

Table I. Frequencies, Intensities, and Assignment of the Vibrational Bands

Alanine						
Obsd frequency, ^b cm ⁻¹	Absorbance ^b	$\Delta A \times 10^5$ for L-alanine ^b	Calcd frequency, ^c cm ⁻¹	Raman frequency, ^d cm ⁻¹	CH ₃ CHFCl, ^a obsd frequency, cm ⁻¹	Assignment
3007	0.18	+0.8 ± 0.5 ^e	3062	3002	3012	$\nu_{\text{C-H}}$
2987	0.24	-1.5 ± 0.5	3011	2988	2985	$\nu_{\text{asym,CH}_3}$
		+4.5 ± 0.7	3010	2964	2974	$\nu_{\text{asym,CH}_3}$
2949	0.20	+1.5 ± 0.5	2921	2932	2945	$\nu_{\text{sym,CH}_3}$
2894	0.07			2891	2894	CH ₃ deformation overtones, combination bands

^a Reference 6. ^b This work. ^c Reference 7. ^d Reference 5. ^e Although some of the reported ΔA values exhibits a very low signal-to-noise ratio, the observed VCD is reliable within the error limits indicated, since the same spectral features have been reproduced on numerous occasions.

duced significantly, resulting in an improved infrared transmission between 3.2 and 3.5 μ .

The VCD spectra in Figure 1 are direct strip chart reproductions without further data treatment. The ΔA values listed in Table I were measured at the VCD peaks, which are near but do not correspond to the absorption peaks. Owing to low solubility, DL-alanine baseline spectra could not be run; however, "absorption baselines"⁴ showed a small baseline dependence on the overall transmission, and followed the average of the D and L spectral curves in Figure 1.

Vibrational frequencies and intensities of alanine and frequencies of 1-chloro-1-fluoroethane are summarized in Table I. To date most infrared studies on alanine were performed in salt pellets, precluding a detailed analysis of the C-H stretching frequencies. As a result, our observed vibrational bands were assigned using alanine single-crystal Raman data by Wang and Storms⁵ and the detailed vibrational analysis of 1-chloro-1-fluoroethane published by Durig et al.⁶ The latter molecule was chosen because the masses of fluorine and chlorine are close to the masses of the amine and acid functions in alanine, respectively.

Barron⁹⁻¹¹ has shown, both experimentally and theoretically, that degenerate asymmetric methyl deformation modes are split by a perturbing chiral environment to yield two components having equal and opposite optical activity. Barron's theoretical arguments are general^{10,11} and apply equally well to Raman optical activity in degenerate asymmetric methyl stretching vibrations. Preliminary theoretical work indicates that similar couplets should appear for degenerate methyl vibrations in VCD.¹³ These preliminary considerations, together with the observation of a couplet in the region of the two asymmetric methyl stretching modes, leads one to the following hypothesis regarding the origin of the VCD spectrum. A conservative bisignate couplet is centered at the peak of the asymmetric methyl stretching absorption band at 2987 cm⁻¹. The high frequency component of this couplet overlaps a VCD band of opposite sign arising from the C α -H stretching mode, reducing the magnitude of these opposing bands. The low frequency component of the couplet overlaps a VCD band of the same sign in the symmetric methyl stretching region, resulting in a low frequency tail.

The observed spectrum is not entirely consistent with this proposed interpretation since the zero crossing of the couplet should be on the high frequency rather than the low frequency side of the absorption maximum. This discrepancy may be due to the mixing of other vibrational modes by the chiral perturbation leading to an inherently asymmetric couplet.^{10,11} In addition, other mechanisms may be responsible for the form of the VCD spectrum; however, they are difficult to estimate and tend to prevent a simple interpretation. These effects include Fermi resonance interactions with combination bands,¹⁴ hydrogen-bonding interactions, and conformational splittings within the absorption envelope. However, the dominant de-

generate methyl couplets observed in Raman optical activity and the large couplet observed in alanine and in certain other methyl-containing compounds reported previously³ suggest that degenerate methyl stretches may play a significant and useful role in the understanding of VCD spectra. A detailed normal coordinate analysis combined with a VCD intensity calculation is in progress to determine the degree of vibrational mixing and to test our interpretation of the VCD spectrum.

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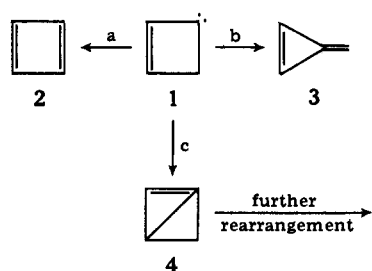
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Rearrangement of Cyclobutenylidene

Sir:

There is considerable interest in carbene rearrangements as routes to unique high energy species.¹ Particularly fascinating examples are provided by the vinyl carbenes which

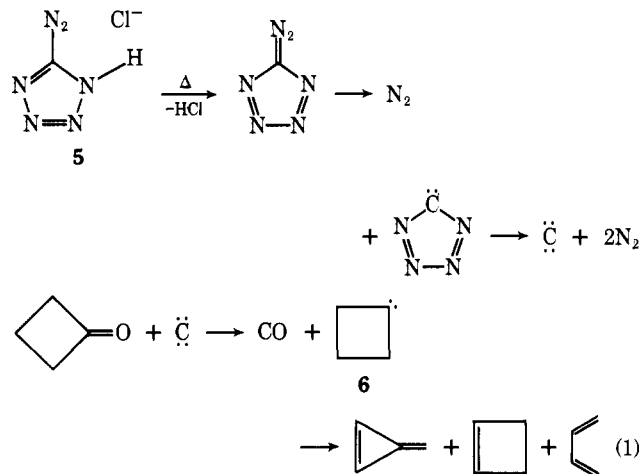
Scheme I



rearrange by a variety of intriguing pathways.² We report here a study of the rearrangement of the novel carbene cyclobutenylidene, **1**. Both a study of the products of this rearrangement and molecular orbital calculations of possible reaction coordinates indicate an interesting bicyclobutene-like transition state.

Cyclobutenylidene, **1**, appears to have a choice between the three reaction paths which are illustrated in Scheme I. Path a leads, via a 1,2-hydrogen migration, to cyclobutadiene (**2**), an energetic species which has recently been characterized by low temperature matrix spectroscopy.³ Ring contraction in **1** yields methylene cyclopropene (**3**, path b), a molecule whose existence has recently been inferred from trapping experiments.⁴ Finally, path c leads to bicyclo[1.1.0]butene, **4**, via a vinyl carbene rearrangement. Bicyclo[1.1.0]butene has been calculated to be extremely energetic⁵ and would probably rearrange further under the conditions of its formation.

Skell and Plonka⁶ have found that deoxygenation of carbonyl compounds with atomic carbon is an excellent method for generating carbenes. We have recently reported that atomic carbon generated by the thermolysis of 5-tetrazoyldiazonium chloride, **5**, deoxygenates cyclobutanone to produce cyclobutenylidene, **6** (eq 1),⁷ which yields products similar to those reported in the literature.⁸



We now report the application of this reaction to the deoxygenation of cyclobutenone (**7**, eq 2) to produce carbene **1**, using the methodology previously reported.⁹ When **5** (9.8×10^{-2} mmol) is decomposed at 85 °C in the presence of cyclobutenone¹⁰ (2.7×10^{-2} mmol), the products are carbon monoxide (5.4×10^{-3} mmol) and vinylacetylene, **8** (3.1×10^{-4} mmol), as the only isolable C_4H_4 product. Since 66% of the

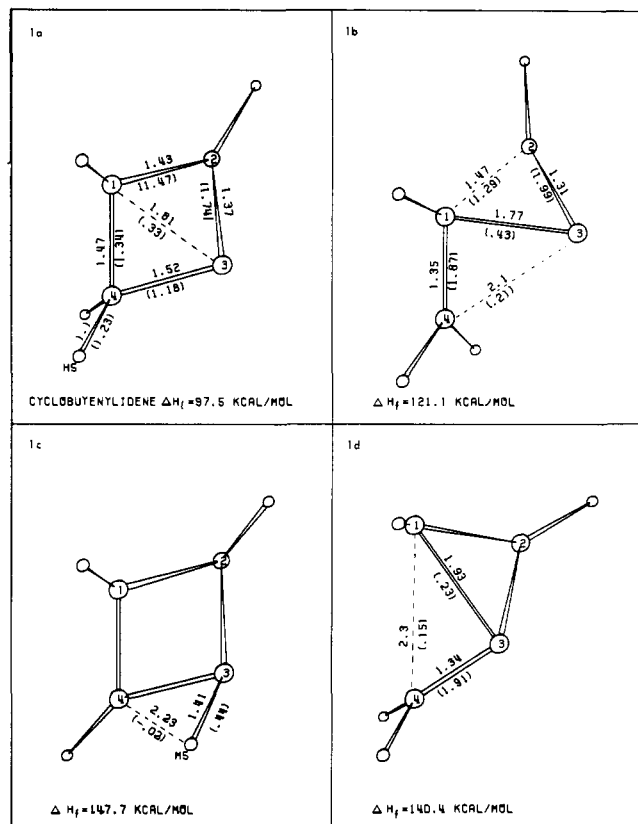
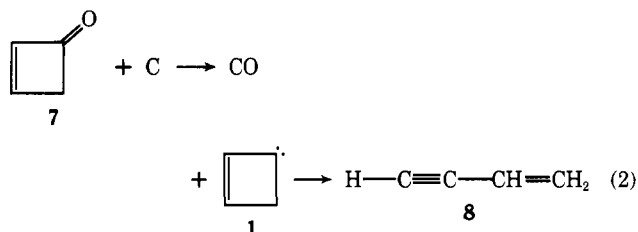
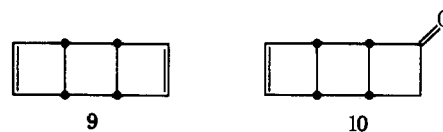


Figure 1. Equilibrium geometry of carbene **1** and geometries of transition states for rearrangement of **1** to **2**, **3**, and **4** calculated by MINDO/3. The numbers on the figure are relevant interatomic distances in ångströms, while numbers enclosed in parentheses are relevant overlap populations.

cyclobutenone is recovered after the reaction, the yield of **8** based on consumed ketone is 3.4%. However, heating **7** under the reaction conditions in a flask in which **5** had been previously decomposed results in a 20% loss of **7** with no production of **8**. This result suggests that some **7** is lost by thermal and/or acid-catalyzed decomposition and that the yield of **8** from carbene **1** must be higher than 3.4%.

The fact that the CO yield exceeds that of **8** is undoubtedly due to other reactions of carbon which produce CO. Among these are the facile reaction of $C(^3P)$ with molecular oxygen¹¹ and the carbon atom deoxygenation of oxygen containing impurities. High yields of carbon monoxide are often a hallmark of reactions of atomic carbon.¹²

It is expected that, were cyclobutadiene formed in this system, it would be detected either as syn dimer **9** or as the adduct **10** which would result from a Diels–Alder reaction between



cyclobutenone and **2**.¹³ An extensive analysis of reaction products by mass spectrometry and GC–mass spectrometry failed to reveal any evidence for **9** or **10**. Since low yields of **9** or **10** could have been detected in this analysis, we feel that **1** has little tendency to rearrange to **2**. Inasmuch as very little is known about the chemistry of **3**, it is difficult to predict its behavior in the absence of trapping agents. However, in analogy with the trapping experiments of Billups, Blakeney, and Chamberlain,⁴ one would expect that the addition of alcohols to **3** would be rapid. To this end we have sought to trap **3** by addition of gaseous methanol immediately after reaction. This experiment did not lead to the isolation of any products

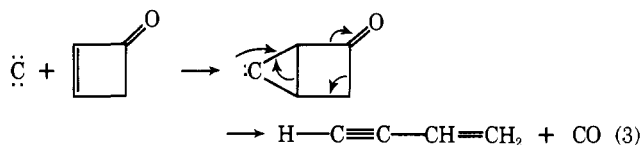
Table I. Calculated Heats of Reaction and Activation Enthalpies for Rearrangement of **1**.

Product formed	Enthalpy, kcal/mol			
	MINDO/3		STO-3G ^a	
	ΔH	ΔH^\ddagger	ΔH	ΔH^\ddagger
2	-2	50.3	-15.3	97.7
3	-16	42.9	-30.4	56.0
8	-36	23.6	-66.6	9.6

^a STO-3G energies of **2**, **3**, and **8** are from ref 5. All other STO-3G values were calculated using the geometries in Figure 1.

with mass spectra corresponding to that of an adduct of **3** with methanol.

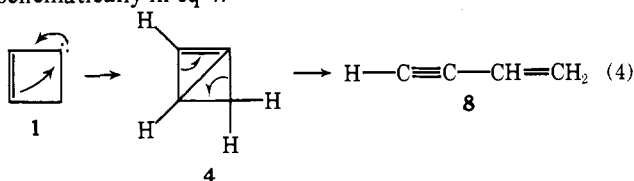
The known rearrangement of bicyclobutanylidene to **8**¹⁴ has led a referee to suggest an alternative mechanism for the formation of vinylacetylene involving the addition of carbon atoms to the double bond (eq 3). However, the decomposition of [¹⁴C]-**5**⁹ in the presence of **7** leads to **8** whose specific activity



is only 4% that of starting tetrazole. Hence, the pathway shown in eq 3 cannot account for more than 4% of the vinylacetylene in this system. This result serves to emphasize the known tendency of atomic carbon to react at the point of highest electron density.¹²

Hence, it appears that rearrangement to vinylacetylene is the most favorable pathway for carbene **1**. To explain the reactivity of **1**, we have carried out MINDO/3^{15,16} semiempirical molecular orbital calculations of the reaction coordinates for the formation of **2**, **3**, and **8** from **1**; a MINDO/3 study of **2** has been reported by Dewar and Kollmar.¹⁷ The calculated equilibrium geometry of carbene **1** as well as the geometries of the transition states for the three reactions are shown in Figure 1.

The reaction coordinate for the rearrangement of **1** to **8** was the C(3)-C(4) distance. Lengthening this bond carried the molecule through the transition state in Figure 1b to a point where the C(4)-C(3)-C(2) angle was 85°. At this point the angle was slowly opened to 180° generating the remainder of the reaction coordinate. It is interesting that lengthening the C(3)-C(4) bond results in an immediate increase in the bonding interaction between C(1) and C(3). In other words this rearrangement proceeds via a transition state (rather than an intermediate) resembling bicyclobutene, a process depicted schematically in eq 4.



The reaction coordinate for the rearrangement of **1** to **2** is the C(3)-C(4)-H(5) angle. A systematic decrease in this angle carries the molecule over the energy barrier shown in Figure 1c to a nonplanar structure which collapses to **2** when the C(4)-H(5) distance is lengthened. A reaction coordinate for the production of **3** is achieved by lengthening the C(1)-C(4) distance causing the molecule to collapse to **3** via the transition state in Figure 1d.

The calculated heats of reaction and activation enthalpies for these reactions are shown in Table I. As a check on the accuracy of the MINDO/3 results, Table I also lists ab initio STO-3G values for ΔH and ΔH^\ddagger . These values were obtained

from the STO-3G calculations of Pople and Hehre on **2**, **3**, and **8**⁵ and our STO-3G calculations¹⁸ on the molecular geometries shown in Figure 1.

Table I shows that both MINDO/3 and STO-3G calculations rationalize the observed formation of **8** and the absence of **2** and **3** in the rearrangement of **1**. Both the ΔH and the ΔH^\ddagger strongly favor rearrangement of **1** to **8**. This suggests that the exothermicity of the reaction controls product formation. An examination of the Mulliken overlap populations,¹⁹ shown in Figure 1, reveals that bonding in the transition states resembles the bonding in the products rather than the bonding in the starting carbene. Hence, these are late transition states with energies which reflect the heats of formation of the products. This consideration results in the observed rearrangement of **1** to the most thermodynamically stable product.

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Species and Equilibria in the Methylmercury(II)-Imidazole System

Sir:

Although the acidity of the "pyrrole" nitrogen of metal-complexed imidazole and the subsequent reaction of the deprotonated pyrrole nitrogen as a ligand have been studied ex-