G_{298}°		73.6	19.7	44.2	1.3

^a Absolute energies (E_h), -354.130 91, -353.995 86.

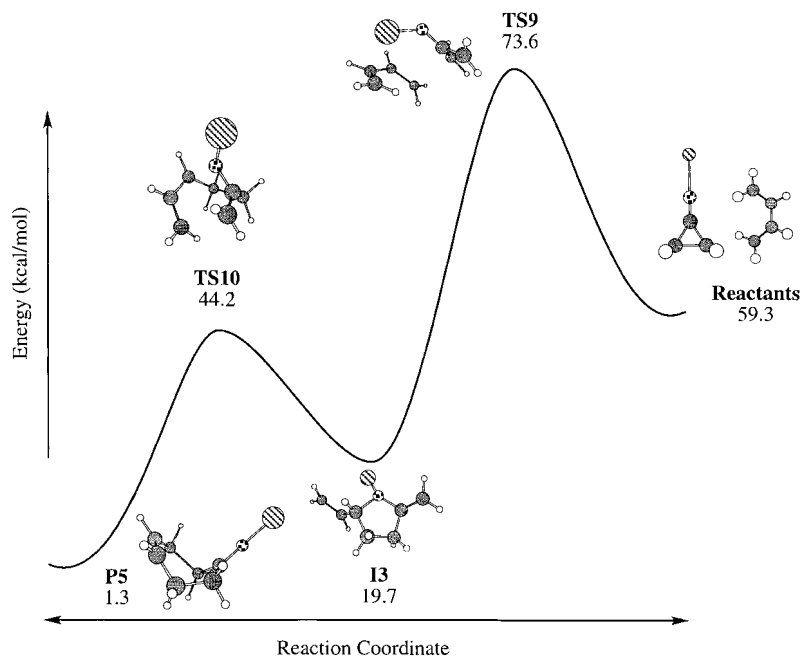


Figure 4. IRC (mass scaled internal coordinates) for concerted enol [3 + 2] cycloaddition of lithium oxyallyl cation with 1,3-butadiene and subsequent Claisen rearrangement. Energies are at the composite G°_{298} level

energies associated with these structures are given in Table 4.

Substitution of sodium for lithium has relatively little effect on the energetics associated with any of the bimolecular reactions. Again, the lowest energy structure for formation of a single C—C bond, **TS11**, is higher in energy than are transition state structures for concerted [4 + 3] closure (**TS12**) or concerted [3 + 2] closure (**TS13**), where the [3 + 2] pathway delivers a sodium-complexed 3*H*-dihydrofuran as an intermediate (**I4**). The

TS structure associated with this [3 + 2] closure is again the lowest energy TS, but the range of energies spanned by **TS11–TS13** is reduced to 4.4 kcal mol⁻¹ (composite G°_{298}), which is slightly smaller than the analogous range found for lithium.

Since stepwise bond formation again corresponds to the least favorable reaction pathway between the two reactants, further characterization of stepwise processes was not considered. The concerted, asynchronous [4 + 3] reaction leads to extended product **P6**, which

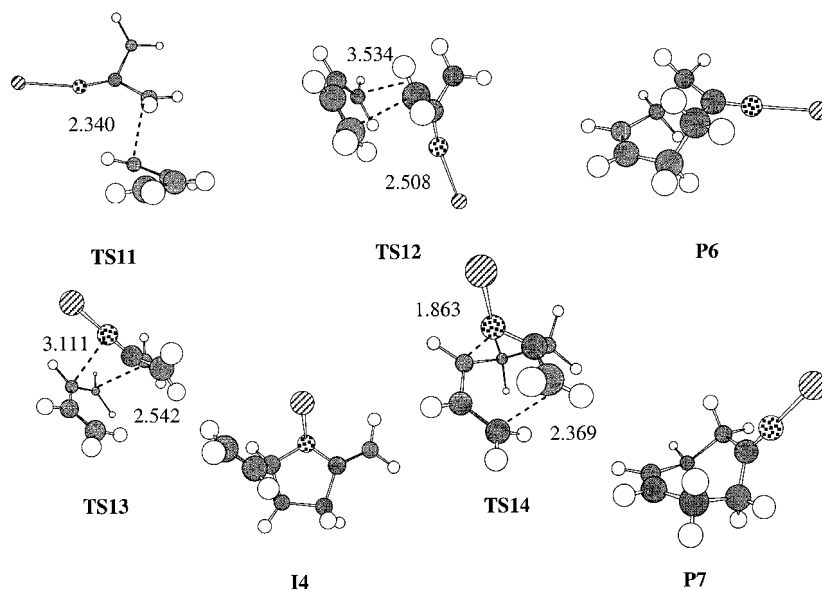


Figure 5. MP2/6–31G* optimized structures of stationary points on the potential energy surface for the reaction of 1,3-butadiene with sodium oxyallyl cation. Forming and breaking heavy atom bond lengths are shown in ångströms

Table 4. Relative energies (kcal mol⁻¹) of stationary points for the reaction of **1** and **4**

Reactants and TS for stepwise C—C bond formation:				
	Reactants	TS11		
MP2/6-31G*	76.3	91.5		
Composite G°_{298}	58.8	83.6		
Concerted [4 + 3] reaction path in extended sense:				
	TS12	P6 ^a		
MP2/6-31G*	88.5	0.0		
Composite G°_{298}	80.0	0.0		
Concerted [3 + 2] cycloaddition/Claisen rearrangement:				
	TS13	I4	TS14	P7
MP2/6-31G*	90.4	21.1	47.4	0.6
Composite G°_{298}	79.2	20.1	45.5	0.0

^a Absolute energies (E_h), -508.532 18, -508.398 74.

structure is the global minimum of those considered. The 3*H*-dihydrofuran intermediate **I4** can again undergo exergonic Claisen rearrangement, and this process has a free-energy of activation quite similar to that found for the lithium analog (25.4 kcal mol⁻¹, via structure **TS14**). The product of Claisen rearrangement, **P7**, is the stereoisomer of sodium-complexed cycloheptenone cation expected from compact [4 + 3] cycloaddition. The intrinsic reaction coordinate for the [3 + 2]/Claisen process, which is the lowest energy path for seven-membered ring formation, albeit by only a small margin compared with extended [4 + 3] cycloaddition, is illustrated in Fig. 6.

Oxyallyl + *s-cis*-1,3-butadiene (**1** + **5**)

Figure 7 illustrates the critical stationary points associated with the potential energy surface for reactions of **1** and **5**. Relative energies and 298 K composite free energies associated with these structures are given in Table 5.

For this uncharged potential energy surface, no transition state structures corresponding to formation of only one C—C bond could be found—optimizations inevitably led to cycloaddition transition state structures. Because removal of the coordinating cation renders oxyallyl symmetric, we first attempted to characterize

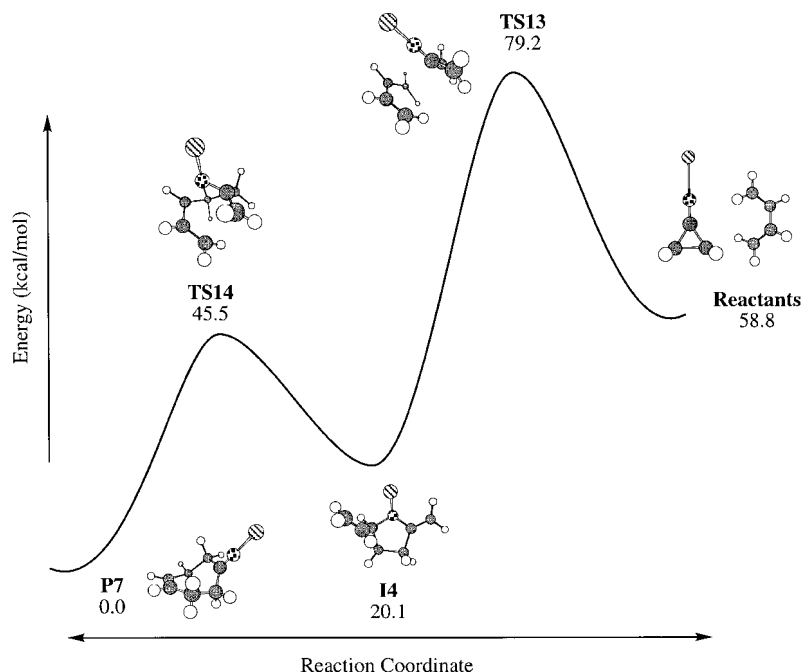


Figure 6. IRC (mass scaled internal coordinates) for concerted enol [3 + 2] cycloaddition of sodium oxyallyl cation with 1,3-butadiene and subsequent Claisen rearrangement. Energies are at the composite G°_{298} level

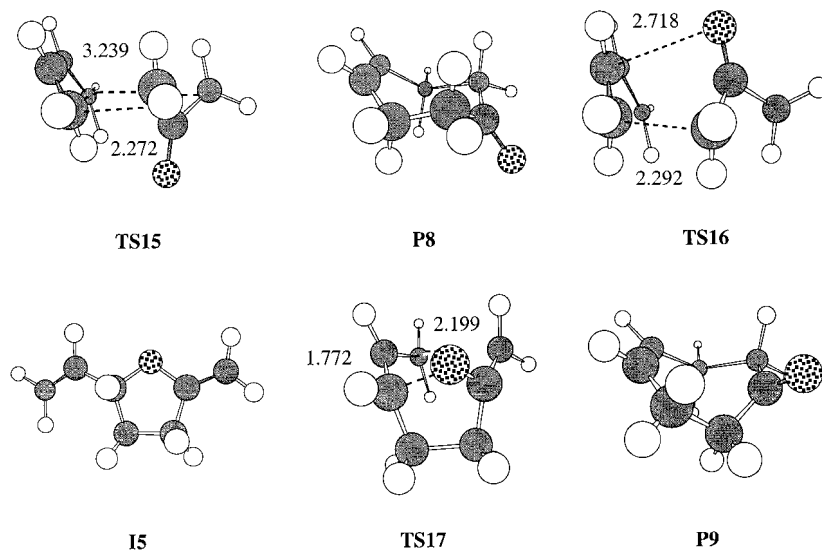


Figure 7. MP2/6-31G* optimized structures of stationary points on the potential energy surface for the reaction of 1,3-butadiene with oxyallyl. Forming and breaking heavy atom bond lengths are shown in ångströms

synchronous [4 + 3] cycloaddition transition state structures, i.e. structures constrained to C_s symmetry. Such structures, however, always corresponded to hilltops (e.g., at the MP2/6-31G* level, a synchronous TS structure for extended [4 + 3] cycloaddition having C—C bond lengths of 2.900 Å was characterized by two imaginary frequencies of magnitudes $75i$ and $395i$ cm^{-1}). Relaxation of symmetry constraints in synchronous extended structures led to a TS for a highly asynchronous but still concerted [4 + 3] cycloaddition (**TS15** leading to product **P8**; see Fig. 8 for IRC corresponding to this TS structure). In the compact mode of cycloaddition, relaxation of symmetry constraints led to [3 + 2] cycloaddition TS structure **TS16**, which produces 3*H*-dihydrofuran intermediate **I5**. As observed for its charged analogs above, **I5** can undergo Claisen rearrangement with a moderate free energy of activation to deliver product **P9** (see Fig. 9 for the corresponding IRC). All attempts to find all-carbon [3 + 2] cycloaddition TS structures led smoothly to enol [3 + 2] structure **TS16**.

Qualitative trends and comparisons with experimental data

The changes in reactivity evidenced for reaction of **1** with increasingly less electrophilic **2–5** are in keeping with intuition and prior experimental analysis.³ With the most electrophilic reactant **2**, single C—C bond formation proceeds at lower energy than is the case for concerted cycloadditions, even though the latter are predicted to have highly asynchronous transition states. When metal atoms better able than a proton to carry a significant portion of the formal positive charge are coordinated to oxygen in the cases of **3** and **4**, the concerted cycloaddition pathways become preferred over single C—C bond formation. Finally, in weakly electrophilic **5**, the formation of a single C—C bond would result in a zwitterionic structure, and this is so unfavorable in the gas phase that no corresponding transition state could be found—only cycloaddition transition states are accessible.

Some insight into the relative energetics of the

Table 5. Relative energies (kcal mol⁻¹) of stationary points for the reaction of **1** and **5**

Reactants and concerted [4 + 3] reaction path in extended sense:		TS15	P8^a
	Reactants		
MP2/6-31G*	71.2	100.5	0.0
Composite G_{298}°	51.7	94.0	0.0
Concerted [3 + 2] cycloaddition/Claisen rearrangement:		I5	P9
	TS16		
MP2/6-31G*	102.0	22.9	49.5
Composite G_{298}°	94.7	21.3	43.9

^a Absolute energies (E_h), -346.814 66, -346.678 24.

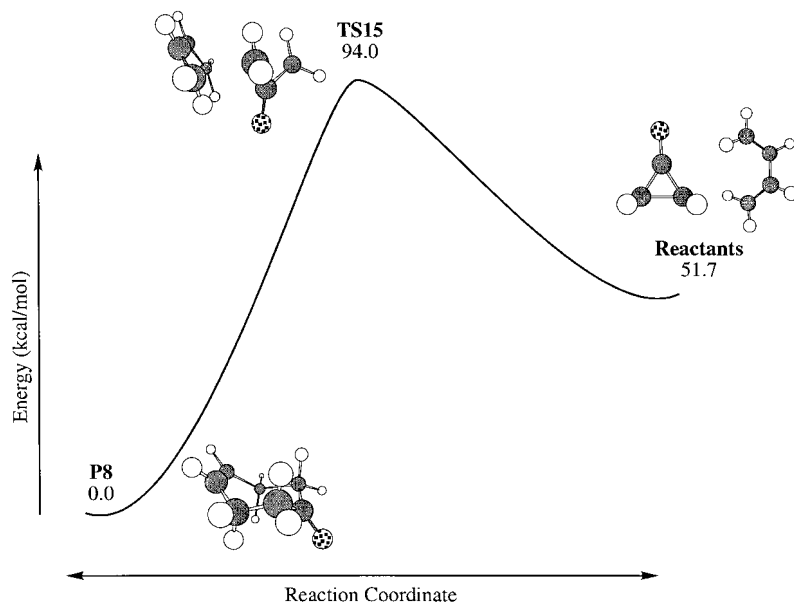


Figure 8. IRC (mass scaled internal coordinates) for concerted [4 + 3] cycloaddition of oxyallyl with 1,3-butadiene. Energies are at the composite G°_{298} level

transition states for single C—C bond formation vs [4 + 3] cycloaddition can be gained from analysis of the geometries of the respective transition state structures. The length of the forming C—C bond in structures **TS2**, **TS7** and **TS11** is not very sensitive to the cation coordinated to oxygen; the observed lengths for this bond, of the order of 2.4 ± 0.1 Å, indicate that a moderate degree of covalent character is present in the TS structure. For the concerted [4 + 3] cycloadditions, on the other hand, the more electrophilic allyl cations have

much looser TS structures. The shorter ones of the two forming C—C bonds have lengths of 3.014, 2.609, 2.508 and 2.272 Å in structures **TS1**, **TS8**, **TS12** and **TS15**, respectively. The same ordering is observed for the longer ones of the two forming C—C bonds, where the lengths are 4.067, 3.621, 3.534 and 3.239 Å, respectively. In **TS1**, then, very little covalent interaction has developed between the bonding atoms, and the TS structure is, as a result, not well stabilized. The development of covalent character increases with de-

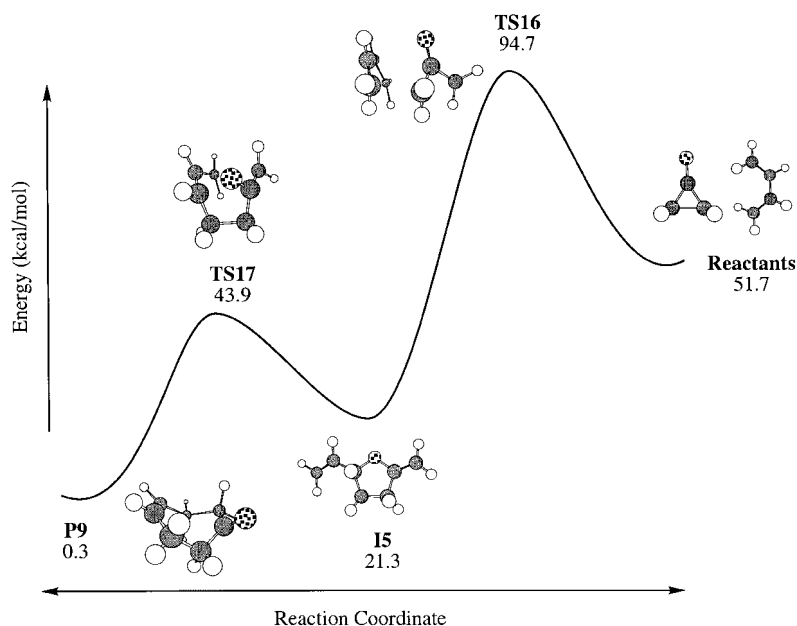


Figure 9. IRC (mass scaled internal coordinates) for concerted enol [3 + 2] cycloaddition of oxyallyl with 1,3-butadiene and subsequent Claisen rearrangement. Energies are at the composite G°_{298} level

creased reactant electrophilicity, and thus the concerted [4 + 3] transition states, which involve the formation of *two* C—C bonds, are stabilized relative to competing *single* C—C bond formation. For **3** compared with **2** as a reactant, the stabilization is sufficient to invert the energetic ordering of the two TS structures, although in the former case a concerted [3 + 2] pathway also exists with still lower activation free energy.

The situation described above for the [4 + 3] cycloaddition TS structures may at first glance seem to be something of a paradox. Cycloaddition reactions of the stronger electrophiles are more exothermic and thus, consistent with the Hammond postulate,³² the TS structures are more reactant like (i.e. looser). However, while more reactant-like TS structures should have lower barriers, the preference for concerted cycloaddition *decreases* for stronger electrophiles. The distinction which must be made in this analysis is that the comparison being made is between two different transition states, not between reactants and transition states. The barrier heights for the cycloadditions relative to the separated reactants are in perfect accord with the Hammond postulate, increasing in the order **2–5** (as noted above, solvation will increase all of the barriers for this reaction, but that is not our focus here). Since single C—C bond formation is much less exothermic than concerted cycloaddition, the Hammond postulate predicts a smaller variation as a function of reactant structure, and hence the inversion in the relative energies of the two kinds of transition states is rationalized.

Hence only the reaction of **1** and **2** favors the formation of an open-chain allyl cation as an intermediate. As the subsequent reactions of this intermediate have been analyzed in some detail elsewhere,⁷ we shall consider here primarily trends for the different concerted cycloadditions. With respect to reaction of **II**, we note only that the weak preference for C—O closure in a [3 + 2] sense via **TS4** (which presumably goes on via Claisen rearrangement ultimately to deliver [4 + 3] products) vs C—C closure in a [3 + 2] sense via **TS6** is entirely consistent with the observation of analogous all-carbon [3 + 2] products in reactions of the highly electrophilic zinc oxyallyl cation with isoprene.³³

In classifying the [4 + 3] reactions of oxyallyl cations with dienes, Hoffmann³ ascribed the formation of furanoid products to stepwise reactions analogous to closure of **II** via **TS4** (Hoffmann refers to such stepwise pathways as 'Class C' pathways). However, structures **TS9**, **TS13** and **TS16** suggest that such products may in some cases alternatively derive from concerted [3 + 2] cycloadditions. Indeed, these furanoid cycloadducts may be intermediates in many [4 + 3] cycloadditions; however, the thermochemical driving force for these species to undergo Claisen rearrangement is such that they are unlikely to be observed unless analysis of product mixtures is undertaken at an intermediate stage of reaction.

Hoffmann³ also suggested that concerted [4 + 3] cycloaddition in a compact sense becomes increasingly less favorable relative to cycloaddition in an extended sense as reactant electrophilicity increases. Our calculations do not necessarily provide support for that hypothesis. The calculations indicate that, at least for model systems **3**, **4** and **5**, compact [4 + 3] products derive from [3 + 2]/Claisen processes, so the relevant comparison of barrier heights is between extended [4 + 3] barriers and corresponding [3 + 2] barriers (the Claisen barrier is never predicted to be rate determining). For reactants **3**, **4** and **5**, the energy of the extended [4 + 3] TS structure relative to the [3 + 2] TS structure is 2.8, 0.8 and -0.7 kcal mol⁻¹, i.e. the extended structure is increasingly preferred with *weaker* electrophilicity. However, the narrow separation between the free energies of activation for the two alternative reaction paths suggests that steric effects may play at least as large a role as electronic effects in realistic situations. The steric bulk of the metal atoms coordinating the oxygen atom would be expected to be fairly large under many sets of experimental conditions [e.g. alkali metal cations in highly coordinating ethereal solvents, or the very bulky Lewis acid Fe₂(CO)₉], and in such systems increased preference for the less sterically crowded extended transition state may be manifested in spite of a competing electronic preference.

It is important to note, however, that if strong electrophiles can access single C—C bond forming TS structures, as is the case for reaction of **1** and **2**, then indeed our calculations predict a strong preference for a stepwise closure mimicking the [3 + 2]/Claisen process and generating a compact cycloadduct compared to a stepwise closure mimicking the [4 + 3] process and generating an extended cycloadduct.

CONCLUSIONS

The highly electrophilic hydroxyallyl cation prefers to react with 1,3-butadiene in a stepwise fashion; subsequent second bond closures can proceed to generate products equivalent to those that would arise from concerted [4 + 3] and [3 + 2] cycloadditions. In the less electrophilic cases of lithium and sodium allyl oxide, however, transition state structures for concerted, highly asynchronous cycloadditions are lower in energy than are transition states for closure of a single C—C bond. In the case of the very weak electrophile, uncharged 2-oxyallyl, no transition state for single C—C bond formation can be found—only transition state structures for concerted cycloadditions were located. These data, consistent with results from a prior study of hydroxyallyl cation reacting with dienes of varying nucleophilicity,⁷ indicate that concerted cycloaddition pathways are preferred over stepwise ones for [4 + 3] cycloadditions when the 'gap' between the electrophilicity of the allyl component and

the electrofugacity of the 4π component is not too large. The Hammond postulate rationalizes variations in free energies of activation for different processes as a function of allyl electrophilicity.

Although transition states for concerted [4 + 3] cycloaddition in an extended sense were found for each allyl electrophile examined here, in no case was a transition state structure located for [4 + 3] cycloaddition in a compact sense. Instead, trial geometries always led to transition state structures for concerted [3 + 2] cycloadditions to form 3*H*-dihydrofuran intermediates. These intermediates upon Claisen rearrangement provide products indistinguishable from compact [4 + 3] cycloadditions; Claisen rearrangement barriers are sufficiently small (about 25 kcal mol⁻¹) and rearrangement is moreover sufficiently exergonic that a significant buildup of the intermediates may not occur under many sets of experimental conditions. Finally, small differences in barrier heights for stereochemically divergent reaction paths suggest that the role of steric interactions in these cycloadditions can be significant when bulky substituents are present.

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