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Staggered Models for Asymmetric Induction: Attack Trajectories and Conformations of Allylic Bonds from ab Initio Transition Structures of Addition Reactions

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Abstract: The transition structures for additions of a model electrophile, nucleophile, and radical to propene have been obtained by ab initio calculations with the split-valence 3-21G basis set and gradient techniques. BH_3, H^-, and $H\cdot$ transition structures are reported. The trajectories of approach of these species to alkenes are quite different, but the allylic CH bonds of the methyl group are always aligned so as to be staggered with respect to the forming bond and the partially pyramidalized carbon undergoing attack. The barriers to methyl rotation are generally 2–3 kcal/mol in these transition structures. Consequences for models for asymmetric induction are discussed.

The origin of asymmetric induction has attracted much interest, spurred by the considerable practical import that such processes have gained for the stereospecific synthesis of natural products.[2] For stereoselective reactions, empirical models have been proposed to rationalize the preference for attack on the "top" or "bottom" of an alkene with diastereotopic faces. Three common models of this type are summarized in Figure 1.[2-12] These models differ by the choice of the conformation of the chiral center with respect to the center at which a new bond is being made and by the positioning of large (L), medium (M), and small (S) allylic substituents on the chiral center. In the epoxidation of allylic alcohols, the hydrogen-bonding potential of the allylic hydroxyl substituent, rather than the size of the group, is frequently invoked to rationalize the preferred position of the hydroxyl group. The "X-eclipsed" (double-bond eclipsed) model is based on the assumption that a conformation similar to that of the isolated alkene or carbonyl is maintained in the transition structure.[4,7a,9,11] The "R-eclipsed" (single-bond eclipsed) model incorporates a conformation that is an energy maximum in the reactants.[3,7b] An intermediate geometry is assumed for the "perpendicular" model.[5,6,8,10]

Previous calculations on model geometries for the transition structures for attack of nucleophiles on carbonyls[6] or nucleophiles, radicals, and electrophiles on substituted alkenes[13] indicate that allylic bonds are staggered with respect to partially formed bonds in the transition states of addition reactions. Such conformations also allow staggering of the partially pyramidalized carbon[14] undergoing attack with respect to the allylic bonds. Since the arrangement of allylic bonds appears to be dictated by the forming bond, the exact conformation of the chiral center in the transition state may depend upon the trajectory of attack, which changes as the reagent is altered.[15,16] We report the first ab initio gradient calculations of transition structures of additions to substituted alkenes. The results imply that the models shown in Figure 2, for which we proposed the generic term "staggered models", best represent the trajectories and allylic conformations for attack of nucleophiles, radicals, and electrophiles on double bonds. These results also allow the rational construction of models to rationalize and predict asymmetric induction in reactions of chiral alkenes.

Results and Discussion

Transition structures for reactions that are representative of nucleophilic, radical, and electrophilic additions to substituted alkenes were obtained by gradient searches with ab initio calculations and the 3-21G basis set[17,18] using the current version of GAUSSIAN80, implemented on the Carnegie-Mellon University Chemistry Department VAX-11/780.[19]

BH_3 represents a mildly electrophilic species. A model for the bridged propyl cation,[20] which is formed from propene and H^+

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(1) Present address: New South Wales Institute of Technology, Australia.

(2) For a general survey, see: Morrison, J. D.; Mosher, H. S. "Asymmetric Organic Reactions"; Prentice-Hall: New York, 1971; reprinted by the American Chemical Society, 1976. Bartlett, P. A. *Tetrahedron* **1980**, *36*, 2.

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(9) Kishi, Y. *Aldrichimica Acta* **1980**, *13*, 23. Johnson, M. R.; Kishi, Y. *Tetrahedron Lett.* **1979**, 4347. Hasan, I.; Kishi, Y. *Ibid.* **1980**, 4229. See also: Narula, A. S. *Ibid.* **1981**, *22*, 2017. Sharpless has proposed a similar model for t-BuOOH/VO(acac)$_2$ peroxidations: Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979**, *18*, 63.

(10) Itoh, T.; Jitsukawa, K.; Kaneda, K.; Teranishi, S. *J. Am. Chem. Soc.* **1979**, *101*, 159. These authors also propose a transition state for t-BuOOH/VO(acac)$_2$ epoxidations like the perpendicular model, but with A = OH and attack occurring eclipsed to the OH group.

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(17) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. Although few tests of the validity of these calculations for transition structures of bimolecular reactions have been carried out, the activation energies are reasonable (4.1 and 7.1 kcal/mol for $H\cdot$ and BH_3 attack and −3.6 kcal/mol for H^- attack), since there is a lower energy ion–molecule complex preceding this transition state. The predictions of conformations and barriers are excellent at even the minimal basis level in the absence of strongly polar bonds and adjacent lone pairs: Pople, J. A. *Tetrahedron* **1974**, *30*, 1605.

(18) The gradient searches for transition structures were facilitated by the use of initial guesses for the attack of these reagents on ethylene. The corresponding transition structures for attack of these reagents on ethylene have been reported at the 4-31G basis set level: (a) H^-—Strozier, R. W.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 1340. (b) $H\cdot$—Nagase, S.; Kern, C. W. *Ibid.* **1979**, *101*, 2544. (c) BH_3—Nagase, S.; Ray, N. K.; Morokuma, K. *Ibid.* **1980**, *102*, 4536.

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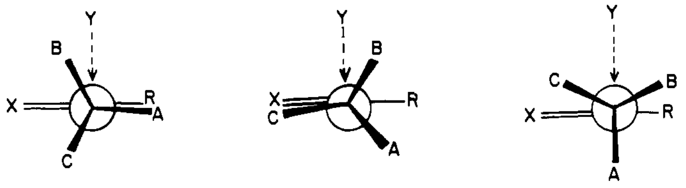

	R-eclipsed	X-eclipsed	Perpendicular
I: X = O Y = nucleophile	Cram[3] A = L, B = S, C = M	Karabatsos[4] A = L, B = S, C = M	Felkin[5], Anh[6] A = L, B = S, C = M
II: X = CR_2 Y = peracid	Boeckman[7b] A = L, B = OH, C = S	Chautemps-Pierre[7a] Kishi[9] A = L, B = OH, C = S	Whitham[8], Teranishi[10] A = L, B = OH, C = S
III: X = CR_2 Y = BH_3		Kishi[11] A = L, B = M, C = S	

Figure 1. Summary of empirical models for 1,2 asymmetric induction in (I) nucleophilic attack on carbonyl compounds, (II) peracid oxidation of alkenes, and (III) hydroboration of alkenes. S, M, and L refer to small, medium, and large groups, and OH refers to a hydroxyl group.

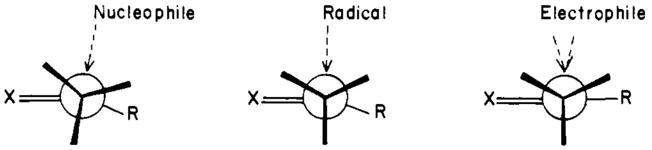

Figure 2. Staggered models for nucleophilic, radical, and electrophilic attack on double bonds.

without activation, is representative of the interaction of a more potent electrophile with propene. The addition of the hydrogen atom to propene is an example of a radical addition, while hydride represents a nucleophile. The transition structures for attack of H^- and H· at the substituted carbon of propene, BH_3 in both orientations, and the model for the bridged propyl cation are shown in Figure 3.[21]

The transition structures for the different types of attack are quite varied. This has important bearing on Baldwin's rules for ring closure,[15] which are based upon the trajectories of attack of various types of reagents but focus on the type of carbon undergoing attack rather than the character of the reagent that attacks the carbon. In particular, the nucleophilic reagent attacks with a CC–H angle of 123°, somewhat larger than that deduced previously for the attack of nucleophiles on carbonyls.[16] We have reported a similar trajectory for the attack of hydride on ethylene.[18a] No successful computations on the transition structures for charged nucleophile attack on a carbonyl have been reported, since such reactions apparently have no activation energies in the gas phase.[16,22,31] Radical (H·) attack is at a much less obtuse angle, while the mildly electrophilic borane B–C bond-forming process occurs at an acute angle. Other electrophiles are expected to attack at an acute angle; while it is not possible to determine transition structures for charged electrophile attack on alkenes, the bridged propyl cation structure[20] provides a suitable model for attack of charged electrophiles.

While only one example of each type of reaction has been studied, we believe that the trajectories found here are characteristic of a variety of reagents. For example, the angle of approach of H^- to acetylene, which has a very early transition state, and of NH_3 to HC≡CCN, which has a very late transition state, are quite similar (C═C—nucleophile angles are 127° and 121°, respectively, by 4-31G and STO-3G, respectively).[18a,23] The transition structures for HO· addition to ethylene and propene also have similar O—C═C angles to the approach angle for H· addition.[24] Highly electrophilic carbenes attack with an only slightly off-center approach, while as the carbene becomes more nucleophilic, the attack occurs with a more nearly perpendicular approach, with respect to one terminus of the double bond.[25]

The trajectories of attack are quite compatible with qualitative predictions of frontier molecular orbital theory.[16,18a,26,27] In particular, the attack of an electrophile at an acute X—C═C angle may be attributed to the favorable interaction of the electrophile LUMO with the alkene HOMO, which is a π bonding orbital. This interaction is maximized when the electrophile LUMO approaches the center of the double bond, unless powerful unsymmetrical donor substitution makes the HOMO appreciably unsymmetrical. This interaction can occur without any appreciable distortion of the alkene except stretching, which raises the HOMO and facilitates interaction with the electrophile LUMO. The obtuse angle of nucleophilic attack occurs in order to maximize interaction of the nucleophile HOMO with the alkene LUMO and to minimize overlap of the nucleophile HOMO with the alkene HOMO. Both of these interactions are facilitated by trans-bending of the alkene.[18a,27] The radical attack occurs in a more nearly perpendicular fashion, since the interactions of the singly occupied orbital of the radical with both the HOMO and the LUMO of the alkene are stabilizing. The radical seeks a compromise between maximization of overlap with the HOMO (best for an acute angle of attack) and with the LUMO (obtuse angle of attack). The direction of approach is expected to vary from acute to obtuse as the electrophile is varied from relatively electrophilic to relatively nucleophilic.

Although the transition structure represents the highest energy point along the lowest energy transit from reactants to products, reactants are expected to select a variety of geometries if they

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(20) This species was "manufactured" by the placement of a standard methyl on the STO-3G bridged ethyl cation (Williams, J. E.; Buss, V.; Allen, L. C.; Schleyer, P. v. R.; Latham, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 2141) and the optimization of the methyl rotational angle. Upon relaxation, this structure would collapse to the 2-propyl cation: Radom, L.; Pople, J. A.; Buss, V.; Schleyer, P. v. R. *Ibid.* **1972**, *94*, 311.

(21) (a) The attack of H· at C-1 of propene is 1.6 kcal/mol more favorable than attack at C-2, and the methyl remains eclipsed with C═C upon C-1 attack. (b) Because of the anti bending of the alkene moiety, C-1 attack of H^- is also accompanied by methyl rotation. Attack at C-2 is favored by .4 kcal/mol. (c) Transition structure C is 3.71 kcal/mol lower in energy than transition structure D at the 3-21G level. This difference drops to 2.1 kcal/mol at the MP2/6-31G* level with these geometries.

(22) Scheiner, S.; Lipscomb, W. N.; Kleier, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 4770.

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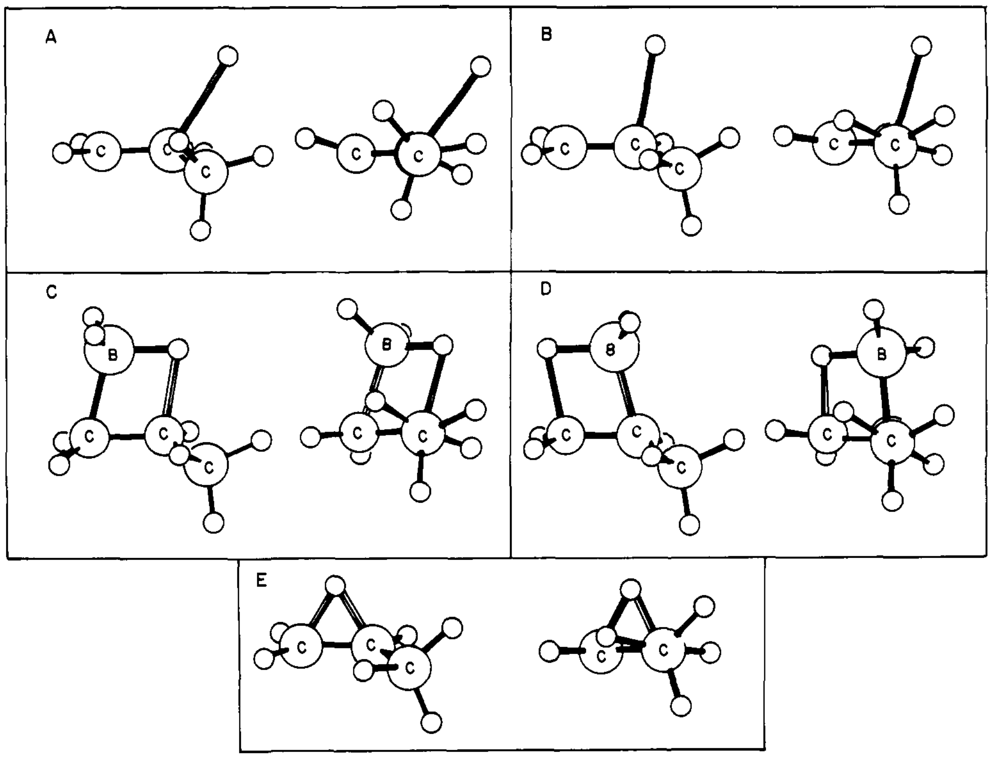
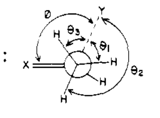


Figure 3. 3-21G transition structures for the addition of (A) hydride, (B) hydrogen atom, and borane in (C) favored and (D) disfavored orientations to propene. E is the STO-3G model for the bridged propyl cation.[20] The unshaded bonds are those partially formed in the transition state. Each structure is shown both in a side view and in a Newman projection looking down the CC bond from the methyl group. The unlabeled atoms are hydrogens.

Table I. Summary of Trajectories and Methyl Conformational Preferences for Additions to C-2 of Propene

attacking reagent (Y)	attack distance r_{Y-C}, Å	trajectory ϕ, deg[a]	conformation $\theta_1, \theta_2, \theta_3$, deg[a]	total energy (3-21G), au	E_{rel}, kcal/mol, 180° methyl rotation[b]	E'_{rel}, kcal/mol, 180° methyl rotation in absence of Y[c]
H^-	2,08	123	39, 162, −79	−116,83042	+3.0 +2,8 (MP2/6-31G*)[d]	−0.2
H·	1,96	102	41, 160, −80	−116.91361	+1.8	+1,3
BH_3 (B at C-2)	1.75	73	68, 188, −52	−142,64407	+3,0 +2,7 (MP2/6-31G*)[d] +2,5 (3-21G reopt)[e]	+1,8
BH_3 (H at C-2)	1,68	101	50, 169, −72	−142.64998	+3.0	+1,4
H^+[f]	1,34	59	71, 189, −51	−166,69668	+2.0	+1.5
$H_2O + CH_3CHO$ (STO-3G[g])	1,69	90[h]	58, 177, −65	−225,84206 (STO-3G)	+3,1	+1,3

[a] Angle of attack:

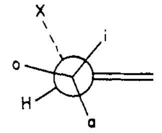


[b] Rigid rotation of methyl, unless specified otherwise. [c] Calculations were carried out on transition structures with attacking species (Y) removed. [d] On 3-21G geometries. [e] Transition state redetermined with Y–CCH fixed at 0°. [f] See ref 20. [g] STO-3G geometry provided by R. Schowen and G. Maggiora; see ref 28. [h] Angle O–C=O.

are reasonably close in energy to the transition structure. In order to obtain a qualitative estimate of the energetic cost of varying the trajectory of reagent from the preferred one, we performed computations in which the H^- or H· was bent away by 5° from the preferred angle of approach in the transition structures. For hydride attack, a 5° in-plane (CCH^-) bend toward C=C, or away from C=C, increases the energy by 0.38 and 0.36 kcal/mol, respectively. A 5° out-of-plane (CCH^-) bend causes a 0.28 kcal/mol increase in energy. The hydrogen atom attack is not as stiff, with energy increases of 0.19, 0.17, and 0.14 kcal/mol, respectively, for the distortions described above. The distortion energies for the H^- and H· transition states are about one-half and one-quarter, respectively, as large as those for the same distortions of ethane. To provide a measure of the amount by which the transition structure is preferred over non-ideal transition geometries, we have calculated the amount of angular distortion away from the ideal arrangement that would cause a tenfold decrease in reaction rate at room temperature, or a 1.36 kcal/mol increase in energy. Assuming that the bending is harmonic and quadratic, a change of in-plane angle by 10° or out-of-plane angle by 11° causes a 1.36 kcal/mol increase in energy for hydride attack. For hydrogen atom attack, these angles are 14° and 16°, respectively. However, these estimates overestimate the flexibility of the transition structures, since recomputations of the transition structures for hydride attack on ethylene with a fixed angle of attack of 116° (cf. 126° for H^- plus ethylene), 136°, and 10° out-of-plane give activation energies of 1.69, 1.55, and 1.19 kcal/mol, respectively, higher than those found for the unconstrained transition structures.

As suggested in the introduction, in each transition structure the methyl group has rotated into a conformation that is staggered with respect both to the partially formed bond and to the partially

Table II. STO-3G Relative Energies of Model Transition Structures for Attack of Hydride and Borane on Butene[a]



methyl position	H^- at C-2 TS[b]	H^- at C-2 butene only[c]	BH_3 (B at C-2) TS[b]	BH_3 (B at C-2) butene only[c]
anti (a)	0	0	0	0
outside (o)	+2.36	+0.63	0.56	0.93
inside (i)	+1.03	+2.17	5.41	3.35

[a] Model transition structures were built by replacing each of the methyl hydrogens, in turn, in the corresponding propene transition structure with a standard methyl group. The STO-3G basis was used, since the exaggeration of charge separations in the 3-21G basis set produces anomalous results for the hydride–butene case. 3-21G and STO-3G results are essentially identical in the borane–butene case. [b] Transition structure. [c] The H^- or BH_3 was removed, and relative energies were determined for butene distorted into the propene transition-state geometry.

pyramidalized carbon undergoing attack. The staggering is coupled to the direction of attack, so that the conformations of allylic substituents with respect to the alkene will be significantly different for nucleophiles, radicals, and electrophiles.

We have assessed the degree of preference of these staggered transition structures by computing the relative energies of other transition-state conformations at various levels of sophistication. Some of these results are summarized in Table I. The energies required to rotate the methyl groups in the absence of the reagent are also shown. For each transition structure, the rotational barrier (2–3 kcal/mol) is nearly as large as that in the final product, regardless of the theoretical level used. In one case, the eclipsed transition structure was recomputed in order to show that the results are not an artifact of the rigid rotor approximation. For H^+ and BH_3, more than half of the methyl conformational preference is due to the pyramidalization of C-2 in the transition state, while the remainder arises from avoidance of eclipsing with the partially formed bond. For the nucleophilic (but four-center) addition of water studied by Schowen and Maggiora,[28] the avoidance of eclipsing of allylic substituents with the partially formed bond is the dominant effect. For hydride attack, the two structures are approximately identical in energy, apparently a compromise between the preference for CH eclipsing with the double bond and the tendency of the vicinal CH bonds to avoid eclipsing. We attribute the large preference for staggering in the transition structure to the especially pronounced closed-shell repulsion between allylic bonds and the partially formed bond from the electron-rich reagent to the alkene.

Regardless of the trajectory of attack, there is a larger preference for staggering of the allylic bonds with respect to the forming bond and the partially pyramidalized carbon. This preference is that deduced in 1968 by Felkin for nucleophilic attack on carbonyls.[5] In all of these structures, the allylic carbon–hydrogen bond that is antiperiplanar to the partially formed bond is stretched by 0.002–0.017 Å relative to the bonds to the other two hydrogens, but this hyperconjugative interation[29] is insignificant compared to the obviously different steric requirements of the three allylic positions. Indeed, similar rotational barriers are obtained for a rigid standard methyl or an optimized methyl. We conclude that the factors which cause alkanes to be staggered are also present in the transition structures to approximately the same extent.

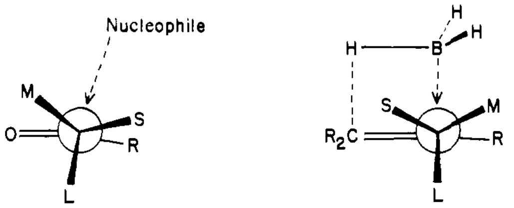


Figure 4. Staggered models to rationalize the stereoselectivities of nucleophilic attack on carbonyls and the hydroboration of alkenes.

While detailed applications of these ideas to stereoselectivity in general will be forthcoming, we note here that the different steric demand placed on "outside" and "inside" allylic substituents in nucleophilic and electrophilic attack provides reasonable rationales of the opposite stereochemical preferences observed in Cram's-rule-type nucleophilic additions[2,3] and Kishi's hydroborations.[9,32]

In order to assess the steric requirements of groups in the stereochemically distinct allylic positions in the transition structure for nucleophilic attack and for hydroboration, we carried out calculations in which one of the methyl hydrogens was replaced by a standard methyl group. Table II shows the results of these calculations. The position antiperiplanar to the attacking reagent is least crowded for both reactions, but the relative steric requirements of outside and inside positions are opposite for the two reactions. The trajectory of hydride attack makes the outside position more crowded than the inside because the outside position is sandwiched between the hydrogen attached to the alkene and the attacking reagent. An increase in size of either of these groups should further crowd the outside position. By contrast, the inside position is most crowded for hydroboration, since a group here is trapped between the attacking reagent and the partial double bond, and it is also near the remaining bulk of the attacking borane.

The "butene only" columns in Table II indicate relative energies of different conformations of the alkene fragment of the transition structures in the absence of attacking reagent. These model calculations support the idea that the inside and outside allylic groups are disfavored both by the partial eclipsing with the alkene bonds, relative to the nicely staggered anti position, and by additional partial eclipsing with the forming bond, and steric repulsions with the approaching reagent. In spite of reactant-like geometries, the types of torsional and steric interactions that develop in the product are already highly developed in the transition structures. The structure of 1-butene itself provides an interesting comparison to the transition structures. Here, the preferred conformation has one ethyl CH bond eclipsed with the double bond, while the conformation with the methyl eclipsed is only 0.6 kcal/mol higher in energy.[30] Conformations where an ethyl CH or CMe bond is anti to C=C are ≈2 kcal/mol higher in energy than the lowest energy conformation.[30]

In the resulting models for nucleophilic and borane addition shown in Figure 4, the largest allylic substituent takes the sterically least hindered position in each case, but the sterically most crowded position is outside for nucleophilic attack and inside for electrophilic attack. The model for nucleophilic attack is the same as the Felkin[5]–Anh[6] model, while the model for hydroborations differs in detail but not in gross predictions made from the Kishi model.[9]

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(28) Schowen, R. L.; Maggiora, G. M., unpublished results on acetaldehyde–water. The transition structures for the formaldehyde–water reaction have been published: Williams, I. H.; Maggiora, G. M.; Schowen, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 7831. Williams, I. H.; Spangler, D.; Femec, D. A.; Maggiora, G. M.; Schowen, R. L. **1980**, *102*, 6619. These reactions have four-centered transition states, geometrically like the hydroboration reaction.

(29) This factor has recently been proposed as the controlling factor in stereoselective nucleophilic additions to carbonyls: Cieplak, A. S. *J. Am. Chem. Soc.* **1981**, *103*, 4540.

(30) Van Hemelrijk, D; Van den Enden, L.; Giese, H. J.; Sellers, H. L.; Schafer, L. *J. Am. Chem. Soc.* **1980**, *102*, 2189.

(31) **Note Added in Proof**: The transition structure for BH_4^- attack on formaldehyde has now been determined. The H---CO angle is 115°, and the transition structure is very near products: Eisenstein, O.; Schlegel, H. B.; Kayser, M. M. *J. Org. Chem.*, **1982**, *47*, 2886.

(32) **Note Added in Proof**: Professor M. Mark Midland has recently discovered that reductions of chiral carbonyl compounds with alkylboranes and borohydrides give "anti-Cram" and "Cram" products, respectively. We thank Professor Midland for communicating these results to us.

Our investigations to date have concentrated on torsional and steric interactions involving nonpolar allylic groups. Studies are in progress to determine how electronic factors that may develop with polar allylic bonds may cause different types of substituents to prefer one or another of the three nonequivalent allylic conformations in addition transition structures.

Acknowledgment. We are grateful to Professor John A. Pople and Michael Frisch for assistance with the CMU version of GAUSSIAN80, the CMU Chemistry Department VAX 11/780, and to the National Science Foundation for financial support of this research. The drawings in Figure 3 were prepared on PROPHET, a computer resource sponsored by the Division of Research Resources of the National Institutes of Health, with the expert assistance of Nancy Woodring.

Registry No. BH_3, 13283-31-3; H^-, 12184-88-2; H·, 12385-13-6; propene, 115-07-1.

Noninterconverting Stereoisomeric Bicyclo[4.4.1] Bridgehead Alkenes

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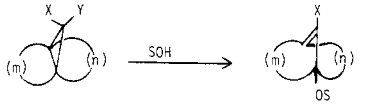
Abstract: The Ag^+-promoted hydrolysis products from epimeric bromochlorides **3a** and **3b** are reported. It is found that the bridgehead olefin-derived products fall into separate sets, depending upon the stereochemistry of their precursor. Importantly, participation of the Δ^3 double bond leading to one of the products derived from **3a** but not from **3b** provides evidence for rehybridization of the intermediate bridgehead olefins at both sp^2 carbon atoms of the bridgehead double bond. Also, hydrolysis of **3c** and **3d** is shown to be stereospecific, again implicating rehybridized bridgehead olefin intermediates.

The generation of bridgehead alkenes of the bicyclo[*m*.*n*.1]alk-1(*m* + *n* + 3)-ene (**2**) variety via solvolysis of (*m* + *n* + 3)-halo[*m*.*n*.1] propellanes (**1**) is now a well-accepted reaction,[3] the first example having been reported less than a decade ago.[4] For some time we have been seeking chemical information regarding the structure of **2**, particularly with respect to the question of rehybridization.[5] Recently, we reported[6] that **2** (*m* = *n* = 4, X = Cl) maintains an unsymmetrical structure during its lifetime in aqueous solution; a rehybridized structure was deemed most reasonable. We now report on the generation and chemistry of stereoisomeric bridgehead olefins from the epimeric propellane pairs **3a** and **3b**, and **3c** and **3d**.



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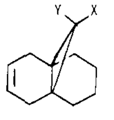
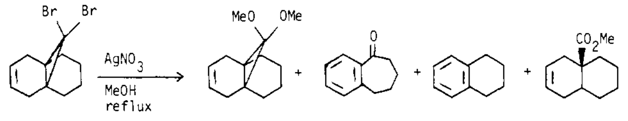
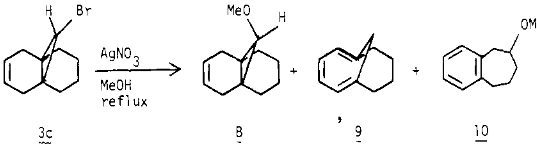


3 a, X=Br, Y=Cl
b, X=Cl, Y=Br
c, X=Br, Y=H
d, X=H, Y=Br

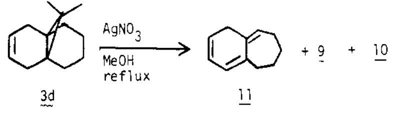
Previously, the methanolysis of **3e** (X = Y = Br) has been reported[7] to produce **4**–**7** in the yields shown. The stereochemistry of **7** (trans) is opposite to the major isomer we observe; we will address this point later. The methanolyses of **3c** and **3d** have also been studied;[8] the reported products are shown below.



3e 4 (20%) 5 (31%) 6 (7%) 7 (3%)



3c 8 (12%) 9 (46%) 10 (19%)



3d 11 (12%) (73%) (2-3%)

Results

Compounds **3a** and **3b** were simultaneously prepared via the addition of CBrCl to dihydrotetralin.[6] Because separation of these was extremely tedious (especially for **3a**, which required ca. 25

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[1] Alfred P. Sloan Foundation Fellow, 1976-1980.

[2] NSF Trainee, 1974-1977.

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[9] Warner, P.; Lu, S.; Chang, S.-C. *Tetrahedron Lett.* **1978**, 1947.