tivation for this process is 99.1 kcal mol^{-1} at 25 °C, appreciably less than the calculated value.

An instructive comparison with the results in Table IV are the bond dissociation energies of the corresponding hydrocarbons (Table VI), for which all of the group values required for the calculation of $D(PhCH_2\text{–}R)$ were available.[1d,8] The agreement between the estimated and experimental values for these hydrocarbons is quite good. The large difference between the bond dissociation energies of the first member of each series is of course caused mainly by the intrinsic difference in C–F and C–H bond strengths. As the side chain is lengthened, the differences between the two series decreases until at the propylbenzene stage relatively little difference remains.

In summary, we have shown that within rather broad limits a correlation exits between the differences in group enthalpies of formation for radicals $\{[^{\bullet}C\text{-}(X)(Y)(Z)] - [^{\bullet}C\text{-}(H)(Y)(Z)]\}$ and for molecules $\{[C\text{-}(H)(X)(Y)(Z)] - [C\text{-}(H)_2(Y)(Z)]\}$ and that this correlation can be used for estimating new group values when the other three group values in the set are known or can be estimated. A better correlation exists in some cases if it is limited to only one X group. These correlations should be useful in cases where enthalpies of formation are unavailable.

Acknowledgment. I thank A. N. Syverud, S. W. Benson, A. S. Kende, E. S. Huyser, and K. N. Houk for helpful discussions and information.

Registry No. $PhCF_3$, 98-08-8; $PhCF_2CF_3$, 309-11-5; $PhCF_2CF_2CF_3$, 378-98-3.

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Experimental and Computational Evidence Indicating That the Initial Carbene Conformation Is Product Determining in the Reactions of Cyclopropylmethylene

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The decomposition of cyclopropyldiazomethane, **2**, to generate cyclopropylmethylene, **1**, was carried out from 573 to 773 K under flash vacuum pyrolysis (FVP) conditions and from 77 to 303 K photolytically in hydrocarbon solvents. An examination of the ratio of ring-expanded products (RE, butadiene and cyclobutene) to those of cleavage (C, ethylene and acetylene) as a funciton of temperature leads to the conclusion that RE is favored over C by 2.3 kcal/mol in the FVP of **2**. Ab initio calculations (MP2/6-31G*//3-21G) predict that decomposition of **2** to give the conformer of **1** in which the ring methyne hydrogen and the α-hydrogen are cis (**1a**) is more favorable than formation of the trans conformer (**1b**) by 1.1 kcal/mol. The calculated activation parameters for the formation of **1a** and **1b** have been combined with those calculated previously for the reactions of **1a** and **1b**, which indicate the RE is favored from **1a** while **1b** gives C, to give theoretical values of RE:C as a function of temperature which lead to a computed difference in E_a between RE and C of 2.7 kcal/mol, in good agreement with the 2.3 kcal observed experimentally. Photolysis of **2** gives a higher ratio of C to RE than does FVP. This may be a consequence of the fact that a more energetic carbene is produced in the photolysis than in the thermolysis.

The reactions of cyclopropylmethylene, **1**, are interesting in that this carbene does not undergo the 1,2-hydrogen migration common to most carbenes with β-hydrogens. Instead, the strain of the cyclopropane ring and the conformation of the carbene dictate rearrangement via a C–C insertion to give cyclobutene and an unusual cleavage of two β C–C bonds to generate ethylene and acetylene.[1,2] Theoretical work has indicated that **1** exists in the two conformations, **1a** (cis) and **1b** (trans) (Scheme I), in which the empty p orbital on the carbene carbon is stabilized by electron donation from the antisymmetric Walsh orbital of the ring.[3-6] In a recent computational investigation of this interesting carbene, we have predicted that **1a** is likely to ring expand to cyclobutene ($k_4 > k_6$) while the most favorable reaction of **1b** is expected to be cleavage to ethylene and acetylene ($k_5 > k_7$, Scheme I).[4] Since these calculations indicate that the barrier to the interconversion of **1a** and **1b** is higher than the respective rates of ring expansion (RE, $k_4 > k_3$) and cleavage (C, $k_5 > k_{-3}$), we have proposed that RE:C ratio in **1** is dictated by the conformation in which the carbene finds itself at birth.[7]

Scheme I

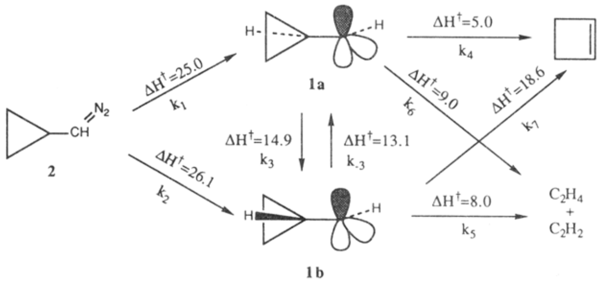

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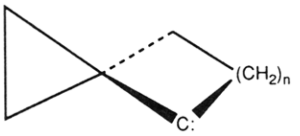
Table I. Ratios of Ring-Expanded Products (RE) to Those of Cleavage (C) When Carbene 1 Is Generated under Various Conditions

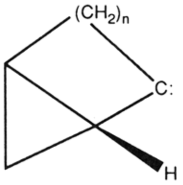
T, °K	[RE]/[C]	conditions
77	5.69	$h\nu$, Pyrex, hydrocarbon solvent
153	5.0	$h\nu$, Pyrex, hydrocarbon solvent
203	3.84	$h\nu$, Pyrex, hydrocarbon solvent
253	3.58	$h\nu$, Pyrex, hydrocarbon solvent
303	3.05	$h\nu$, Pyrex, hydrocarbon solvent
473	20.3	FVP
573	13.9	FVP
673	10.1	FVP
773	7.94	FVP
263	0.27	$h\nu$, λ = 300–320 nm, hydrocarbon solvent
298	0.93	$h\nu$, Pyrex, gas phase[a]
77	0.9	C atoms + cyclopropanecarboxaldehyde[b]
453	6	tosylhydrazone salt decomposition in solution[c]

[a] Reference 2. [b] Reference 31. [c] Reference 1.

Experimental evidence to support this proposal is sparse. Although carbenes such as **3**, which are locked into the cis conformation, do rearrange by RE,[10-12] the corresponding cleavage would result in a strained cycloalkyne. Likewise derivatives of **1**, such as **4**, which are held in a trans conformation by a ring fusion, undergo predominate cleavage. However, RE would generate a bridgehead double bond in the fused cyclobutene of the product.[13] Certain derivatives of **1** in which large groups on the ring may force a trans conformation give increased fragmentation.[14] In the present study, we report an investigation of the thermolysis and photolysis of cyclopropyldiazomethane, **2**, which provides evidence to support the above hypothesis concerning product-determining conformations of **1**.



3; n=2,3



4; n=2,3

Results and Discussion

In order to measure the differences in activation energies and entropies for the process leading to RE and C, we have examined the ratio of RE products to those of C as a function of temperature in the thermolysis and photolysis of **2**. The thermolysis of **2** was examined under flash vacuum pyrolysis (FVP) conditions over a temperature range of 573–773 K while the photolysis were carried out from 77 to 303 K in hydrocarbon solvents. The photochemical decomposition of **2** gave only ethylene, acetylene, and cyclobutene as expected from Scheme I. However, in the FVP experiments, the products were ethylene, acetylene, and 1,3-butadiene. In this case, the 1,3-butadiene is formed by electrocyclic ring opening of the initially formed cyclobutene. The fact that ring opening to butadiene occurs in this system reflects the high exothermicity associated with reactions of **1**. The RE of **1a** is calculated to be exothermic by 66.7 kcal/mol. Since the barrier to electrocyclic ring opening in cyclobutene is only 32.5 kcal/mol[15] and little deactivation is expected in the gas phase, there is ample energy available for butadiene formation. Other cases in which **1** is generated in the gas phase also result in the formation of butadiene and very little cyclobutene.[2,16]

Table II. Absolute Energies (hartrees) of Various Species on the $C_4H_6N_2$ Surface

	3-21G	6-31G*	MP2/6-31G*	ZPE-(NEV)[a]
2a	−262.246 12	−263.745 44	−264.585 38	64.28 (0)
2b	−262.245 82	−263.743 86	−264.585 80	64.34 (1)
2c	−262.247 59	−263.747 90	−264.589 78	64.43 (0)
TS2-1a	−262.217 68	−263.721 06	−264.546 98	62.55 (1)
TS2-1b	−262.215 02	−263.785 30	−264.545 08	62.47 (1)

[a] Zero point energy (kcal/mol) and the number of imaginary frequences in parentheses.

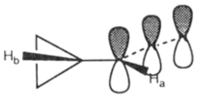
Table III. Relative Energies (kcal/mol) of Various Species on the $C_4H_6N_2$ Surface

	3-21G	6-31G*	MP2/6-31G*	MP2/6-31G* + ZPE
2a	0.92	1.54	2.76	2.61
2b	1.11	2.54	2.50	2.41
2c	0.00	0.00	0.00	0.00
TS2-1a	18.77	16.84	26.86	24.98
TS2-1b	20.44	18.44	28.05	26.09

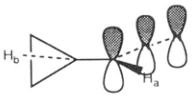
Table I summarizes the ratios of RE to C observed in the present study and when **1** is generated under several other conditions. Figure 1 shows a plot of log [RE products]/[C products] vs $1/T$. If E_C and E_{RE} are the activation energies and $\Delta S^{\ddagger}{}_C$ and $\Delta S^{\ddagger}{}_{RE}$ the activation entropies for the formation of C and RE products, Figure 1 yields and $E_C - E_{RE} = 2.3$ kcal/mol and a $\Delta S^{\ddagger}{}_{RE} - \Delta S^{\ddagger}{}_C = 1.2$ cal/(mol deg) for the thermolysis of **2**. The dependence of log RE/C on $1/T$ in the photolysis is also shown in Figure 1.

Scheme I shows possible pathways to the RE and C products from **2**. We know from the differences in the calculated enthalpy and entropy barriers that k_3, k_{-3}, and k_7 are small compared to k_4, k_5, and k_6 over the temperature range of the thermolysis, and these processes may be neglected. However at the temperatures employed here, k_6 is calculated to become competitive with k_4, and some cleavage will result from **1a**. In the absence of interconversion of **1a** and **1b**, the mole fraction of RE products (X_{RE}) is simply $X_{1a}(k_4/(k_4 + k_6))$. The mole fraction of **1a**, X_{1a}, in turn, could be characteristic of an equilibrium constant between different conformers of **2** leading to **1a** and **1b**, the ratio of k_1:k_2, or a combination of these factors.

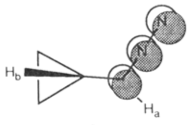
Conformers of **2**, which lead directly to **1a** and **1b**, are **2a** and **2b**, respectively. The gauche conformer, **2c**, could presumably lead to either conformer of the carbene. In order to evaluate the conformational preference in **2**, we have measured the vicinal coupling constant between H_a and H_b in the ^1H NMR spectrum of **2**. H_a appears as a doublet at δ = 3.76 ppm whose coupling constant increases from 1.76 to 2.57 Hz upon increasing the temperature from



2 a



2 b



2 c

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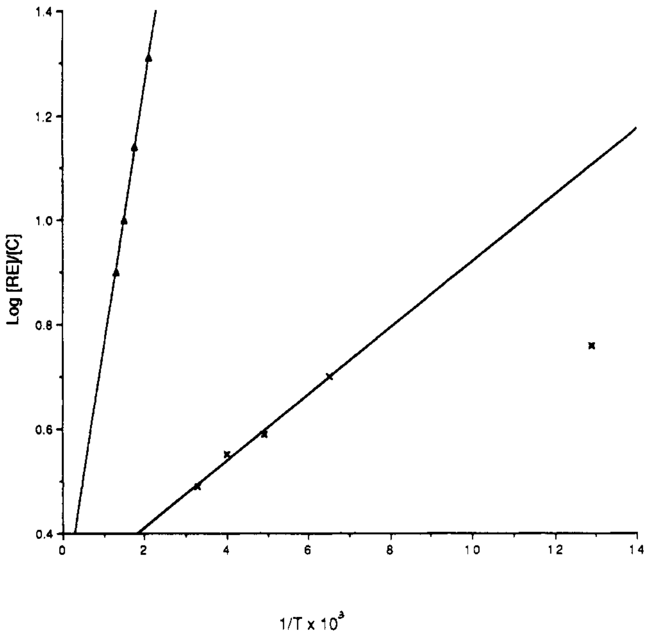

Figure 1. Dependence of log [RE]/[C] products on inverse temperature for: (Δ) the FVP of 2; (×) the broad-band photolysis of 2.

153 to 303 K. Surprisingly, this small coupling constant appears to be characteristic of a predominance of neither syn or anti conformer **2a** or **2b**. Instead, this value indicates the predominance of the gauche conformer, **2c**.

In order to evaluate the conformational preferences in 2, computationally we have carried out molecular orbital calculations of the energies of the various conformers of 2. In these calculations, which utilized the GAUSSIAN 82[17] and 86[18] programs, geometries were optimized at the 3-21G level and single point calculations were made on these geometries at the MP2/6-31G* level. Frequencies were calculated at the HF/3-21G level and used to calculate zero-point corrections. Tables II and III give the absolute and relative energies of intermediates and transition states calculated at various levels in this investigation. These calculations tend to bear out the general conclusions resulting from the coupling constant measurements. Thus, the minimum-energy conformation of 2 is calculated to correspond to a gauche species in which the dihedral angle between H_a and H_b is calculated to be 67.8° with conformers **2a** and **2b** calculated to lie 2.6 and 2.4 kcal/mol higher in energy at the MP2/6-31G*//3-21G level. It should be pointed out that **2b** has one negative eigenvector at the 3-21G level and is thus not calculated to be a true intermediate at this level but may be at the higher level. The energy minimum for **2c** appears to be rather broad in that increasing the H_a–H_b dihedral angle to 90° brings about little change in energy.

In principle, one can use the observed coupling constant, J_o, in **2** to calculate an equilibrium constant between conformers which, when combined with temperature dependence data, will give an experimental enthalpy difference between conformers. If it is assumed that **2c** is the lowest energy conformer of **2** and that **2a** and **2b** are of similar energy as indicated by the calculations, the mole fraction of **2c** (X_{2c}) is given by eq 1 in which J_o is the observed coupling constant, J_{2ab} is the sum of the vicinal coupling constants in **2a** and **2b** and J_{2c} is the coupling constant in **2c**. The K_{eq} for the equilibrium between **2c** and a mixture of **2a** and **2b** is thus given by eq 2. In order

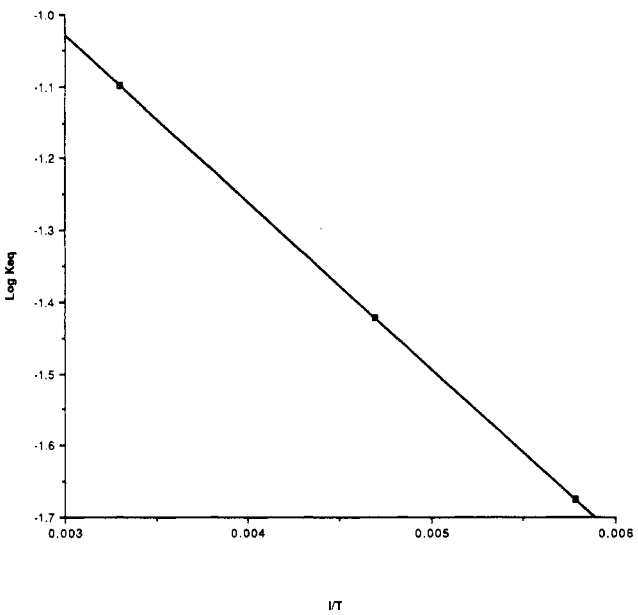

Figure 2. The dependence of the log of the NMR-derived K_{eq} for the reaction 2 **2c** → **2a** + **2b** on inverse temperature.

$$X_{2c} = (J_o - J_{2ab})/(J_{2c} - J_{2ab}) \quad (1)$$

$$K_{eq} = (J_{2c} - J_o)/(J_o - J_{2ab}) \quad (2)$$

to calculate this equilibrium constant, we have used coupling constants that have been estimated for the corresponding conformers of vinylkcyclopropane of 11, 5, and 1.5 Hz for J_{ab} in **2a**, **2b**, and **2c**, respectively.[19,20] A plot of the log of the equilibrium constant, estimated from the NMR data, as a function of $1/T$, shown in Figure 2, leads to an observed enthalpy difference between **2c** and **2a** + **2b** of 0.9 kcal/mol. While this $\Delta\Delta H°$ is only an estimate based on assumed values for J_{ab} in **2a**, **2b**, and **2c**, the fact that the observed coupling constant is small and increases with temperature indicates that **2c** is the most stable conformer of **2**.

These experimental and theoretical results regarding the conformational preference in **2** are in contrast to those found in other substituted cyclopropanes with a p orbital on a carbon adjacent to the ring. For example, the cyclopropylcarbinyl cation,[21,22] cyclopropanecarboxaldehyde[23] as well as **1a** and **1b**[4–6] (Scheme I) are all thought to exist predominately in conformers in which the p orbital on carbon eclipses the antisymmetric Walsh orbital of the ring. In these compounds, this conformation provides for stabilization of the electron deficient p orbital by the electrons in the antisymmetric Walsh orbital of the ring. However, in **2**, this p orbital contains an excess of electron density and the conformation in which it eclipses the oc-

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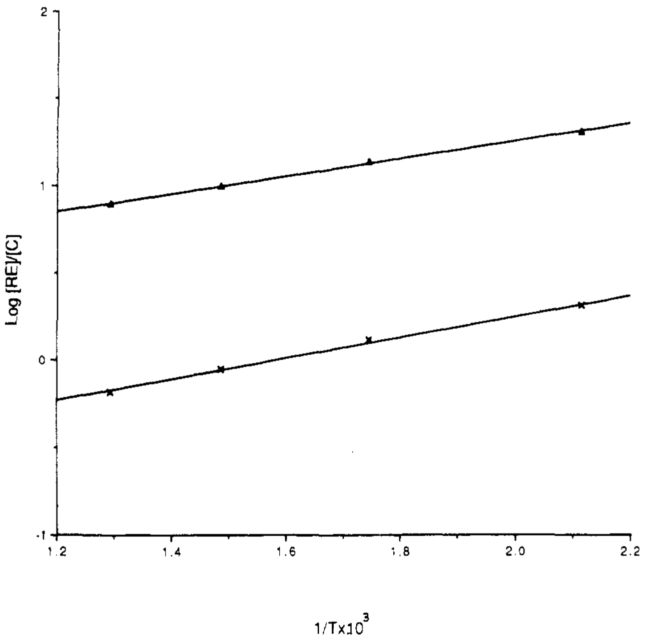

Figure 3. Comparison of the dependence of theoretical (×) and experimental (Δ) log [RE]/[C] values on inverse temperature.

cupied antisymmetric Walsh orbital of the ring is destabilizing.[24] A similar situation exists in cyclopropylamine which exists in a conformation similar to **2c** with the nitrogen lone pair cis to the cyclopropane ring.[29]

If the most stable conformer of **2** is **2c**, this species could lead to either carbene **1a** or carbene **1b**, and the ratio of carbene conformers would simply reflect the value of k_1/k_2. Accordingly, we have calculated (MP2/6-31G* + ZPC//3-21G) the energies of the transition states for loss of nitrogen from **2c** leading to carbenes **1a** and **1b** (**TS2-1a** and **TS2-1b**). The results of these calculations, shown in Tables II and III, indicate that loss of N_2 from **2c** to give **1a** ($\Delta H^{\ddagger} = 25.0$ kcal/mol, $\Delta S^{\ddagger} = 0.3$ cal/(mol deg)) is more favorable than formation of **1b** ($\Delta H^{\ddagger} = 26.1$ kcal/mol, $\Delta S^{\ddagger} = 0.4$ cal/(mol deg)) by 1.1 kcal/mol.

We may use the activation parameters calculated here for steps corresponding to k_1 and k_2 in Scheme I to estimate X_{1a} and X_{1b} at various temperatures, assuming, as indicated by our earlier calculations, that these carbenes do not interconvert. If we make the further assumption, again justified by previous calculations, that k_7 is small compared to k_4, k_5, and k_6, we may combine X_{1a} with the calculated values of k_4, k_5, and k_6 to obtain $X_{RE} = (k_1/(k_1 + k_2))(k_4/(k_4 + k_6))$ and theoretical RE:C ratios at various temperatures. Figures 3 shows a plot of the log of both the theoretical and the experimental RE/C values vs $1/T$. The data from Figure 3 yield a computed $E_C - E_{RE} = 2.7$ kcal/mol and a $\Delta S^{\ddagger}_{RE} - \Delta S^{\ddagger}_{C} = -4.34$ cal/(mol deg) which may be compared to the experimental values of 2.3 kcal/mol and 1.2 cal/(mol deg). While there is excellent agreement between theoretical and experimental activation energy differences, the $\Delta\Delta S^{\ddagger}$ values do not agree as well, perhaps due to the failure of the computational technique to calculate accurate entropies.

The above results combined with our previous calculations lead to the conclusion that the slowest step in Scheme I is loss of N_2 from **2** and that, once formed, carbenes **1a** and **1b** do not interconvert but that **1a** gives both RE and C while **1b** gives only C. This reasoning is consistent with the calculations which predict barriers of 25–26 kcal/mol for carbene formation and barriers of 5 and 9 kcal/mol for RE and C, respectively, from **1a** and a barrier of 8 kcal/mol for C from **1b**. An alternate explanation, which is, however, inconsistent with the calculations, is rapid interconversion of **1a** and **1b** followed by rate determining RE and C of the carbenes. If this were the mechanism, the RE:C ratio would be $k_4/(k_5 + k_6)$, and the process corresponding to C would undoubtedly have the more positive $\Delta S^{\ddagger}$. In this case, the experimentally measured $\Delta\Delta S^{\ddagger}$ should be less than zero. The calculated $\Delta\Delta S^{\ddagger}$ assuming rapid carbene interconversion and the calculated value of $k_4/(k_5 + k_6)$ is −5.4 eu. The experimental observation of a $\Delta\Delta S^{\ddagger}$ of +1.2 eu is clearly inconsistent with a mechanism involving equilibration of carbene conformers.

The dependence of log RE/C on inverse temperature shown in Figure 1 for the photolysis of **2** is somewhat complicated by the fact that the point at 77 K does not fall on the line. However, **2** was not completely soluble in the propane solvent at this temperature, and some photolysis of solid diazo compound may have occurred in this case. It is interesting that the ratio of C products to those of RE is larger in the photolysis than in the thermolysis despite the fact that the former is carried out at far lower temperatures. This result is made more striking by the fact that our calculations indicate that, if thermally equilibrated carbenes are involved at the low temperatures employed in the photolysis, $k_4 \gg k_6$ and cleavage from **1a** may be ignored ($k_4/k_6 = 86$ at 303 K). Hence, we must conclude that photolysis of **2** either generates a smaller **1a**:**1b** ratio than does thermolysis or that **1** is born with excess energy at a point on the potential energy surface which channels into the cleavage mode. Since **1** + N_2 is calculated to lie only 23.5 kcal/mol above **2c** and aliphatic diazo compounds have a λ_{max} in their absorption spectrum corresponding to an energy of 60 kcal/mol,[30] it is possible that photolytically generated **1** is born with more energy than that generated by thermolysis. Table I demonstrates that gas-phase photolysis of **2** produces an even smaller value of [RE]/[C] than we report here for photolysis in solution.[2] When **1** is generated by the carbon atom deoxygenation of cyclopropanecarboxaldehyde, a reaction which should be exothermic by over 80 kcal/mol, a small [RE]/[C] is also observed (Table I).[31] In order to increase the average energy imparted to **2** in the present study, we have carried out the photolysis at 263 K using filtered light of 300–320 nm. As shown in Table I, this results in a dramatic decrease of [RE]/[C] from 3–3.5 to 0.27. The above data indicate that cleavage becomes more important as the energy increases and more molecules of **1** are produced at the point on the energy surface where funnelling into the cleavage mode becomes more favorable.

Conclusions

These results indicate that the chemistry of **1** is dictated by the initial conformation of the carbene. This hypothesis is consistent with the results of calculations[4] and with the

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[24] A referee has pointed out that vinylcyclopropane, with an occupied p orbital adjacent to the ring, also adopts a conformation similar to **1**.[19,20,26-27] In vinylcyclopropane, this conformation is stabilized by an interaction between the occupied Walsh orbital and the π^* orbital of the vinyl group.[28] In **2**, the LUMO that we calculate does not have the proper symmetry for this type of stabilization.

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chemistry of substituted derivatives of 1 of fixed conformation.[10,11] Although there are cases reported in the literature in which different carbene conformers give rise to different products,[32] there has been little evidence that the initial carbene conformation can be product determining. However, the situation in which the initial carbene conformation determines the product formed may be more general in carbene chemistry than is generally supposed. Carbenes often have low barriers to intramolecular reaction, and stabilization of these reactive intermediates by electron delocalization involving adjacent substituents may lead to preferred conformations which undergo intramolecular reaction faster than they interconvert.

Experimental Section

Cyclopropyldiazomethane (2). The diazo compound was prepared in a sequence of reactions starting from cyclopropylmethylamine[33] via 3-(*N*-nitroso-*N*-(cyclopropylmethyl)amino)-3-methyl-2-butanone[34] by the method of Adamson and Kenner.[30] Compound 2 was purified by trap to trap vacuum distillation and stored at 77 K: IR 2073 cm^{-1} ($C{=}N_2$); ^{1}H NMR (pentane-d_{12}, 213 K) δ 3.76 (d, 1 H, J = 2.0 Hz), 1.55 (m, 1 H), 0.78 (m, 2 H), 0.44 (m, 2 H).

Flash Vacuum Pyrolysis of 2. Compound 2 (0.42 mmol) was distilled at 0.2 Torr through a 25 mm × 50 cm quartz tube packed with quartz chips and heated by an external furnace to the desired temperature. The pyrolysis products were trapped in two consecutive traps at 77 K. Products were vacuum transferred to an NMR tube, and the ethylene–1,3-butadiene ratio was determined by NMR integration in $CDCl_3$ solvent. Observed integrations were corrected for a small difference in solubilities of gaseous butadiene and ethylene through the use of a standard of known concentration. Absolute yields were determined by NMR integration using *p*-dioxane as an internal standard. Total product yields were typically 70%. No cyclobutenes could be detected by the NMR analysis.

Low-Temperature Photolysis of 2. Compound 2 was condensed into a pyrex NMR tube and sealed off. The solvent was isopentane except for the 77 K photolysis in which propane was used. The tube containing 2 was then placed in a pentane bath in a quartz Dewar flask, which could be cooled in a stream of N_2 and photolyzed at various low temperatures with an Oreil 1000-W Hg/Xe medium-pressure lamp until the yellow color of 2 disappeared (about 15 min). After photolysis, NMR analysis of the contents of the tube revealed the presence of cyclobutene (δ 2.52, 5.97), ethylene (δ 5.30), and acetylene (δ 1.87). The ratio of cyclobutene to ethylene was measured by integration of their NMR signals. Photolysis from 300 to 320 nm was accomplished using the same apparatus with light passed through a Photon Technology International Model 001 monochrometer.

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Theoretical Studies of Aldol Stereoselectivity: The Development of a Force Field Model for Enol Borinates and the Investigation of Chiral Enolate π-Face Selectivity

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Ab initio calculations on enol borinate structures have been used to generate empirical force field parameters for the title systems. The optimized structures of enol borinates are nonplanar with the BR_2 group twisted out of the enolate plane, rendering the enolate π-faces nonequivalent. The resulting force field model has been used for a preliminary investigation of the aldol stereoselectivity of enol borinates with chiral groups attached either to boron or to the carbonyl carbon. This suggests that the π-facial selectivity of *Z*-enol diisopinocampheyl borinates derived from ethyl ketones may be explained by the conformational bias of the enolate and a Zimmerman–Traxler chair transition state with the aldehyde. The reversed aldehyde enantioface selectivity observed for enol diisopinocampheyl borinates derived from methyl ketones does not fit this pathway, and alternative boat transition states are required.

The aldol addition reaction of enol borinates is an important method for attaining absolute stereocontrol in the synthesis of β-hydroxy carbonyl compounds (Scheme I). This process often relies on a specially designed chiral auxiliary R^1 built into the starting carbonyl compound 1, which then controls the enolate π-face selectivity in addition to an aldehyde.[1] For the *Z* enolates of certain chiral ethyl ketones or propionimides, i.e., 2 for R^2 = Me, a high level of π-face selectivity is accompanied by high syn diastereoselectivity leading to selective formation of aldol adducts 4 or 5. The use of enol borinate derivatives of α-alkoxy ketones, 6,[2] α-silyl ketones, 7,[3] and oxazolidinone imides, 8,[4] are noteworthy examples (Table I, entries 1–3).

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