2b can be made by adding 3 kcal/mol (estimate of the reverse reaction) to the heat of reaction. Likewise, an estimate of the barrier of reaction for eq 3b can be made by adding 15 kcal/mol (addition of BH_3 to B_5H_9, a stable boron hydride) to the heat of reaction. Heats of reaction can be calculated more reliably and therefore an estimate of the reaction barrier for eqs 2b and 3b can be made.

The heat of reaction at the MP2/6-31G*//3-21G+ZPC level for the reaction $B_5H_{11} \rightarrow B_4H_8 + BH_3$ is 32.7 kcal/mol (36.0 kcal/mol at 400 K). The estimated barrier for the reaction is therefore about 39 kcal/mol, which is the heat of reaction (36 kcal/mol) plus the reverse barrier for addition of BH_3 to a reactive boron hydride, B_4H_8 (3 kcal/mol).

For the decomposition of B_5H_{11}, the estimated barrier for the reaction $B_5H_{11} \rightarrow B_4H_8 + BH_3$ is substantially greater than that observed for decomposition of B_5H_{11} (39 (estimated) and 17.4 kcal/mol (exptl)[5]). It would appear that either the estimated barrier is in error by over 20 kcal/mol or B_5H_{11} decomposes by a different mechanism. Considering the possible errors in the estimation for the reverse activation barrier and errors in the level of theory for determining the heat of reaction, the uncertainty is probably about ±10 kcal/mol. The lower limit of 29 kcal/mol would still indicate that direct decomposition to $B_4H_8 + BH_3$ is not involved. Formation of B_4H_8 catalytically could not explain the discrepancy since the barrier can only be reduced by a maximum of 3 kcal/mol.

An alternative explanation is that the reaction proceeds by a bimolecular rate-determining step (eq 15). The strongest evidence for a bimolecular mechanism is the pre-exponential factor for the decomposition of B_5H_{11} ($1.6 \times 10^7\ s^{-1}$), which is about 10000 times smaller than the low end of unimolecular pre-exponential factors[39] (10^{11}–$10^{15}\ s^{-1}$). Alternatively, eq 15 could represent a pre-equilibrium step followed by a rate-determining step. Although an effort was made, a reasonable series of steps consistent with the known[5,6] kinetics of decomposition of B_5H_{11} could not be found.

$$2B_5H_{11} \rightarrow B_3H_7 + B_5H_9 + B_2H_6 \qquad (15)$$

If the rate data for decomposition of B_5H_{11} from ref 5 is plotted as a second-order reaction, the activation barrier is about 14 kcal/mol, which can be compared to a calculated endothermicity of 7.7 kcal/mol for eq 15.

The decomposition of B_6H_{12} via eq 3b is estimated to proceed with a barrier of 29 kcal/mol (15 kcal/mol reverse barrier for addition of BH_3 to a stable boron hydride and 14 kcal/mol endothermicity of the forward reaction), which is 11 kcal/mol greater than the observed barrier of 17.9 kcal/mol.[8] While the observed barrier is nearly within the 10 kcal/mol uncertainity estimated for the barrier of $B_6H_{12} \rightarrow B_5H_9 + BH_3$, it is possible that B_6H_{12} also decomposes with a mechanism similar to B_5H_{11} since the pre-exponential factor for the observed[8] decomposition of B_6H_{12} ($3.8 \times 10^7\ s^{-1}$) is very similar to the observed pre-exponential factor for the decomposition of B_5H_{11} ($1.6 \times 10^7\ s^{-1}$).

Conclusion

Several reactions of possible significance to pyrolysis of diborane were studied. Two pathways of B_4H_{10} decomposition were considered, elimination of H_2 to form B_4H_8 and production of BH_3 plus B_3H_7. In agreement with experiment, the favored pathway was found to be elimination of H_2 with an activation barrier of 26.8 kcal/mol.

Four isomers of B_4H_8 were optimized at the MP2/6-31G* level, the double-, triple-, and quadruple-bridged isomers. At the [MP4/6-311G**]+ZPC level, the triple-bridged isomer was found to 4.0 kcal/mol more stable than the double-bridged isomer.

Decomposition of B_5H_{11} and B_6H_{12} by H_2 elimination is found to be inhibited due to high activation barriers. The experimental decomposition of B_5H_{11} is predicted not to occur by a unimolecular pathway to $B_4H_8 + BH_3$ due to an excessively high heat of reaction for formation of unimolecular products. The first step of an alternative mechanism is suggested which involves two B_5H_{11} molecules forming B_3H_7, B_5H_9, and B_2H_6. This alternative mechanism is supported by an experimental pre-exponential factor that is in the range of bimolecular reactions.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. Computer time for this study was made available by the Auburn University Computer Center, the Alabama Supercomputer Network, and the NSF-supported Pittsburgh Supercomputer Center. We thank the IBM Corp. for access to an IBM 3090 computer at the Los Angeles Scientific Center under Grant RSP 1039. I also acknowledge Dr. W. N. Lipscomb in whose laboratory this work was started.

Supplementary Material Available: The computer-generated coordinates (Z matrix) of small boron hydrides optimized at the MP2/6-31G* level and the $B_5H_{11} \rightarrow B_5H_9 + H_2$ and $B_6H_{12} \rightarrow B_6H_{10} + H_2$ transition states optimized at the HF/3-21G level (5 pages). Ordering information is given on any current masthead page.

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Electrocyclic Ring Openings of Dialkylcyclobutenes: Anomalies Explained

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Abstract: The electrocyclic reactions of dialkylcyclobutenes were examined with use of ab initio molecular orbital theory. *cis*-3,4-Dimethylcyclobutene possesses a destabilizing steric interaction that elevates the energy of the ground state and leads to a faster rate of reaction than expected on the basis of methyl groups effects in other systems. The ring openings of 3-alkyl-3-methylcyclobutenes were shown by Curry and Stevens to involve inward rotation of the larger group in some cases. Calculations on 3-ethyl-3-methylcyclobutene show that the product distribution can be explained as a result of more favorable gauche interactions upon inward rotation of the larger ethyl group. An extremely large stereochemical dependence of torsional barriers of alkyl groups is revealed in these calculations.

Introduction

During the last 5 years the stereoselectivities of cyclobutene ring openings have been studied intensively from both the theoretical and experimental points of view.[1-4] In the original derivation of substituent effects upon outward or inward conrotation of substituents in the electrocyclization of cyclobutenes, additivity

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[1] Carpenter, B. *Tetrahedron* **1978**, *34*, 1977.

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Table I. Product Ratios in the Ring Opening of 3-Methyl-3-alkyl- and 3-Methyl-3-arylcyclobutenes at 180 °C[5]

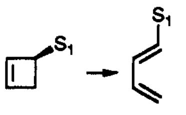
alkyl or aryl group	(*Z*)-diene: (*E*)-diene	alkyl or aryl group	(*Z*)-diene: (*E*)-diene
ethyl	68:32	phenyl	30:70
propyl	62:38	4-methoxyphenyl	52:48
isopropyl	66:34	3-methoxyphenyl	32:68
cyclopropyl	43:57	4-cyanophenyl	45:55
tert-butyl	32:68		

Table II. Calculated and Experimental Methyl Group Effects on Activation Energies, Relative to Cyclobutene

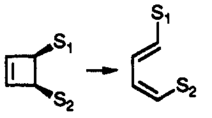
cyclobutene	E_a(calcd)	ΔE_a(calcd)	E_a(exptl)	ΔE_a(exptl)
parent	41.6[a]	0	32.5[c]	0
3-methyl- (out)	40.9[b]	−0.7	31.6[d]	−0.9
3-methyl- (in)	47.3[b]	+5.7		
3,3-dimethyl-	46.4	+4.8	36.1[e]	+3.6
cis-3,4-dimethyl-	44.4	+2.8	34.0[f]	+1.5
trans-3,4-dimethyl- (out)	40.4[a]	−1.2	30.6[g]	−1.9
trans-3,4-dimethyl- (in)	53.4[a]	+11.8		

[a] Reference 3. [b] Reference 11. [c] Cooper, W.; Walters, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 4220. [d] Frey, H. M.; Marshall, D. C. *Trans. Faraday Soc.* **1965**, *61*, 1715. [e] Reference 5. [f] Srinivasan, R. *J. Am. Chem. Soc.* **1969**, *91*, 7557. [g] Reference 2.

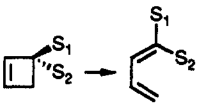
of substituent effects was assumed.[2] For example, the influence of a substituent rotating outward (S_1 in eq 1) is assumed to hold also for eq 2, where S_2 simultaneously rotates inward.



(1)



(2)



(3)

If the substituent effects are, indeed, independent of the presence of other substituents, then the activation energies of the reactions in eqs 2 and 3 will be the same. However, cis-3,4-disubstituted cyclobutenes react considerably faster than 3,3-disubstituted cyclobutenes.[1,5,6] The activation energy measured for *cis*-3,4-dimethylcyclobutene opening (34.0 kcal/mol) is 2 kcal/mol less than that for 3,3-dimethylcyclobutene (36.1 kcal/mol). Rickborn pointed out that *cis*-3,4-dimethoxycyclobutene has an activation energy for conrotatory opening that is 4 kcal/mol less than that of 3,3-dimethoxycyclobutene.[6]

Another oddity is observed in the conrotatory opening of various 3-alkyl-3-methylcyclobutenes. Well before our proposed explanations of cyclobutene stereoselectivity,[2,3] Curry and Stevens[5] showed that the larger substituent rotates inward preferentially in several 3,3-disubstituted cases, as shown in Table I. In the first three cases, the more crowded product is formed. This led Curry and Stevens to propose that an electronic effect, the acceptor character of the substituent, might be important in such systems.

Computational Methods

All stationary points (reactants, transition states, and products) in the parent *cis*-3,4-dimethyl- and 3,3-dimethylcyclobutenes and the six transition states in the ring opening of 3-ethyl-3-methylcyclobutene were fully optimized by use of restricted Hartree–Fock theory (RHF) employing the split valence 3-21G basis set implemented in the GAUSSIAN 86 program of Pople and co-workers.[7] The nature of each stationary point was confirmed by analysis of the vibrational frequencies computed analytically. The activation energies are given in Table II and the computed energies and geometries are available as supplementary material. The reactants had all real vibrational frequencies, while the transition states had one imaginary frequency each. The *trans*-3,4-dimethylcyclobutene calculations were performed earlier by Rondan.[2] In the model study probing the 3-alkyl-3-methylcyclobutenes, steric crowding of the transition states was analyzed with Allinger's MM2 program.[8a]

Table III. Influence of 3- or 4-Substituents upon Activation Energies for Conrotatory Electrocyclic Reactions of Cyclobutenes

	direction of rotation		
substituent	outward	inward	cis correction
Me	−1	+5	−2
Cl	−3	+6	
OAc	−5		
OR	−9	+5	−4

Results and Discussion

The Cis Effect. The activation energy for the 3,3-dimethylcyclobutene conrotatory opening was calculated to be 46.4 kcal/mol at the RHF/3-21G level of theory, while that for the *cis*-3,4-dimethyl compound was 44.4 kcal/mol, 2.0 kcal/mol lower. This agrees well with the experimental energy difference of 2.1 kcal/mol.[5] A value for the amount of destabilization caused by inward rotation of a methyl group can be calculated by subtracting the activation energy of the unsubstituted reaction from the activation energy for inward conrotation of a methyl group in 3-methylcyclobutene. This value is 5.7 kcal/mol. Subtracting the activation energy for 3-methyl outward opening from the activation energy for 3,3-dimethylcyclobutene yields 5.5 kcal/mol computationally and 4.5 kcal/mol experimentally. When the same treatment is applied to *cis*-3,4-dimethylcyclobutene, the inward destabilization is calculated to be 3.5 kcal/mol and is 2.4 kcal/mol experimentally. This corresponds to a 2.0 kcal/mol lowering of the cost of inward methyl rotation in the cis compound.

The methyl groups of *cis*-3,4-dimethylcyclobutene are eclipsed. This interaction raises the energy of the ground state relative to the transition state, accounting for the smaller activation energy. *trans*-3,4-Dimethylcyclobutene is calculated to be 1.5 kcal/mol more stable than *cis*-3,4-dimethylcyclobutene. The destabilization upon cis substitution compares quite favorably with the experimentally observed activation barrier lowering for the opening of *cis*-3,4-dimethylcyclobutene.

These calculations allow us to propose a cis correction to the quantities proposed by Kirmse, Rondan, and Houk[3] that quantify the effects of 3- and 4-substitution on the activation energies of substituted electrocyclic ring openings as shown in Table III.

We can also explain Kirmse's dimethoxycyclobutene data[6] in this manner. The 4 kcal/mol difference in activation energies for ring openings of the *cis*- and *gem*-dialkoxycyclobutenes arises from electronic and steric destabilization of the cis isomer. This correction is a 4 kcal/mol lowering of the activation energy for

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Table IV. Calculated Relative Energies and Product Ratios of Transition States for Ring Openings of 3-Ethyl-3-methylcyclobutene

	MM2		3-21G (partial)		AM-1		3-21G (full)		exptl, %
	ΔE^a	BD,[b] %	ΔE	BD, %	ΔE	BD, %	ΔE	BD, %	
				Ethyl Inward					
A	0.7	40	0.0	47	0.4	34	0.0	56	68
C	0.0		0.6		0.3		0.4		
E	1.5		2.3		2.6		2.1		
				Ethyl Outward					
B	0.6	60	0.6	53	0.1	66	0.8	44	32
D	0.0		0.6		0.2		0.8		
F	0.0		0.2		0.0		0.5		

[a] In kilocalories per mole. [b] Boltzmann distributions.

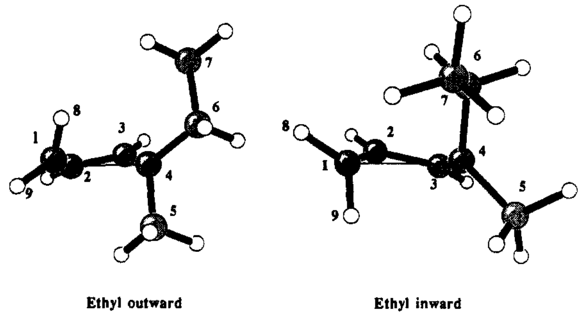

Figure 1. Lowest energy transition structures for the conrotatory electrocyclization of 3-ethyl-3-methylcyclobutene. The ethyl inward structure is 0.5 kcal/mol more stable than the ethyl outward structure.

Table V. Energies and Geometries for Transition Structures of the Ring Opening of 3-Ethyl-3-methylcyclobutene and 3,3-Dimethylcyclobutene

transition structure	3-21G (full) geometry[a]		$E_{(3\text{-}21G)}$, au	E_{rel}, kcal/mol
A	C1–C4	2.184	−270.421 15	0.0
	C1C4C6	95.1		
	C1C4C5	129.5		
	C4C1H8	136.2		
	C4C1H9	83.8		
	C5C4C6	113.6		
	H8C1H9	114.2		
	C1C2C3C4	22.3		
B	C1–C4	2.184	−270.41982	0.8
	C1C4C5	94.5		
	C1C4C6	130.7		
	C4C1H9	135.3		
	C4C1H8	83.2		
	C5C4C6	112.9		
	H8C1H9	114.3		
	C1C2C3C4	22.3		
C	C1–C4	2.196	−270.42055	0.4
	C4C1H8	136.4		
	C4C1H9	82.8		
	C1C4C6	94.9		
	C1C4C5	128.9		
	H8C1H9	114.4		
	C5C4C6	114.4		
	C1C2C3C4	22.6		
D	C1–C4	2.191	−270.41981	0.8
	C4C1H9	135.8		
	C4C1H8	83.1		
	C1C4C5	94.4		
	C1C4C6	129.8		
	H8C1H9	114.4		
	C5C4C6	113.3		
	C1C2C3C4	22.4		
E	C1–C4	2.196	−270.41780	2.1
	C4C1H8	137.3		
	C4C1H9	82.3		
	C1C4C6	97.4		
	C1C4C5	128.4		
	H8C1H9	114.3		
	C5C4C6	110.9		
	C1C2C3C4	22.5		
F	C1–C4	2.191	−270.42040	0.5
	C4C1H9	135.7		
	C4C1H8	83.4		
	C1C4C5	94.4		
	C1C4C6	130.9		
	H8C1H9	114.4		
	C5C4C6	111.9		
	C1C2C3C4	22.6		
3,3-dimethylcyclobutene ring opening				
	C1–C4	2.183		
	C4C1H9	135.6		
	C4C1H8	83.5		
	C1C4C5	94.6		
	C1C4C6	130.3		
	H8C1H9	114.4		
	C5C4C6	112.2		
	C1C2C3C4	22.4		

[a] Distances in angstroms and angles in degrees.

cis-3,4-dimethoxycyclobutene opening.

3-Alkyl-3-methylcyclobutenes. Frey and co-workers found that the activation energy of ring opening of 3,3-diethylcyclobutene was 1.4 kcal/mol less than that of 3,3-dimethylcyclobutene.[10] Curry and Stevens found that 3-ethyl-3-methylcyclobutene gave a (*Z*)-diene as a major isomer in thermolysis.[5] Other 3-alkyl-3-methylcyclobutenes also exhibit outward methyl rotation, except 3-cyclopropyl-3-methylcyclobutene and 3-*tert*-butyl-3-methylcyclobutene (see Table I).[5] It was suggested that the acceptor character of the larger alkyl groups might promote inward rotation.

Modeling methods developed in recent years have met significant success in dealing with the problems of stereoselectivity in chemical reactions.[9] We first attempted to apply such techniques to this problem. By use of the RHF/3-21G geometry for the transition structure of the ring opening of 3,3-dimethylcyclobutene, the effects of other alkyl substituents were modeled with Allinger's MM2 program.[8a] The cyclobutene ring geometry was held constant, and the substituent geometries were optimized. These constraints are reasonable since it has been shown[3,11] that variation of the substitution pattern only slightly influences the geometry of the ring. However, in this case, unsatisfactory results were obtained. The Boltzmann distributions over the various conformations for inward and outward rotation at 180 °C predicted 60% of inward rotation of the methyl group for 3-ethyl-3-methylcyclobutene, 77% for 3-isopropyl-3-methylcyclobutene, and 97% for the 3-*tert*-butyl derivative. Because of this failure, ab initio calculations were carried out in order to probe the subtle effects of dialkyl substitution on the transition-state geometry.

All the six possible conformations for 3-ethyl-3-methylcyclobutene opening were calculated by use of the 3-21G basis set with all the ring atoms and the two carbon atoms connected to the ring frozen in the geometry of the 3,3-dimethylcyclobutene transition structure. These partial optimizations gave the same trend as those from MM2 calculations, favoring outward rotation of the ethyl group. This caused us to undertake full optimizations of the six transition structures of 3-ethyl-3-methylcyclobutene electrocyclization.

Dewar's semiempirical method, AM-1,[8b] was also tested, but full optimization of all six transition structures gave results in disagreement with experimental results (see Table IV).

The full optimizations of the six transition structures were accomplished with the RHF/3-21G basis set. The results are summarized in Table V. The two transition states shown in Figure 1 represent the two conformations of the lowest energies for ethyl inward and outward rotation. The product ratios calculated from a Boltzmann distribution with relative activation energies at 180 °C are summarized in Table IV. The ratio from full optimization agrees well with the experimental results.

Compared with the geometry of the transition state of 3,3-dimethylcyclobutene ring opening, there are slight changes of the

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Views from Inward (left) and Outward Methyl Groups of the TS of 3,3-Dimethylcyclobutene

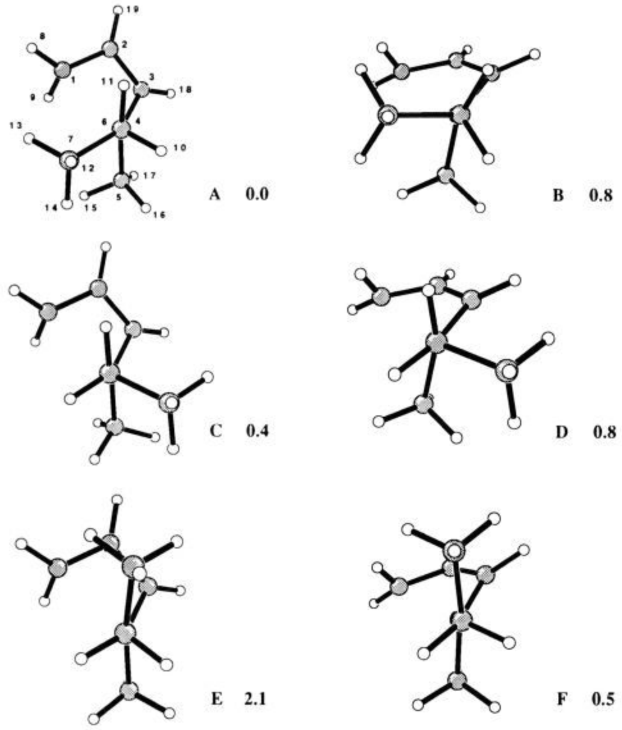

Figure 2. Newman projections looking along the C6–C4 bond for the 3,3-dimethylcyclobutene and 3-ethyl-3-methylcyclobutene transition structures.

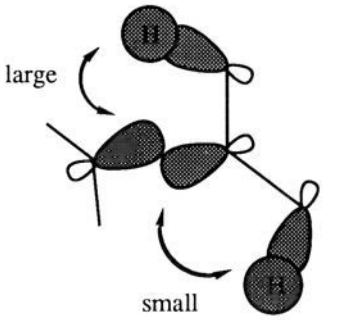

Figure 3. Interactions of C–H bonds of outwardly and inwardly rotating methyl groups with the C–C breaking bond.

geometries in all the ethyl inward transition structures; however, there are no apparent changes in the ethyl outward transition structures. Similarly, the ethyl outward transition structures showed little decrease in energy from the values obtained by partial optimization, but substantial energy decreases were found in all the cases for ethyl inward transition states. This is why the MM2 calculation and the 3-21G partial optimizations failed to reproduce the experimental ratios. Two somewhat different structures are actually involved for outward and inward transition states with two substituents of different size.

By examining the six transition states, it was determined that the energy differences are related to the type and magnitude of the gauche methyl–alkyl interactions. We will compare similar conformers for ethyl group inward or outward rotation. That is, we compare A with B, C with D and E with F. The Newman projections and relative energies are shown in Figure 2, and the geometries and energies are summarized in Table V. First, note that the transition structures for ethyl inward rotation have conformers with dihedral angles essentially identical with those of the dimethylcyclobutene transition structure, shown at the top of Figure 2. This indicates that there are no large steric repulsions in A, C, or E. By contrast, B and D are significantly rotated. A and C have gauche methyl groups, and these are relatively unstrained as compared to the anti conformer E, which is destabilized by interaction of the methyl group with not only C1 and C3 but also C2–H of the cyclobutene. The corresponding anti conformer F is the best of the ethyl outward transition states, while the outward gauche conformers B and D are destabilized by a relatively small amount of 0.3 kcal/mol, as compared to 0.9 kcal/mol for butane.[12] To understand the origin of the different energies of A and B, or of C and D, we must describe the remarkable differences between the methyl rotational barriers for outward and inward methyl rotations. Calculations on the transition states for 3-methylcyclobutene opening show that upon outward rotation the methyl group remains staggered and the barrier to a 60° rotation is about 3.7 kcal/mol, approximately normal for a propane unit. However, for outward rotation the barrier is much smaller, only 0.5 kcal/mol.

As shown in Figure 3, the CH–CC repulsions are as large, or even larger, than normal upon inward rotation because there is large overlap of a CH bond orbital with the breaking CC bond orbital. Upon outward rotation, this overlap is much smaller. An outwardly rotating methyl group experiences a small rotation barrier, akin to that of a methyl attached to a radical or an aromatic ring. These differences are responsible for the differences between the conformation of the methyl group with respect to the C4–C5 bond in A (C) and B (D). Upon inward rotation of the methyl group (and outward rotation of the ethyl group), the methyl stays essentially perfectly staggered about the C4–C5 bond. This causes the hydrogens (especially, e.g., in B) H15 to experience considerable repulsion with the ethyl hydrogen, H14, only 2.40 Å away, even after the rotation of the ethyl group. This ethyl rotation has caused H13 and H8 repulsion. Upon outward rotation of the methyl group (e.g., in A), upon which the rotational barrier is small about C5–C6, the conformation changes readily, increasing the distance between H14 and H15 to 2.51 Å.

Such effects are related to torquoelectronic effects in general. Any outwardly rotating group will behave conformationally as if it were attached to a slightly pyramidal radical. By contrast, an inwardly rotating group will experience major conformational barriers typical of attachment to sp^3 centers, but magnified.

If we assume the gauche interaction to be additive, the stereoselectivities of ring opening of other 3-methyl-3-alkylcyclobutenes can be deduced qualitatively. There are six 3-methyl-3-isopropylcyclobutene transition structures that can be formed by replacing a hydrogen on C6 of A–F by a methyl group. For isopropyl inward the energies are 0.4, 2.1, and 2.5 kcal/mol; for isopropyl outward the energies are 1.3, 1.3, and 1.6 kcal/mol. A Boltzmann distribution at 180 °C predicts 66% isopropyl inward rotation. In 3-methyl-3-*tert*-butylcyclobutene, *tert*-butyl outward rotation is favored. There is only one transition structure for *tert*-butyl group inward rotation ($E = 2.5$ kcal/mol) and one for outward rotation ($E = 2.1$ kcal/mol), and a 62% *tert*-butyl outward rotation is predicted. These predictions are in excellent accord with experimental results.

Conclusion

Cis substitution of cyclobutenes causes a destabilizing steric interaction that lowers the activation barrier for conrotatory electrocyclic ring opening.

The ring opening of 3-ethyl-3-methylcyclobutene was shown to give a diene with methyl group outward rotation as a major product. The cyclobutene rings are slightly different in transition

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states for outward rotation and inward rotation. The product distribution was mainly determined by and parallel to the magnitude of the gauche interactions, which are larger in the methyl group inward transition states.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research, Dr. Nelson G. Rondan (Dow Chemical) for preliminary results, and the UCLA Office of Academic Computing and the San Diego Supercomputer Center for computer time used in this work.

Supplementary Material Available: Listing of computed energies and geometries (3 pages). Ordering information is given on any current masthead page.

Theoretical Study on the Insertion of Formaldehyde into the Cobalt–Hydrogen Bond

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Received December 26, 1989

Abstract: Theoretical calculations, based on density functional theory, have been carried out on the insertion of formaldehyde into the Co–H bond of $\mathrm{HCo(CO)_3}$. The first step of the process was considered to involve the initial formation of a π-complex between $\mathrm{HCo(CO)_3}$ and $\mathrm{H_2CO}$. The second step was modeled by a migration of the hydride to either carbon or oxygen on formaldehyde under the formation of a methoxy or hydroxymethyl intermediate. Several structures of the precursor π-complex as well as the methoxy and hydroxymethyl intermediate were fully optimized. The π-complexes were found to have a trigonal bipyramidal structure with $\mathrm{H_2CO}$ in either the axial or equatorial position. The equatorial site was favored by 50 kJ/mol. The methoxy and hydroxymethyl groups were found to favor axial coordination with a β-hydrogen in the equatorial position interacting in an agostic manner with cobalt. The corresponding equatorial coordination was calculated to be less stable by 27 (methoxy) and 44 kJ/mol (hydroxymethyl), respectively. The methoxy intermediates were found to be more stable than the corresponding hydroxymethyl intermediates by as much as 40 kJ/mol, primarily as a result of oxygen forming stronger bonds with cobalt than carbon. The reaction profile for the hydride migration was modeled by a linear transit procedure. The formation of methoxy was calculated to have a reaction enthalpy of 6 kJ/mol and an activation barrier of less than 5 kJ/mol. The formation of hydroxymethyl has a reaction enthalpy of 40 kJ/mol and an activation barrier of 15 kJ/mol. It is concluded that the catalytic conversion of aldehydes to alcohols, polyols and esters, by $\mathrm{HCo(CO)_3}$, most likely proceeds via the formation of a methoxy intermediate.

I. Introduction

The insertion of an olefin into the cobalt–hydrogen bond, as depicted in eq 1, is one of the key reactions in the hydroformylation process. The insertion process relies on the ability of olefins to

$$\mathrm{HCo(CO)_3 + C_2H_4 \rightarrow HCo(CO)_3{-}C_2H_4} \tag{1a}$$

$$\mathrm{HCo(CO)_3{-}C_2H_4 \rightarrow Co(CO)_3{-}C_2H_5} \tag{1b}$$

form π-complexes, eq 1a, as well as their susceptibility to nucleophilic attacks at the olefinic carbon, eq 1b. There have in recent years been a number of studies[1–5] on the insertion of olefins into the metal–hydrogen bond, including a few[4,5] involving the process given in eq 1.

The electronic structure of the C=O linkage in aldehydes bears some resemblance to olefinic double bonds. One might thus anticipate that aldehydes can undergo insertion processes analogous to those of olefins. In fact, the insertion of aldehydes into a cobalt–hydrogen bond, eq 2, has been postulated[6] in connection with the catalytic reduction of aldehydes to alcohols.

$$\mathrm{HCo(CO)_3 + H_2CO \rightarrow HCo(CO)_3{-}H_2CO} \tag{2a}$$

$$\mathrm{HCo(CO)_3{-}H_2CO \rightarrow Co(CO)_3{-}H_2CO(H)} \tag{2b}$$

We shall here investigate the two reactions given in eq 2 using the Hartree–Fock–Slater method[7,8] as our computational model. The emphasis of the investigation lies on the identification of the equilibrium geometries and the relative energies of stable configurations for the π-complex $\mathrm{HCo(CO)_3{-}(\eta^2{-}H_2CO)}$ and the coordinatively unsaturated intermediate $\mathrm{Co(CO)_3{-}H_2CO(H)}$. However, we shall also attempt to model the energy profile for the formaldehyde insertion into the Co–H bond by an approximate linear transit procedure. We shall further emphasize similarities and differences between the processes in eq 1 and eq 2. The olefin insertion has been investigated in a previous study.[5]

An important aspect of the reactions between metal centers and aldehydes is the fact that the π-complex $\mathrm{HM(CO)_n{-}H_2CO}$ is believed to be the precursor for the catalytic conversion of aldehydes to alcohols, esters, and polyalcohols.[6b,9] The reaction is, as already mentioned, proposed to proceed via the insertion of the aldehyde group into the metal–hydride bond. The latter process possesses two channels by which the different sets of products can be attained. The first channel, eq 3, proceeds via

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