

(t, CH₂); IR (KBr) 2225 and 2220 (C≡N) cm⁻¹; mass spectrum, *m/e* 279.082 (M⁺; calcd 279.083).

Anal. Calcd for C₁₆H₁₃N₃S (M, 279.365): C, 68.79; H, 4.69; N, 15.04. Found: C, 68.65; H, 4.88; N, 14.86.

Reaction of (E)-7 in Toluene. A solution of (E)-7 (0.35 g, 1.3 mmol) in 10 mL of toluene was heated at 110 °C for 90 h. After removal of the solvent under reduced pressure, the remaining solid was triturated with methanol to yield pure **14** in a yield of 90%.

Methyl cis-2,3,10,10a-Tetrahydro-10-(methoxycarbonyl)-1H-[1-benzothieno[3,2-b]pyrrolizine-3,3,10a-d₃-10-acetate-d (16a). A solution of (E)-8 (0.35 g, 1 mmol) in 10 mL of 1-butanol was heated at 118 °C for 15 h. After removal of the solvent under reduced pressure a 7:3 mixture of **16a** and **17a**, respectively, was obtained from which **16a** was isolated as a white solid by trituration with methanol: yield 48%; mp 137–139 °C (methanol); ¹H NMR δ 7.7–6.9 (m, 4 H, Ar H), 3.73 and 3.72 (s, 3 H, OCH₃), 2.77 (br s, 1 H, CHDE), 2.2–1.4 (m, 4 H, CH₂); mass spectrum, *m/e* 349.129 (M⁺; calcd 349.129).

Anal. Calcd for C₁₈H₁₅D₄NO₄S (M, 349.453): C, 61.87; H + D, 6.63; N, 4.01. Found: C, 61.95; H + D, 6.53; N, 3.94.

Methyl trans-2,3,10,10a-Tetrahydro-10-(methoxycarbonyl)-1H-[1-benzothieno[3,2-b]pyrrolizine-3,3,10a-d₃-10-acetate-d (17a). A solution of (E)-8 (0.35 g, 1 mmol) in 10 mL of toluene was heated at 110 °C for 78 h. After removal of the solvent under reduced pressure, the remaining solid was triturated with ethanol to give **17a** as a white crystalline compound: yield 72%; mp 95–97 °C (ethanol); ¹H NMR δ 7.7–6.9 (m, 4 H, Ar H), 3.80 and 3.56 (s, 3 H, OCH₃), 3.12 (br s, 1 H, CHDE), 2.1–1.5 (m, 4 H, CH₂); mass spectrum, *m/e* 349.126 (M⁺; calcd 349.129).

Anal. Calcd for C₁₈H₁₅D₄NO₄S (M, 349.453): C, 61.87; H + D, 6.63; N, 4.01. Found: C, 61.88; H + D, 6.55; N, 3.94.

Thermal Rearrangement of (Z)-8 in 1-Butanol. A solution of (Z)-8 (35 mg, 0.1 mmol) in 3 mL of 1-butanol was heated at 118 °C for 16 h. After removal of the solvent, the ¹H NMR spectrum of the crude reaction mixture revealed the presence of (Z)-8, **16b**, and **17b** in a ratio of 4:7:3, respectively.

16b: ¹H NMR δ 3.99 (br s, 1 H, CHDE).

17b: ¹H NMR δ 2.97 (br s, 1 H, CHDE).

Kinetic Studies of the Thermal Rearrangement of (E)-5, (Z)-5, and (E)-8. A sealed ¹H NMR tube containing a solution of (E)-5, (Z)-5, or (E)-8 (30 mg) in 0.4 mL of toluene-*d*₈ was heated in an oil bath at 110 °C and withdrawn at regular intervals for ¹H NMR analysis. The rate of conversion was monitored by measuring the ratio of the intensity of the low-field methoxy signals of the starting material and of the corresponding benzothieno[3,2-b]pyrrolizine. All the reactions fitted first-order kinetics and for the rate constants *k* of the rearrangements of (E)-5, (Z)-5, and (E)-8, values of (2.6 ± 0.1) × 10⁻⁵, (5.0 ± 0.1) × 10⁻⁶, and (1.8 ± 0.1) × 10⁻⁵ s⁻¹, respectively, were calculated. The same procedure was followed using a solution of (E)-5 (30 mg) in 0.4 mL of toluene-*d*₈ and acetic acid-*d*₄, respectively, but these reactions were performed at 100 °C. For the rate constants of the rearrangement of (E)-5 in toluene-*d*₈ and acetic acid-*d*₄ values of (9.7 ± 0.1) × 10⁻⁶ and (3.6 ± 0.1) × 10⁻⁴ s⁻¹, respectively, were calculated.

Acknowledgment. We are grateful for the financial support of this work by the "Koningin Wilhelmina Fonds". We express our gratitude to G. M. de Boer for his contribution to a part of the experimental work. We also acknowledge J. M. Visser and J. L. M. Vrielink for recording the NMR spectra and T. W. Stevens for recording the mass spectra. Dr. R. Visser is gratefully acknowledged for a detailed discussion of the NMR spectra.

Registry No. 1, 85923-93-9; **3a**, 67395-14-6; **3b**, 67395-15-7; **4**, 19983-26-7; (E)-5, 83466-94-8; (Z)-5, 83466-97-1; **6**, 85923-94-0; (E)-7, 85923-95-1; (Z)-7, 85923-96-2; (E)-8, 85923-97-3; (Z)-8, 85923-98-4; **9**, 85924-00-1; **10a**, 83466-93-7; **10b**, 85924-01-2; **11**, 83466-96-0; **12**, 83466-95-9; **13**, 85924-02-3; **14**, 85924-03-4; **16a**, 85924-04-5; **16b**, 85955-80-2; **17a**, 85993-32-4; **17b**, 85955-81-3; DMAD, 762-42-5; 1-(3,4-dihydro-1-naphthalenyl)pyrrolidine, 7007-34-3; methyl propionate, 922-67-8; **4-d₄**, 85923-99-5; 2-mercaptobenzo[b]thiophene, 30214-04-1; pyrrolidine-2,2,5,5-*d*₄, 42403-25-8.

Transition-State Geometries and Stereoselectivity of Alkylidenecarbene Addition to Olefins. An Experimental and Theoretical Investigation

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Abstract: A careful investigation of the addition of unsymmetrical alkylidenecarbenes R(CH₃)C=C:, where R = Et, *i*-Pr, and *t*-Bu, to two unsymmetrical olefins, isobutylene and *tert*-butylethylene, was carried out. In all cases, the *E* adduct predominated over the *Z* adduct, with increasing stereoselectivity being observed upon going from R = Et to R = *t*-Bu in the carbene. Greater stereoselectivity was also observed with *tert*-butylethylene as substrate compared with isobutylene. Detailed theoretical calculations were carried out on the reaction pathways and transition-state geometries of unsaturated carbene-olefin interactions. Model studies on the H₂C=C: + H₂C=CH₂ system were done both by MNDO and by standard ab initio methods at the STO-3G level, whereas the more substituted systems were evaluated by the MNDO method. These calculations indicate that attack of R(CH₃)C=C: on (CH₃)₂C=CH₂ leads to favored "C₂-inward" transition states, which yield the observed *E* adducts. For *t*-BuCH=CH₂, the preferred pathway is through anti "C₂-semiperpendicular" transition states that collapse to "C₂-inward" conformations and then to the *E* products. This pathway also nicely explains the observed relative reactivities of alkylidenecarbenes.

Carbenes are mechanistically interesting as well as synthetically useful reactive intermediates.¹ Recently unsaturated carbenes have been extensively investigated.² Two of the major unanswered questions in unsaturated carbene chemistry are the exact mode of approach of the carbene toward the π-system of olefins and

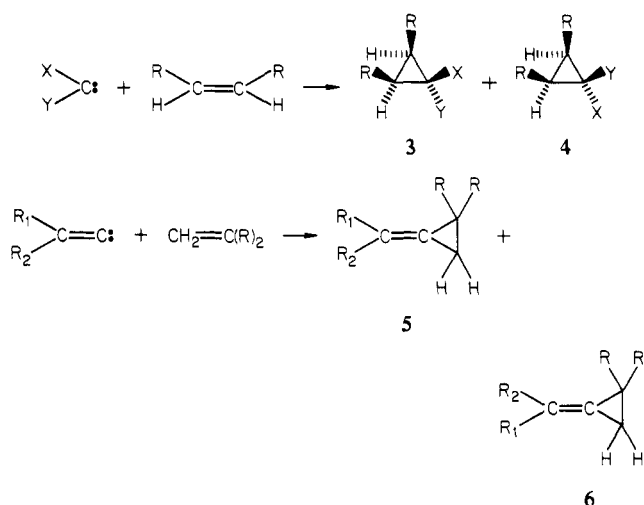
the precise nature of the transition state in carbene-alkene addition reactions. Whereas the potential surfaces of methylene and related carbene additions to olefins have been investigated theoretically,^{3,4}

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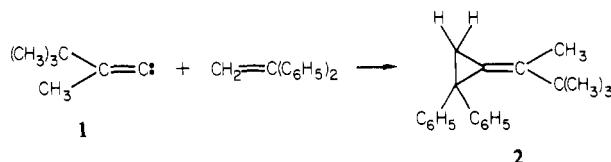
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(2) For a review see: Stang, P. J. *Chem. Rev.* 1978, 78, 383.

Scheme I



as well as probed experimentally by means of stereochemistry,¹ no comparable data exist for unsaturated carbenes.

In 1970 Newman and Patrick⁵ reported that the addition of alkylidenecarbene **1** to 1,1-diphenylethylene gave the more strained *Z* isomer **2** as the major product and on the basis of this data proposed a two-step process and a highly polar intermediate as the proper reaction pathway:



However, the assignment of *Z* stereochemistry to methylenecyclopropane **2** was based solely on tenuous NMR data that was further complicated by the subsequently discovered thermal rearrangement of such ring-substituted diphenylmethylenecyclopropanes to indenes under relatively mild conditions.^{2,6}

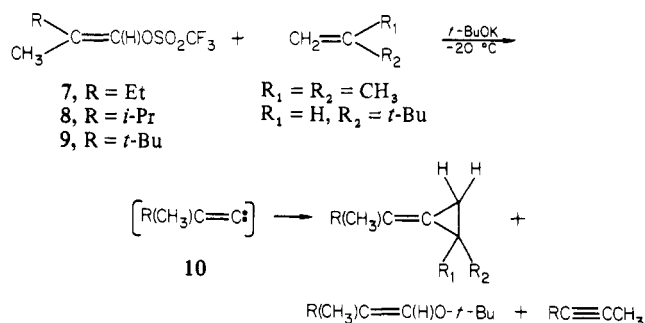
Moreover, in the absence of gas-phase data, due to the lack of suitable modes of gas-phase generation of unsaturated carbenes, it is essential for meaningful interpretation of solution data that the carbene be an unencumbered species rather than a carbenoid. Furthermore, for stereoselectivity to be a valid probe of the geometry of the carbene-olefin interaction, the carbene must react in the singlet state, as triplet reactions, and the concomitant diradicals would lead to ambiguous stereochemical results and consequent errors of interpretation. Alkylidenecarbenes generated by means of *t*-BuOK-initiated α -elimination of primary vinyl triflates have been shown to be singlet⁷ unencumbered⁸ species and consequently are well suited as probes of transition-state geometries.

Hence, we decided to undertake and herein report the results of a detailed experimental and concomitant theoretical investigation of the reaction pathways and transition-state geometries of alkylidenecarbene additions to olefins.

Results and Discussion

A. Experimental Studies. The stereochemical outcome of the addition of a dissymmetrically substituted carbene to an unsymmetrical olefin is a reflection of the path of approach and con-

Scheme II



sequent transition-state geometry of the carbene-olefin interaction. In the case of saturated carbenes such a reaction results in syn and anti adducts **3** and **4**, whereas with unsaturated carbenes the results are (*E*)- and (*Z*)-alkylidenecyclopropanes **5** and **6**, shown in Scheme I.

Limited data on alkyl-substituted carbenes as well as a plethora of data on halogen-, alkoxy-, carbalkoxy-, and aryl-substituted carbenes indicate that carbene-olefin addition reactions are generally stereoselective but seldom stereospecific.^{1,9,10} In order to assess the steric factors involved in alkylidenecarbene-olefin interactions, a series of differing β -alkyl-substituted vinyl triflates, **7–9**, were prepared and reacted in isobutylene as well as *tert*-butylethylene.

Preparation of Vinyl Triflates 7–9. Vinyl triflates **7–9** were prepared as previously described¹¹ from the corresponding substituted butanals via their silyl enol ethers. Specifically, vinyl triflate **7** was obtained from commercial 2-methylbutanal, whereas the necessary 2,3-dimethylbutanal for **8** was prepared in three steps from isovaleraldehyde by literature procedures.^{12,13} In addition, the required 2,3,3-trimethylbutanal for **9** was prepared by chromyl chloride oxidation¹⁴ of commercial 2,3,3-trimethyl-1-butene. In all instances mixtures of (*E*)- and (*Z*)-triflates were obtained, with the *E* isomer predominating in all cases, as determined by NMR (see Experimental Section).

Reaction of Vinyl Triflates 7–9 with Unsymmetrical Olefins. Each of the vinyl triflates **7–9** (as a mixture of *E* and *Z* isomers) was reacted at -15 °C to -20 °C in a large excess of both pure isobutylene and pure *tert*-butylethylene containing 50% excess *t*-BuOK. Reactions were monitored by GC and analyzed after the disappearance of all starting triflate. In all cases three types of products, adducts, enol ethers, and alkynes, were observed, as shown in Scheme II. It is obvious that the alkynes are the result of known² intramolecular migrations in carbene **10** and the enol ethers are the consequence of carbene "insertion" into the *tert*-butyl alcohol formed in the reaction. The exact product distributions, including the *E/Z* isomer ratios, are given in Table I.

After analytical analysis of the original reaction mixtures, all products were collected by preparative GC and the previously unknown adducts and enol ethers characterized by spectral means as described in the Experimental Section. Alkynes were identified either by spectral comparison with authentic material when isolated or by coinjection with authentic material on two different GC columns.

Critical to any discussion of the significance and implication of these results to transition-state geometry and reaction pathways is the stability and exact assignment of stereochemistry of the adducts. Use of only alkyl-substituted olefins as substrates rather

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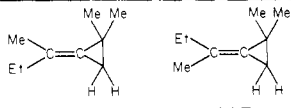
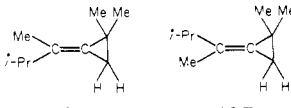
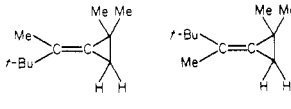
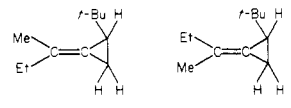
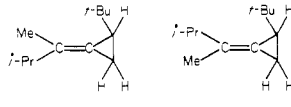
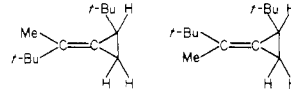
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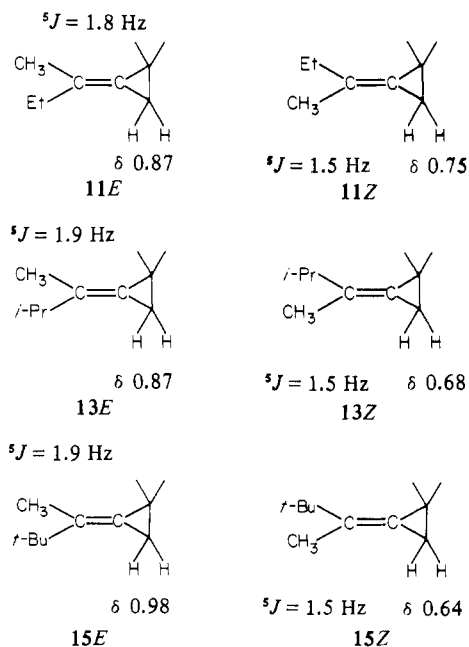
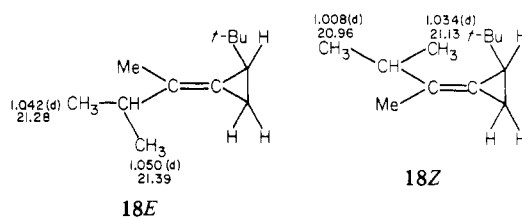
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Table I. Products of Reaction of Vinyl Triflates 7-9 in Isobutylene and *tert*-Butylethylene at -20°C

| triflate | % adduct (<i>E/Z</i> ratio) ^a | % <i>tert</i> -butyl vinyl ether (<i>E/Z</i> ratio) ^a | % alkyne ^a |
|---|--|--|----------------------------------|
| Et(Me)C=CHOTf 7, <i>E</i> + <i>Z</i> |  11 <i>E</i> 11 <i>Z</i> 67 (57/43) | Et(Me)C=C(H)O- <i>t</i> -Bu 12, 23 (71/29) | MeC≡CEt, 10 |
| <i>i</i> -Pr(Me)C=CHOTf 8, <i>E</i> + <i>Z</i> |  13 <i>E</i> 13 <i>Z</i> 74 (60/40) | <i>i</i> -Pr(Me)C=C(H)O- <i>t</i> -Bu 14, 23 (77/23) ^b | MeC≡C- <i>i</i> -Pr, 3 |
| <i>t</i> -Bu(Me)C=CHOTf 9, <i>E</i> + <i>Z</i> |  15 <i>E</i> 15 <i>Z</i> 15 (67/33) | <i>t</i> -Bu(Me)C=C(H)O- <i>t</i> -Bu 16, 47 (100/0) | MeC≡C- <i>t</i> -Bu, 38 |
| Et(Me)C=CHOTf 7, <i>E</i> + <i>Z</i> |  17 <i>E</i> 17 <i>Z</i> 48 (67/33) | Et(Me)C=C(H)O- <i>t</i> -Bu 12, 22 (73/27) | MeC≡CEt, 30 |
| <i>i</i> -Pr(Me)C=CHOTf 8, <i>E</i> + <i>Z</i> |  18 <i>E</i> 18 <i>Z</i> 59 (75/25) | <i>i</i> -Pr(Me)C=C(H)O- <i>t</i> -Bu 14, 41 (78/22) | MeC≡C- <i>i</i> -Pr ^c |
| <i>t</i> -Bu(Me)C=CHOTf 9, <i>E</i> + <i>Z</i> |  19 <i>E</i> 19 <i>Z</i> 28 (90/10) | <i>t</i> -Bu(Me)C=C(H)O- <i>t</i> -Bu 16, 16 (100/0) | MeC≡C- <i>t</i> -Bu, 56 |

^a Relative (uncorrected) GC areas, $\pm 2\%$. ^b Determined by NMR. ^c Not determined.Chart I. ^1H NMR of Isobutylene Adducts 11, 13, and 15Chart II. 300-MHz ^1H and ^{13}C NMR of *tert*-Butylethylene Adducts 18*E* and 18*Z*

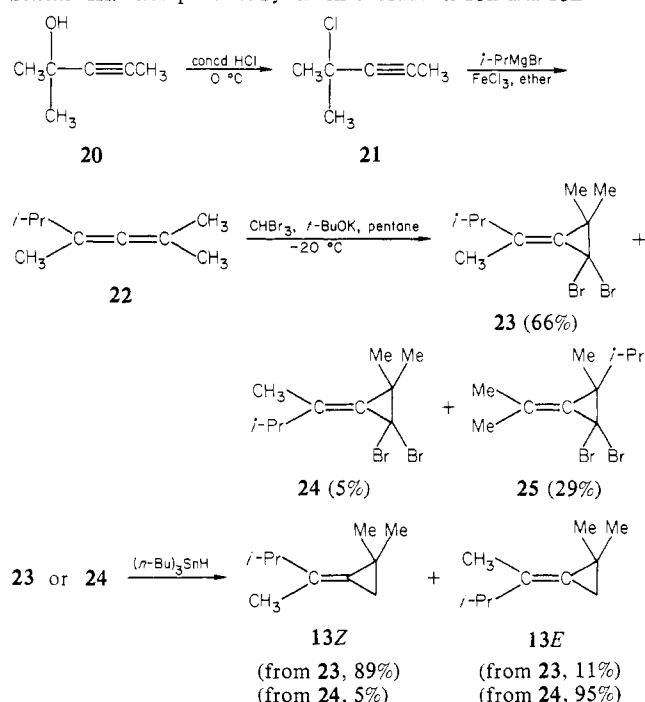
the reaction conditions or upon GC analysis and workup.

Stereochemistry of Alkylidenecarbene Adducts. The adduct stereochemistry was assigned by critical analysis of the NMR data coupled with the independent synthesis of one of the adduct pairs. The important features of the proton NMR of the *pairs* of all isobutylene adducts are summarized in Chart I. Two trends are clearly evident and consistent with the stereochemical assignments from the data in Chart I. First, as expected,¹⁵ the homoallylic coupling between the exocyclic methyl and the cyclopropane hydrogens is always larger for the *E* isomer (i.e., anti or trans coupling) than for the corresponding *Z* isomer (i.e., syn or cis coupling). Second, the qualitative expectation of van der Waals deshielding^{16,17} for the cyclopropyl protons in the *E* isomers, with

than aryl-substituted alkenes avoids the problem of thermal isomerization to indenenes. Moreover, control experiments with adduct 18 established that no product isomerization occurs under

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Scheme III. Independent Synthesis of Adducts **13Z** and **13E**

the bulky substituents on the same side as the cyclopropyl protons, is clearly seen. The same trend, although somewhat more complicated and less pronounced, was also seen for all pairs of the *tert*-butylethylene adducts **17**, **18**, and **19**.

Next, the 300-MHz ^1H as well as the ^{13}C NMR spectra of adducts **18E** and **18Z** were scrutinized (Chart II). In these adducts the methyls of the isopropyl group are diastereotopic because of the presence of the chiral center. It is evident from the spectra that both the proton and the carbon-13 chemical shift differences between the diastereotopic methyls are *larger* in the *Z* isomer than in the *E* isomer. Since the chemical shift difference of diastereotopic protons or groups is a function^{17,18} of proximity to a chiral center, these data further confirm our stereochemical assignment.

Finally, to unambiguously assign stereochemistry, adducts **13E** and **13Z** were independently synthesized as outlined in Scheme III. Reaction of commercial pentynol **20** with HCl gave propargyl chloride **21**.¹⁹ FeCl_3 -catalyzed addition of isopropyl-Grignard to **21** gave allene **22** and some alkyne.²⁰ Addition of dibromocyclopropane to this allene gave three adducts in the ratio indicated. These product ratios are in accord with expectations based on the selectivity of dibromocyclopropane²¹ and on analogies of dibromocyclopropane addition to similar allenes.^{22,23} Adducts **23–25** were separated by preparative gas chromatography and fully characterized by spectral means and literature analogies.^{22,23} Each of adducts **23** and **24** was separately reduced to the corresponding alkylidenecyclopropanes **13** with $(n\text{-Bu})_3\text{SnH}$.^{22,24} Although, as shown in Scheme III, some isomerization occurred in the final

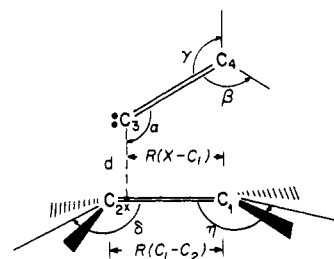


Figure 1. Definition of the geometrical parameters for the addition of alkylidenecarbenes to olefins.

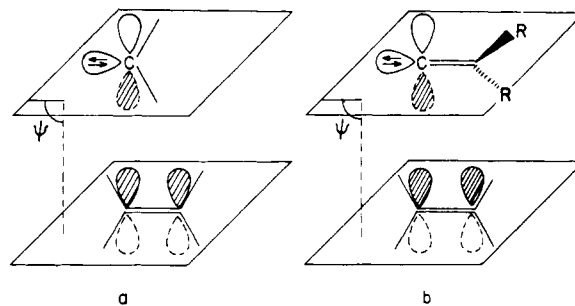


Figure 2. Electrophilic approaches of carbenes to olefins: (a) for a saturated carbene; (b) for an alkylidenecarbene.

tin hydride reduction, this is in accord with known²⁵ minor isomerization of allylic halide reductions (presumably via allylic radicals) with R_3SnH and the purported existence²⁶ of allylic radicals in some alkylidenecyclopropanes. Adducts **13Z** and **13E** prepared in Scheme III were identical with the appropriate alkylidenecarbene adducts of Table I.

Perusal of the data in Table I reveals a number of interesting trends. In general the total amount of adduct vs. products resulting from "insertion" and alkyl migration decreases²⁷ as the steric bulk of the carbene increases from ethyl to *tert*-butyl. Moreover, all addition reactions and most "insertion" reactions are stereoselective but not stereospecific. The stereoselectivity increases upon going from ethyl to *tert*-butyl substitution in the carbene and is more pronounced in the *tert*-butylethylene adducts than in the isobutylene adducts. All of these results are in accord with intuitive and qualitative expectations based upon the steric requirements of an *electrophilic, singlet* alkylidenecarbene-olefin interaction. Furthermore, in all cases there is a clear preference for formation of the sterically less demanding *E* adduct, clearly implying a very specific approach of the carbene to the olefin and a concomitant specific transition state for these reactions. In order to account for this preference and obtain further insight into the transition state, extensive and detailed theoretical calculations were carried out on these unsaturated carbene-olefin interactions.

B. Theoretical Studies. Theoretical molecular orbital calculations have provided important insights into the mechanism for reaction of saturated carbenes,^{3,4} but no calculations are available for the addition of alkylidenecarbenes to olefins. A priori, the only prediction that can be made is that the "least-motion" linear approach of alkylidenecarbenes to olefins is "symmetry forbidden" and is therefore expected to be high in energy.²⁸ In order to gain further insight into the reaction mechanism, we have investigated computationally the potential energy surface for the addition reactions of several alkylidenecarbenes, $\text{RR}'\text{C}=\text{C}$: ($\text{R} = \text{R}' = \text{H}$; $\text{R} = \text{H}$ and $\text{R}' = \text{CH}_3$, *i*-Pr, *t*-Bu; $\text{R} = \text{CH}_3$, $\text{R}' = \text{C}_2\text{H}_5$), to four olefins, $\text{RR}'\text{C}=\text{CH}_2$ ($\text{R} = \text{R}' = \text{H}$; $\text{R} = \text{H}$, $\text{R}' = \text{CH}_3$; $\text{R} = \text{H}$, $\text{R}' = t\text{-Bu}$; $\text{R} = \text{R}' = \text{CH}_3$). Most calculations were performed

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(23) Battioni, P.; Vo-Quang, L.; Vo-Quang, Y. *Bull. Soc. Chim. Fr.* **1970**, 3938.

(24) Seyferth, D.; Yamazaki, H.; Alleston, D. L. *J. Org. Chem.* **1963**, *28*, 703.

(25) Hoyte, R. M.; Denney, D. B. *J. Org. Chem.* **1974**, *39*, 2607.

(26) Lunazzi, L.; Placucci, G.; Grossi, L. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1063.

(27) The isopropyl system seems to be an anomaly for reasons that are not clear.

(28) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: Weinheim, 1970.

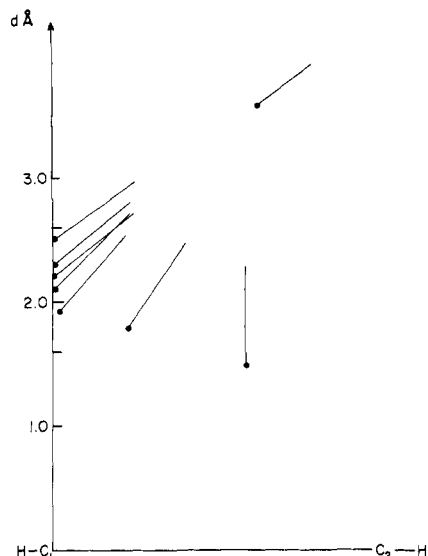
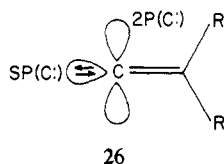


Figure 3. Geometry of approach of methylenecarbene to ethylene. The ethylene and carbene are seen edge on. The abscissa denotes the ethylenic bond length. The dots indicate successive positions of the carbenic carbon and the attached tails indicate the carbenic double bond.

with the MNDO method,²⁹ but the parent $\text{H}_2\text{C}=\text{C} + \text{H}_2\text{C}=\text{CH}_2$ system was also studied by standard ab initio methods at the minimal basis set (STO-3G³⁰) level. We study here only the reactions of singlet alkylidenecarbenes, because the triplet states are known to be 40–50 kcal mol⁻¹ higher in energy.² Experimental data support this choice.⁷ Only the most important conclusions of the calculations are discussed. More details will be published elsewhere.³¹

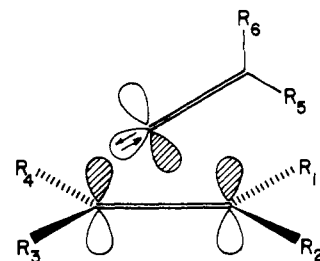
We have followed the usual practice of plotting the energy as a function of a suitable reaction coordinate, which we chose as the vertical distance between the carbene and the ethylenic C_1C_2 bond (Figure 1). The carbene's C_3 was connected to a "dummy" floating point X, which was allowed to slide along the C_1C_2 axis. At each value of d , the energy was optimized with respect to all the geometric parameters (Figure 1) unless otherwise stated, except that in the STO-3G calculations the C–H bond lengths were fixed at the MNDO values.

1. $\text{H}_2\text{C}=\text{C} + \text{H}_2\text{C}=\text{CH}_2$. Singlet alkylidenecarbenes (**26**) have an empty 2p orbital and a filled sp orbital. Qualitatively,

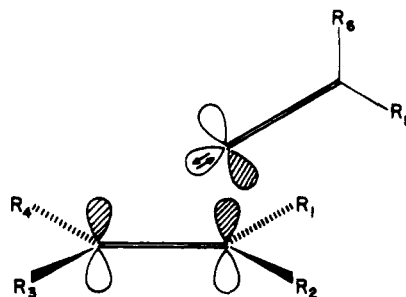


the favored approach of **26** to ethylene should be related to that of a saturated carbene and involve, at relatively large separations, interaction between the vacant 2p(C:) orbital and the ethylenic π bond (π approach³ or electrophilic phase⁴). At shorter distances, the carbene's lone pair would then become involved in bonding (σ approach³ or nucleophilic phase⁴). Comparison of the respective approaches (Figure 2) suggests that steric factors should be more important for alkylidenecarbenes.

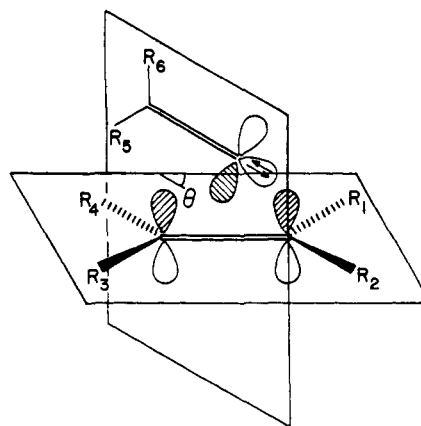
Four approaches of $\text{H}_2\text{C}=\text{C}$ to ethylene were investigated in detail. Three electrophilic approaches represented by **27a**–**29a**



- 27a**, $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{R}_4 = \text{R}_5 = \text{R}_6 = \text{H}$
27b, $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{R}_4 = \text{R}_6 = \text{H}$, $\text{R}_5 = \text{CH}_3$
27c, $\text{R}_3 = \text{R}_4 = \text{R}_6 = \text{H}$; $\text{R}_1 = \text{R}_2 = \text{R}_5 = \text{CH}_3$
27d, $\text{R}_1 = \text{R}_2 = \text{R}_6 = \text{H}$; $\text{R}_3 = \text{R}_4 = \text{R}_5 = \text{CH}_3$
27e, $\text{R}_1 = \text{R}_2 = \text{R}_4 = \text{R}_6 = \text{H}$; $\text{R}_3 = \text{R}_5 = \text{CH}_3$
27f, $\text{R}_1 = \text{R}_2 = \text{R}_4 = \text{R}_6 = \text{H}$; $\text{R}_3 = t\text{-Bu}$; $\text{R}_5 = \text{CH}_3$
27g, $\text{R}_3 = \text{R}_4 = \text{H}$; $\text{R}_1 = \text{R}_2 = \text{R}_5 = \text{CH}_3$; $\text{R}_6 = \text{Et}, i\text{-Pr}, \text{ or } t\text{-Bu}$



- 28a**, $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{R}_4 = \text{R}_5 = \text{R}_6 = \text{H}$
28b, $\text{R}_1 = \text{R}_2 = \text{R}_6 = \text{H}$; $\text{R}_3 = \text{R}_4 = \text{R}_5 = \text{CH}_3$
28c, $\text{R}_1 = \text{R}_2 = \text{R}_4 = \text{R}_6 = \text{H}$; $\text{R}_3 = \text{R}_5 = \text{CH}_3$



- 29a**, $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{R}_4 = \text{R}_5 = \text{R}_6 = \text{H}$
29b, $\text{R}_1 = \text{R}_2 = \text{R}_6 = \text{H}$; $\text{R}_3 = \text{R}_4 = \text{R}_5 = \text{CH}_3$; $\theta = 90^\circ$
29c, $\text{R}_1 = \text{R}_2 = \text{R}_4 = \text{R}_6 = \text{H}$; $\text{R}_3 = \text{R}_5 = \text{CH}_3$; $\theta < 90^\circ$
29d, $\text{R}_1 = \text{R}_2 = \text{R}_4 = \text{R}_6 = \text{H}$; $\text{R}_3 = t\text{-Bu}$; $\text{R}_5 = \text{CH}_3$; $\theta < 90^\circ$
29e, $\text{R}_1 = \text{R}_2 = \text{R}_4 = \text{H}$; $\text{R}_3 = t\text{-Bu}$; $\text{R}_5 = \text{CH}_3$;
 $\text{R}_6 = \text{Et}, i\text{-Pr}, \text{ or } t\text{-Bu}$; $\theta < 90^\circ$

along with the "symmetry-forbidden" least-motion approach were analyzed. The "symmetry-forbidden" pathway was, as expected, highest in energy. Both MNDO and STO-3G calculations show that "inward" approach **27a** provides the lowest reaction path from reactants to products. Qualitative considerations and calculations also caused Hoffmann and co-workers³ to favor the analogous "inward" approach of methylene to ethylene. The "outward" (**28a**) and the "perpendicular" (**29a**, $\theta = 90^\circ$) approaches are higher in energy than **27a** and collapse upon full geometry optimization to **27a**. These reaction paths were studied by holding the floating point X on C_2 and the $\text{C}_1\text{C}_2\text{C}_3\text{C}_4$ dihedral angle at 180° and 90° , respectively. Under these constraints, at $d = 2.2 \text{ \AA}$ for example, **28a** is 2.4 kcal mol⁻¹ higher in energy than **27a**. The perpendicular approach, which has not been considered for saturated carbenes to our knowledge, was studied here as steric factors may favor it for alkylidenecarbenes (see later). A more detailed description

(29) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

(30) (a) Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 2191. (b) Calculations were carried out with the GAUSSIAN 70 series of programs: Hehre, W. J.; Latham, W. A.; Ditchfield, R.; Newton, M.; Pople, J. A., Program No. 236, QCPE, Indiana University, Bloomington, IN.

(31) Apeloig, Y.; Karni, M.; Stang, P. J.; Houk, K. N., manuscript in preparation.

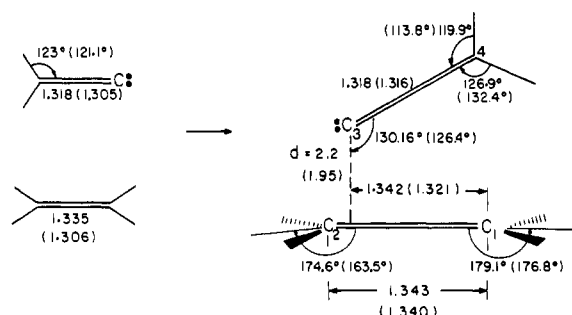


Figure 4. Calculated geometries of the transition state in the addition of $\text{H}_2\text{C}=\text{C}:$ to $\text{H}_2\text{C}=\text{CH}_2$ (MNDO, numbers in brackets are from STO-3G). The optimized geometries of the reactants are given on the left side of the figure.

of the inward approach follows.

a. Reaction Path of the "Inward" Approach. Figure 3 presents "snapshots" along the lowest energy path from reactants to products at MNDO. (Of course, the usual caveat applies that the computed lowest energy path is probably not the true reaction path. The calculations are primarily used here and in the following to locate and characterize transition states.) Even at relatively large separations, e.g., at $d = 2.8$ Å, the carbenic C_3 is located essentially above one of the ethylenic carbons with the carbene at the inward conformation. The carbene remains off center until the transition state is reached at ca. 2.2 Å and then slides "backward" toward the center of the ethylene. The carbene's tilt angle, α , opens simultaneously from ca. 129° – 134° at separations of 2.6–2.1 Å to 180° at 1.5 Å, and the ethylenic double bond lengthens from 1.343 Å at $d = 2.3$ Å to 1.469 Å at $d = 1.5$ Å (1.536 Å in methylenecyclopropane, MNDO). The bond angles of the carbenic hydrogens reflect the steric hindrance inherent in the inward approach, i.e., $\beta > \gamma$. Finally, the length of the carbenic double bond remains essentially unchanged along the entire reaction path.

b. The Transition State. The calculated geometries of the transition state at MNDO and STO-3G are given in Figure 4. With both methods, the transition state is characterized as "early" and possessing an off-center inward conformation.³² Thus, the developing cyclopropane σ bonds are not equal, $\text{C}_2\text{C}_3 = 2.20$ Å compared with $\text{C}_1\text{C}_3 = 2.57$ Å (MNDO; STO-3G values $\text{C}_2\text{C}_3 = 1.95$ Å and $\text{C}_1\text{C}_3 = 2.35$ Å). Similarly the C_3C_2 overlap population is nearly 10 times larger than the C_3C_1 overlap population (STO-3G). Charge transfer from ethylene to the carbene is small (0.13 and 0.06 electron at STO-3G and MNDO, respectively),³³ and the geometries of the carbene and the ethylene fragments at the transition state are very similar to those of the isolated reactants (Figure 4). The small substituent effects on the rates of addition of alkylidenecarbenes to olefins³⁴ are consistent with an "early" transition state. The transition state is reached at $d = 2.20$ and 1.95 Å according to MNDO and STO-3G, respectively. This large difference in the position of the transition state is disturbing. A similar discrepancy was found in the addition of methylene to ethylene.^{4,35} We favor the STO-3G separation because d is even shorter at 3-21G (1.83 Å).³¹ Finally, we note the overall resemblance of this transition state to that in the addition of $\text{Cl}_2\text{C}:$ to ethylene.⁴

The activation energy for the favored inward approach is 9.5 kcal mol⁻¹ (MNDO) and 10.0 kcal mol⁻¹ (STO-3G). These activation energies are probably too high,³⁶ but in the following

Table II. Activation Energies for the Addition of $\text{R}_5\text{R}_6\text{C}=\text{C}:$ to Various Olefins $\text{R}_1\text{R}_2\text{C}=\text{CR}_3\text{R}_4$ (MNDO)

| conformation | ΔH_f° ($d = \infty$), ^a kcal mol ⁻¹ | E_a , kcal mol ⁻¹ | d , Å ^b | θ , deg ^{c,d} |
|--------------|--|-----------------------------------|----------------------|-------------------------------|
| 27a | 136.9 | 9.5 | 2.2 | 0.0 |
| 27b | 125.2 | 11.4 | 2.1 | 0.0 |
| 27c | 107.8 | 13.5 | 2.1 | 0.0 |
| 27c | 107.8 | 14.2 ^e | 2.13 ^e | 0.0 ^{e,f} |
| 27d | 107.8 | 18.0 | 2.1 | 0.0 |
| 27d | 107.8 | 18.0 ^e | 2.08 ^e | 0.0 ^{e,f} |
| 27e | 114.7 | 14.7 | 2.1 | 6.3 ^f |
| 27f | 111.6 | 18.8 | 2.1 | 6.2 ^f |
| 29b | 107.8 | 14.8 | 2.1 | 84.1 ^f |
| 29b | 107.8 | 14.8 ^e | 2.06 ^e | 67.0 ^{e,f} |
| 29c | 114.7 | 11.7 | 2.1 | 42.6 ^f |
| 29d | 111.6 | 13.9 | 2.1 | 64.1 ^f |
| 30a | 121.3 | 14.5 | 2.1 | 0.0 |
| 30b | 119.7 | 14.0 | 2.1 | 0.0 |
| 30c | 102.4 | 18.0 | 2.1 | 15.9 ^f |

^a The sum of the heats of formation for the isolated reactants.

The following ΔH_f° were used (kcal mol⁻¹): $\text{CH}_2=\text{CH}_2$, 15.3; $\text{CH}_2=\text{C}(\text{CH}_3)_2$, -2.0; $\text{CH}_3\text{CH}=\text{CH}_2$, 4.9; $t\text{-BuCH}=\text{CH}_2$, 1.8; $\text{CH}_3\text{CH}=\text{C}:$, 109.8; $i\text{-PrCH}=\text{C}:$ (conformation as in 30), 104.4; $t\text{-BuCH}=\text{C}:$, 106.0. ^b Separation distance at the transition state.

^c The dihedral angle $\text{C}_4\text{C}_3 \times \text{C}_2\text{C}_1$ (Figure 1) at the transition state.

^d Not optimized unless otherwise indicated. ^e Transition state

located by minimizing the scalar gradient of the energy (see text).⁴¹ ^f Optimized.

we are mainly interested in energy differences between various transition states, where errors due to the computational methods are expected to cancel out. Note that at STO-3G the activation energy for the addition of $\text{H}_2\text{C}=\text{C}:$ to ethylene is 10 kcal mol⁻¹ higher than for the addition of methylene to ethylene (where no barrier was found⁴). This difference most likely results from more severe steric interactions in the alkylidenecarbene's transition state (see Figure 2).

2. Substituted Systems $\text{RCH}=\text{C}:$ + $\text{R}_1\text{R}_2\text{C}=\text{CH}_2$. In general, all geometrical parameters were optimized except for the CH bond lengths.³⁷ In analogy to the parent system, point X (Figure 1) was held at a distance of 1.35 Å from C_1 in the perpendicular and the outward approaches. Table II lists the transition states and activation energies obtained for the carbene additions discussed below.

a. $\text{RCH}=\text{C}:$ + $\text{H}_2\text{C}=\text{CH}_2$. Substitution of one of methylenecarbene's hydrogens by an alkyl group generates a set of two possible configurations for each transition state. In one the alkyl group points toward and in the other away from the ethylene. Only disubstituted carbenes have been studied experimentally, so model transition states where the alkyl group points toward the olefin are the most relevant, and these are reported here.³⁸ In addition, the substituent that points away from the olefin has little effect on activation energies (see section B.2b), so these transition states should accurately model those in the experimental systems.

As with methylenecarbene, the lowest reaction path when R

(32) The general features of the transition state remain unchanged at 3-21G.³¹

(33) This contrasts with the suggestion of Patrick and Newman that a dipolar intermediate is formed in these addition reactions.⁵

(34) Stang, P. J.; Madsen, J. R.; Mangum, M. G.; Fox, D. P. *J. Org. Chem.* 1977, 42, 1802.

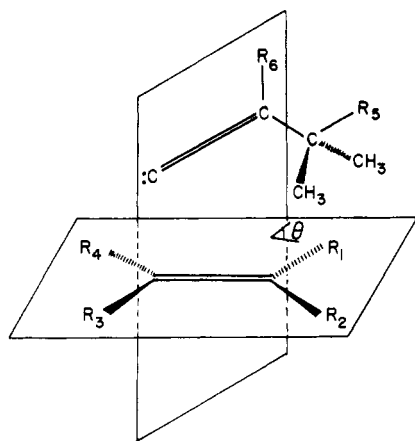
(35) Bodor, N.; Dewar, M. J. S.; Wasson, J. S. *J. Am. Chem. Soc.* 1972, 94, 9095.

(36) See for example: (a) Zurawski, B.; Kutzelnigg, W. *J. Am. Chem. Soc.* 1978, 100, 2654. (b) Bouma, W. J.; Vincent, M. A.; Radom, L. *Int. J. Quantum Chem.* 1978, 14, 767. (c) For example, in the addition of $\text{H}_3\text{P}:$ + $\text{H}_2 \rightarrow \text{PH}_3$, the activation energy is lowered from 116 kcal mol⁻¹ to 93 and 84 kcal mol⁻¹ by the addition of polarization functions and the inclusion of correlation energy, respectively: Kutzelnigg, W.; Wasilewski, J. *J. Am. Chem. Soc.* 1982, 104, 953. (d) A recent study^{36e} shows that calculations give a reasonable estimate of the activation enthalpies for carbene addition to olefins. $\Delta\Delta H^\ddagger$ for the addition of PhCCl to $n\text{-BuCH}=\text{CH}_2$ is -1.5 kcal mol⁻¹,^{36e} which is in reasonable agreement with MINDO/2³⁵ and STO-3G^{4,36a,b} calculations that predict $\Delta\Delta H^\ddagger < 0$. (e) Turro, N. J.; Lehr, G. F.; Butcher, J. A., Jr.; Moss, R. A.; Guo, W. *J. Am. Chem. Soc.* 1982, 104, 1754.

(37) These were held at 1.09 Å for the $\text{C}(\text{sp}^2)\text{-H}$ bonds (i.e., ethylenic or carbenic) and at 1.10 Å for the $\text{C}(\text{sp}^3)\text{-H}$ bonds (i.e., methylenic). This restriction slightly affects the total energy, but the relative energies of the different conformers are not changed by subsequent optimization of the C-H bond lengths.

(38) Inward transition states where the hydrogen points toward the alkene were determined and found to be lower in energy ($\sim 1\text{--}2$ kcal mol⁻¹ for alkyl = Me) than those where the alkyl group points toward the alkene.

= Me goes through inward transition state **27b**. Variation of R from methyl to larger groups increases the activation energy. When the methyl in **27b** is replaced by *tert*-butyl to give **30a**, the



30a, $R_1 = R_2 = R_3 = R_4 = R_5 = H$; $R_6 = CH_3$; inward ($\theta = 0^\circ$)
30b, $R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = H$; inward ($\theta = 0^\circ$)
30c, $R_1 = R_2 = CH_3$; $R_3 = R_4 = R_5 = R_6 = H$; inward ($\theta = 0^\circ$)
30d, $R_1 = R_2 = CH_3$; $R_3 = R_4 = R_5 = R_6 = H$; perpendicular ($\theta = 90^\circ$)

activation energy increases from 11.4 to 14.5 kcal mol⁻¹. The conformation shown in **30a** for the *tert*-butyl group was found to be the lowest energy arrangement for it. Replacement of R_5 with H (**30b**) decreased the activation energy by only 0.5 kcal mol⁻¹.³⁹ This small change indicates that isopropyl held in the indicated conformation should be an acceptable model for *tert*-butyl when more substituted systems are considered.

b. $RCH=C + (CH_3)_2C=CH_2$. In unsymmetrically substituted olefins such as isobutylene, the degeneracy of the olefinic carbons is lifted, and two distinct approaches, i.e., with initial attack at either C_1 or C_2 , exist for each of the reaction paths. We find that with all routes, i.e., inward, outward, or perpendicular, the carbene attacks at the unsubstituted carbon (here designated C_2). This is best rationalized by FMO theory,⁴⁰ which suggests that electrophilic attack should occur at the site with the largest coefficient in the highest occupied orbital (HOMO). In isobutylene these coefficients are 0.650 at C_2 vs. 0.579 at C_1 (STO-3G); attack therefore occurs at C_2 .

Several pathways pertinent to the experimental study were calculated for the addition of $CH_3CH=C$: to isobutylene (**27c**, **27d**, **28b**, and **29b**). As electronic effects override the steric effects in these approaches, structure **27c**, a " C_2 -inward" conformation, represents the lowest transition state. The activation energy is 13.5 kcal mol⁻¹ while that for the related C_1 -inward **27d** is higher at 18.0 kcal mol⁻¹, even though it is less crowded sterically. The " C_2 -perpendicular" (**29b**) and the C_2 -inward (**27c**) reaction paths are separated by a small energy barrier, but these merge at $d = 2.05$ Å; **29b** collapses to **27c** (Figure 5). An activation energy of 14.8 kcal mol⁻¹ was found for **29b**. The " C_2 -outward" **28b** is higher in energy than either **27c** or **29b**. Upon geometry optimization, **28b** collapses to **29b**.

As the $CH_3CH=C + H_2C=C(CH_3)_2$ system is of central importance in the comparison of the theoretical and the experimental results, several of the transition states were more accurately located by minimizing the scalar gradient of the energy and establishing that the Hessian matrix had only one negative eigenvalue.⁴¹ The results (Table II) are almost unchanged from

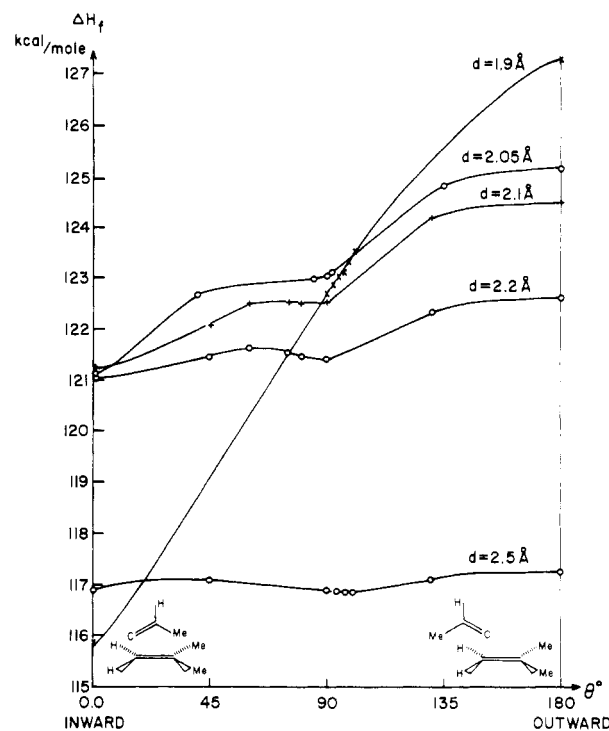


Figure 5. $CH_3CH=C + H_2C=C(CH_3)_2$: reaction energy profiles at various separation distances d for the "out-of-plane" rotation of $CH_3CH=C$: from the C_2 -outward to the C_2 -inward conformation (**28b** ($\theta = 180^\circ$) \rightarrow **29b** ($\theta \sim 90^\circ$) \rightarrow **27c** ($\theta = 0^\circ$), θ is the $C_1C_2C_3C_4$ dihedral angle).

those obtained by the regular Davidson-Fletcher-Powell optimization techniques^{41a} employed throughout this paper.

The lowest reaction path for the addition of *i*-PrCH=C: to isobutylene (isopropyl pointing toward the olefin) is the C_2 -inward approach (**30c**),³⁹ but the C_2 -perpendicular reaction path (**30d**) is only slightly higher in energy. Both **30c** and **30d** are energy minima on the potential energy surface, but only a small barrier separates the two paths. The activation energy for **30c** is 18.0 kcal mol⁻¹. For the similar addition of *t*-BuCH=C: to isobutylene, the activation energy is therefore also ca. 18 kcal mol⁻¹ (see section B.2a).

It was of interest to determine the effect on the transition state of the carbene substituent that points away from the olefin. The activation energies for the addition of $CH_3CH=C$: and of $CH_3CH_2(CH_3)C=C$: to isobutylene via C_2 -inward structures (with the methyl pointing toward the olefin in each case) were calculated and found to be 13.5 and 13.7 kcal mol⁻¹, respectively. This suggests that changing the substituent that points away from the olefin would not significantly affect the activation energies determined in this study.

c. $CH_3CH=C + CH_3CH=CH_2$ or *t*-BuCH=CH₂. With monosubstituted olefins such as propene or *tert*-butylethylene, the approaching carbene can meet either a face that is syn or one that is anti to the olefin's substituent R. The face syn to R is obviously more crowded. Approach of the carbene from the anti face was found to always be lower in energy than the corresponding syn attack.

Since the π bond of propene or *tert*-butylethylene is polarized similarly to that of isobutylene, the carbene was expected to preferentially attack the unsubstituted carbon (C_2). Indeed, for both alkenes the carbene was calculated to follow a path intermediate between the C_2 -inward and the anti C_2 -perpendicular approaches. These pathways are here designated "semiperpendicular" and are represented by structures **29c** and **29d**. At the transition state, the carbene is rotated by 42.6° in **29c** and by 64.1° in **29d** (Table II). Beyond each transition state, the carbene rotates to a C_2 -inward conformation and then collapses to product. Activation energies for addition via **29c** and **29d** are 11.7 and 13.9 kcal mol⁻¹, respectively. The activation energies

(39) The *i*-Pr group was held as in **30b** (i.e., at the same configuration relative to the double bond as in **30a**) even though this conformation is not the lowest in energy.

(40) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: London, 1976.

(41) (a) Fletcher, R.; Powell, M. J. D. *Comput. J.* **1963**, *6*, 163. Davidson, W. C. *Ibid.* **1968**, *10*, 406. Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (b) McIver, J. W., Jr.; Komornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625; **1973**, *95*, 4512. McIver, J. W., Jr. *Acc. Chem. Res.* **1974**, *7*, 72. (c) Dewar, M. J. S.; Ford, G. P.; McKee, M. L.; Rzepa, H. S.; Thiel, W.; Yamaguchi, Y. *J. Mol. Struct.* **1978**, *43*, 135. (d) Poppinger, D. *Chem. Phys. Lett.* **1975**, *35*, 550.

for syn approaches are higher, e.g., by 2.4 kcal mol⁻¹ with propene. As before, the C₂-outward reaction paths are considerably higher in energy and collapse upon geometry optimization to the semiperpendicular conformations.

As anticipated, attack at C₁ was higher in energy than attack at C₂ for both alkenes. The energy difference between the C₂ and C₁ transition states is 3.0 and 4.9 kcal mol⁻¹ for propene (i.e., **29c**–**27e**) and *tert*-butylethylene (i.e., **29d**–**27f**), respectively. For comparison, the energy difference is 4.5 kcal mol⁻¹ when isobutylene is the olefin (i.e., **27c**–**27d**). The lower energy difference for propene compared to isobutylene results from a lower polarization of the HOMO.⁴² Since polarization of the HOMO is essentially identical in CH₃CH=CH₂ and *t*-BuCH=CH₂,⁴² the high energy difference between **27f** and **29d** presumably results from steric effects that increase the activation energy for attack at C₁ more than at C₂. In the C₁-inward transition state, the carbenic C₃ is closer to the *tert*-butyl group on C₁ than in the C₂-semiperpendicular state. Thus, while the C₂-semiperpendicular transition state is 2.2 kcal mol⁻¹ higher with *tert*-butylethylene than with propene, the difference in the corresponding C₁-inward transition states is 4.1 kcal mol⁻¹.

C. Comparison of the Experimental and the Theoretical Results.

1. Stereoselectivity. Complete calculations for the systems that were studied experimentally are prohibitively expensive. To reduce the computation time, we omitted the carbenic substituent that points away from the olefin. This substituent was determined not to affect the activation energy of a particular reaction path relative to other approaches (see section B.2b). CH₃CH=C: can, therefore, serve as a model for approaches of the larger carbenes that were studied experimentally (i.e., *t*-Bu(CH₃)C=C:, *i*-Pr(CH₃)C=C:, and C₂H₅(CH₃)C=C: where the methyl points toward the olefin).

The results of the calculations can be used to predict the major product in the addition of these carbenes to isobutylene and to *tert*-butylethylene. With CH₃CH=C: as a model, the calculations show, *vide supra*, that the lowest transition states for addition to isobutylene and to *tert*-butylethylene are the C₂-inward (i.e., **27g**) and the C₂-semiperpendicular (i.e., **29e**) structures, respectively. Transition states **27g** lead to the *E*-substituted alkylidenecyclopropanes **11E**, **13E**, and **15E**. Similarly, **29e** collapse to the corresponding C₂-inward conformations and then to the corresponding *E* products **17E**, **18E**, and **19E**. Thus, in agreement with experiment (Table I), the calculations predict that the major products in the addition of *t*-Bu(CH₃)C=C:, *i*-Pr(CH₃)C=C:, and C₂H₅(CH₃)C=C: to either isobutylene or *tert*-butylethylene are the *E* isomers.

The determination of the transition states that lead to *Z* products is not as straightforward. The addition of *t*-Bu(CH₃)C=C: to isobutylene is considered first. Two configurations, the C₁-inward (modeled by **27d**, *E*_a = 18.0 kcal mol⁻¹) and the C₂-inward with the *tert*-butyl group pointing toward the olefin (modeled by **30c**, *E*_a ≈ 18 kcal mol⁻¹—see section B.2b), are essentially equal in energy and were found to be the second lowest in energy to **27c** (*E*_a = 13.5 kcal mol⁻¹, model for **27g** with R₆ = *t*-Bu). Both transition states progress to *Z* product which for *t*-Bu(CH₃)C=C: would be **15Z**. The theoretical *E*:*Z* product ratio is determined by the difference between the activation energies of model transition states **27c** and **27d** (or **30c**), which in this case is 4.5 kcal mol⁻¹. The experimental product ratio **15E**:**15Z** is 67:33, which corresponds to an energy difference of only 0.4 kcal mol⁻¹ at 25 °C. The calculations account for the formation of the *E* isomer as the major product but overestimate the degree of stereoselectivity. This is the major shortcoming of using a relatively simple theoretical method such as MNDO for this problem.⁴³ Preliminary MNDO calculations that include correlation energy,⁴⁴ preliminary 3-21G calculations,³¹ and various

qualitative arguments suggest that the reaction path MNDO artificially raises in energy is **27d** rather than **30c**. Therefore, in the addition of *t*-Bu(CH₃)C=C: to isobutylene, the major *E* product is produced via a C₂-inward transition state and the minor *Z* product via a C₁-inward transition state, both with the smaller methyl pointing toward the olefin.

In the addition of *i*-Pr(CH₃)C=C: and of C₂H₅(CH₃)C=C: to isobutylene, the preferred C₂-inward and the C₁-inward configurations are not affected by substituting the remote *tert*-butyl group by isopropyl or ethyl. The same stereoselectivity as with *t*-Bu(CH₃)C=C: should result. However, with *i*-Pr(CH₃)C=C: and C₂H₅(CH₃)C=C:, the C₂-inward structures with the larger groups pointing toward the isobutylene are considerably lower in energy than with *t*-Bu(CH₃)C=C:. This is because the isopropyl and the ethyl substituents can rotate to a conformation in which (as with methyl) only a hydrogen is pointing toward the olefin. Thus, the energy difference between the C₂-inward transition states where either methyl or isopropyl (or ethyl) point toward the olefin is expected to be small, and a very low stereoselectivity should result. With C₂H₅(CH₃)C=C:, the experimental *E*:*Z* product ratio is 57:43, which corresponds to an energy difference of only 0.17 kcal mol⁻¹ (at 25 °C). It can be concluded that in the addition of *i*-Pr(CH₃)C=C: or C₂H₅(CH₃)C=C: to isobutylene both the *E* and *Z* products are produced via C₂-inward transition states with the methyl pointing toward or away, respectively, from the olefin.

The addition of *t*-Bu(CH₃)C=C: to *t*-BuCH=CH₂ is now considered. The lowest transition state is the anti C₂-semiperpendicular one (modeled by **29d**), which leads to the major product **19E**. The *Z* product is obtained via the C₁-inward transition state (modeled by **27f**). As with isobutylene, the calculated *E*:*Z* product ratio is too high. However, the calculations predict correctly the higher stereoselectivity that is observed with *tert*-butylethylene than with isobutylene. The calculated energy differences between the model transition states leading to the *E* and the *Z* products are 4.9 kcal mol⁻¹ for *tert*-butylethylene and 4.5 kcal mol⁻¹ for isobutylene. Thus, in the reaction with *t*-Bu(CH₃)C=C:, *tert*-butylethylene is calculated to be more selective than isobutylene by 0.4 kcal mol⁻¹. This difference is in good agreement with the experimental *E*:*Z* product ratios of 90:10 and 67:33, respectively, that correspond to transition-state free energy differences of 1.3 and 0.4 kcal mol⁻¹, respectively. The stereoselectivity of the addition of *i*-Pr(CH₃)C=C: or of C₂H₅(CH₃)C=C: to *tert*-butylethylene is, as expected from previous discussion, smaller than that of *t*-Bu(CH₃)C=C:.

Predictions for Other Systems. The insight that was gained through the calculations can be used to predict the stereoselectivity in similar addition reactions. The electronic properties of the olefinic substituents can be manipulated to yield the desired stereoselectivity. According to FMO, preferred attack occurs at the atom that possesses the highest coefficient in the relevant frontier orbitals (i.e., the olefinic π bond).⁴⁰ The polarizing effect of various substituents has been analyzed in the literature for monosubstituted olefins.⁴⁵ In most cases, e.g., R = alkyl, vinyl, phenyl, OR, and SR, the HOMO is polarized toward the unsubstituted carbon.^{40,45} An alkylidenecarbene such as *t*-Bu(CH₃)C=C: should then attack each of these alkenes preferentially at C₂ so that the major reaction product would be the *E* isomer. In general, the expectation is that the stronger the polarization of the HOMO, the higher the stereoselectivity should be. The extent of the polarization can be represented by the calculated ratio of the coefficients at the two olefinic centers (C = C₂/C₁). Although the absolute values of the coefficients are

(42) The HOMO (π bond) coefficients are as follows (MNDO): in propene C₁ = 0.667, C₂ = 0.689, C₂/C₁ = 1.033; in isobutylene C₁ = 0.6467, C₂ = 0.678, C₂/C₁ = 1.049; in *tert*-butylethylene C₁ = 0.665, C₂ = 0.688, C₂/C₁ = 1.035.

(43) Other factors such as the effect of solvation or entropy that are not included in the calculations may also contribute to this discrepancy.

(44) Single-point calculations at the optimized MNDO geometries were carried out with the MND0C program, which uses a perturbational approach (BWEN) for calculating the correlation energy. The following heats of formation (kcal mol⁻¹) were obtained: **27c**, 98.7; **27d**, 101.3; **29b**, 98.7. Thus, the **27c**–**27d** energy difference is 2.6 kcal mol⁻¹, which is in closer agreement with experiment than the MNDO results.

(45) (a) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779. Eisenstein, O.; Lefour, J. M.; Anh, N. T.; Hudson, R. F. *Tetrahedron* **1977**, *33*, 523. (b) Houk, K. N. *J. Am. Chem. Soc.* **1973**, *95*, 4092. Houk, K. N.; Sims, J.; Watts, C. R.; Luskus, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 7301.

Table III. Relative Addition Rates of $\text{Cl}_2\text{C}:$, $(\text{CH}_3)_2\text{C}=\text{C}:$, and $(\text{CH}_3)_2\text{C}=\text{C}=\text{C}:$ to Olefins

| olefin | relative rates | | | ionization potential, eV ^d |
|---|--|---|-------------------------------------|---------------------------------------|
| | $(\text{CH}_3)_2\text{C}=\text{C}:$ ^a | $(\text{CH}_3)_2\text{C}=\text{C}=\text{C}:$ ^b | $\text{Cl}_2\text{C}:$ ^c | |
| $(\text{CH}_3)_2\text{C}=\text{CH}_2$ | 1.00 | 1.0 | 1.0 | 9.24 |
| $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$ | 1.55 | | 0.011 | 9.63 |
| <i>cis</i> - $\text{CH}_3\text{CH}=\text{CHCH}_3$ | 8.73 | | 0.23 | 9.12 |
| <i>trans</i> - $\text{CH}_3\text{CH}=\text{CHCH}_3$ | 1.64 | 0.4 | 0.15 | 9.12 |
| cyclohexene | 9.10 | | | 8.94 |
| $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2$ | 2.73 | 2.55 | 3.05 | 8.68 |
| $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$ | 0.24 | 5.55 | 7.41 | 8.27 |
| $\text{H}_2\text{C}=\text{CH}(\text{OEt})$ | 23.0 | | | |

^a Reference 2. ^b Reference 48. ^c Moss, R. A.; Gerstl, R. J. *Org. Chem.* 1967, 32, 2268. ^d Experimental values, see: Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* 1977, 60, 2213.

dependent on the computational method, the trends are not, and they therefore have predictive significance.⁴⁵ Alkyl groups, which are the sole substituents that were tested experimentally, have weak directing effects. Much higher *E:Z* product ratios are predicted for $\text{H}_2\text{C}=\text{CH}(\text{C}_6\text{H}_5)$, $\text{H}_2\text{C}=\text{CH}(\text{SCH}_3)$, and $\text{H}_2\text{C}=\text{CH}(\text{OCH}_3)$ on the basis of their *C* values.⁴⁶ We stress that the *C* values should be regarded only as qualitative guides for stereoselectivity predictions.

The relative sizes of the olefinic and carbenic substituents can also affect the resulting stereoselectivity. For large alkyl substituents in the alkene such as *tert*-butyl, a significant steric effect is anticipated. With $(t\text{-Bu})_2\text{C}=\text{CH}_2$, for example, the electronically favored C_2 -inward transition state should be destabilized significantly by strong steric repulsions, and attack should occur preferentially at C_1 yielding the *Z* product. For the carbenic substituents, only when they differ significantly in their sizes (as in $t\text{-Bu}(\text{CH}_3)\text{C}=\text{C}:$) should high stereoselectivity be expected. In this respect, high stereoselectivity should result when $\text{AdCH}_3\text{C}=\text{C}:$ (Ad = adamantyl) is employed. Approaches of this carbene where the bulky adamantyl group points toward the olefin are essentially blocked.

Finally, when steric and electronic effects do not distinguish one carbon or the other in the alkene (e.g., in propene), low stereoselectivity should be observed. Experimental testing of the preceding predictions is in progress.

2. Relative Rates. Unlike most saturated carbenes⁴⁷ and unsaturated extended carbenes such as $(\text{CH}_3)_2\text{C}=\text{C}=\text{C}:$,⁴⁸ that react faster with the electron-rich tetramethylethylene (TME) than with less substituted alkenes, alkylidenecarbenes react slower (Table III). In addition to the stereoselectivity results, the theoretical model should also account for this different reactivity of alkylidenecarbenes. Unfortunately, calculations of the activation energies for the addition of $(\text{CH}_3)_2\text{C}=\text{C}:$ to all the olefins of interest are prohibitively expensive.

The contrasting behavior of saturated carbenes and alkylidenecarbenes can be understood qualitatively by a combination of electronic and steric effects. Electronically, the higher the energy of the olefin's HOMO (i.e., a lower ionization potential), the faster the addition reaction should occur. Thus, alkyl substitution that lowers the ionization potential of the olefin should increase its reactivity. This is indeed the order of reactivity with electrophilic saturated carbenes^{47,49} and with $(\text{CH}_3)_2\text{C}=\text{C}=\text{C}:$ (Table III). The reactivity order for $(\text{CH}_3)_2\text{C}=\text{C}:$ can be understood

if it is assumed that the transition states for these addition reactions have perpendicular or semiperpendicular geometries (e.g., **29b** or **29c**) rather than inward geometries (e.g., **27c**). With $\text{CH}_3\text{C}=\text{H}=\text{CH}_2$ and with $t\text{-BuCH}=\text{CH}_2$, the calculated transition states indeed possess semiperpendicular geometries (i.e., **29c** and **29d**, respectively). With isobutylene, the semiperpendicular conformation is only 1.3 kcal mol⁻¹ higher than that of the inward conformation (Table II), but the relative energy of these may be reversed at higher levels of theory, as preliminary STO-3G⁵⁰ and MNDOC⁴⁴ calculations indicate. Most importantly, a semiperpendicular geometry at the transition state with isobutylene is fully consistent with the stereoselectivity results (see section C.1).

The results in Table III are consistent with increasing reactivity of the olefin upon additional alkyl substitution (electronic effect) provided that there is reduced steric interaction in the semiperpendicular transition state. The lower reactivity of isobutylene relative to 1-butene results from steric interactions between the alkylidenecarbene and one of the isobutylene methyls that raise the energy of the semiperpendicular transition state. These steric interactions are absent in 1-butene where $(\text{CH}_3)_2\text{C}=\text{C}:$ can attack from the face anti to the ethyl substituent. The higher reactivity of *cis*- compared to *trans*-2-butene can be explained similarly. In *trans*- $\text{CH}_3\text{CH}=\text{CHCH}_3$, attack from either side of the olefin is hindered by a methyl group, while in *cis*- $\text{CH}_3\text{CH}=\text{CHCH}_3$ one side is not hindered to attack. Trimethylethylene reacts faster than *trans*-2-butene because the additional methyl enhances the reactivity electronically without hindering further the semiperpendicular transition state of the carbene. Further addition of a methyl to give $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$ increases the addition rate with saturated electrophilic carbenes. Similarly, $\text{R}_2\text{C}=\text{C}=\text{C}:$ and $\text{R}_2\text{C}=\text{C}=\text{C}=\text{C}:$ (no steric problems for either) react roughly 5 times faster with TME than with isobutylene. In contrast, alkylidenecarbenes react 4 times slower with TME than with isobutylene, or approximately 20 times slower than one would predict on electronic grounds alone, because both sides of the olefin are blocked by two methyls.

Conclusion

We have established experimentally that unsymmetrical alkylidenecarbenes add to unsymmetrical alkenes to give a predominance of the *E* over the *Z* adduct. Stereoselectivity increases as a function of the increasing size of the β -substituent of the carbene and also upon changing the substrate from isobutylene to *tert*-butylethylene. Carbene-olefin additions are highly exothermic, and hence it is not surprising that the highest stereoselectivity observed was only 90/10, an energy difference of only about 1 kcal mol⁻¹ at -20 °C.

The theoretical calculations are in complete qualitative harmony (albeit not in quantitative agreement with the actual energy differences based upon the observed stereoselectivities) with the experimental facts. In particular, the transition states proposed to be favored nicely rationalize both the observed stereoselectivities and the relative reactivities.

Specifically, the favored pathway of approach of $\text{R}(\text{CH}_3)\text{C}=\text{C}:$ to isobutylene is through C_2 -inward transition states that then proceed to the favored *E* adducts. The corresponding transition states for *tert*-butylethylene are anti C_2 -semiperpendicular ones that progress through C_2 -inward conformations to the *E* products. The *Z* adducts arise in both cases from C_1 -inward transition states. Higher stereoselectivity than seen with *tert*-butylethylene is predicted for olefins with strong polarizing substituents such as $\text{H}_2\text{C}=\text{CH}(\text{OCH}_3)$ and styrene. Furthermore, the anti semiperpendicular transition state explains the unusual reactivities of alkylidenecarbenes, i.e., the faster reactivity of *cis* over *trans* substrates, the faster reactivity of a monosubstituted alkene (such as 1-butene) over a 1,1-disubstituted one (isobutylene), and the still higher reactivity of a trisubstituted olefin (trimethylethylene). A rigorous test that our model meets is the satisfactory explanation

(46) *C* values (MNDO): $\text{CH}_3\text{CH}=\text{CH}_2$, 1.033; $t\text{-BuCH}=\text{CH}_2$, 1.035; $\text{CH}_2=\text{C}(\text{CH}_3)_2$, 1.049; $\text{CH}_2=\text{CH}(\text{SCH}_3)$, 1.380; $\text{CH}_2=\text{CH}(\text{OCH}_3)$, 1.384; $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$, 1.393.

(47) Moss, R. A. *Acc. Chem. Res.* 1980, 13, 58.

(48) Stang, P. J.; Fisk, T. E. *J. Am. Chem. Soc.* 1980, 102, 6813.

(49) One exception stands out. $\text{Cl}_2\text{C}:$ reacts with isobutylene 5–6 times faster than with *cis*- or *trans*-2-butene, although the ionization potential of the former is higher. This may be explained, however, by a polar transition state where the partial positive charge on the olefin is better stabilized by a *gem*-dimethyl substituent.

(50) The STO-3G transition states are located at a closer separation distance than the corresponding MNDO transition states (section B.1b). Steric effects are expected, therefore, to be more important with STO-3G.

of the unusually slow reactivity of tetramethylethylene toward alkylidenecarbenes. The fourth substituent has fully sterically "blocked" all the possible low-energy attacks of the alkylidenecarbene and, consequently, has raised the activation energy for this reaction despite the favorable electronic factors.

Experimental Section

General. All boiling points are uncorrected. Analytical weights were measured on a Mettler H33AR or H18 balance. Infrared spectra were recorded on a Beckman IR5A, Beckman Acculab 3, or Perkin-Elmer 298 infrared spectrometer and are reported in wavenumbers (cm^{-1}) calibrated to the 1602-cm^{-1} absorption of polystyrene. ^1H NMR spectra were recorded on a Varian A-60, EM-360, EM-390, or SC300 (300 MHz) spectrometer, and all values are given in δ (ppm) relative to internal tetramethylsilane (Me_4Si , δ 0) except where indicated otherwise. Determinations of isomer or product ratios by ^1H NMR are averages of several integrations. For ^{13}C NMR, a Varian SC300 (75 MHz) spectrometer with Fourier transform capability was utilized. The instrument was locked on internal CDCl_3 , and the shifts given are relative to internal Me_4Si (δ 0). Mass spectra were recorded on an AEI MS-30 mass spectrometer system or on a Varian MAT-112 gas chromatograph-mass spectrometer equipped with GC columns containing either 1% SE-30 or 1% OV-17 as stationary liquid phase. Mass spectra are recorded as m/z (relative intensity). Preparative GC was accomplished on a Varian Aerograph 90-P or 920 gas chromatograph. Analytical GC was carried out on a Hewlett-Packard 700 flame ionization gas chromatograph connected to a Hewlett-Packard 3370B integrator or a Hewlett-Packard 5710A flame ionization gas chromatograph connected to a Hewlett-Packard 3380A integrator. Columns used in this work are as follows: A, 0.25 in. \times 5 ft 10% SF-96 on 60-80 Chromosorb W; B, 0.25 in. \times 5 ft 15% SF-96 on 45-60 Chromosorb W; C, 0.25 in. \times 8 ft 15% Carbowax 20M on 60-80 Chromosorb W; D, 0.25 in. \times 25 ft 20% Apiezon J on 60-80 Chromosorb W; E, 0.375 in. \times 15 ft 15% QF-1 on 45-60 Chromosorb W; F, 0.375 in. \times 25 ft 20% Carbowax 20M on 30-60 Chromosorb W; G, 0.125 in. \times 6 ft 10% UCW-982 on 80-100 Chromosorb W; H, 0.125 in. \times 6 ft 10% Carbowax 20M on 80-100 Chromosorb W; I, 0.125 in. \times 15 ft 15% QF-1 on 100-120 Chromosorb W; J, 0.125 in. \times 20 ft 10% Apiezon J on 100-120 Chromosorb W; K, 0.125 in. \times 25 ft 15% Carbowax 20M on 100-120 Chromosorb W. Columns G and H were stainless steel while all the others were aluminum.

Materials. The preparation of $\text{Me}(\text{Et})\text{C}=\text{C}(\text{H})\text{OSiMe}_3$ and triflate 7 have been previously¹¹ reported as part of the general procedures for the respective synthesis of trimethylsilyl enol ethers and primary vinyl triflates. These procedures were also utilized here for the new enol ethers and triflates prepared in this investigation, with any differences noted. 3,3-Dimethyl-1-butene (*tert*-butylethylene, Aldrich) was distilled from CaH_2 before use. Isobutylene (Phillips Pure Grade, 99 mol % minimum) was used as received. For GC coinjection and spectral comparison, 2-pentyne, 4-methyl-2-pentyne, and 4,4-dimethyl-2-pentyne (all from Chemical Samples) were employed. Sodium borohydride (Alfa) and tri-*n*-butyltin hydride (Alfa) were used as obtained. Potassium *tert*-butoxide was either prepared¹¹ or obtained commercially (Alfa) and then doubly sublimed.

Silyl Enol Ether from 2,3-Dimethylbutanal. 2,3-Dimethylbutanal^{12,13} (23.1 g, 0.23 mol) with the general¹¹ procedure gave after 37 h of reflux (disappearance of aldehyde monitored on column A at 100 °C) and standard workup 31.2 g (78%) of a 63:37 mixture (NMR)⁵¹ of (*E*)- and (*Z*)-trimethyl[(2,3-dimethyl-1-butenyl)oxy]silanes, $\text{Me}(\text{i-Pr})\text{C}=\text{C}(\text{H})\text{OSiMe}_3$: bp 71.5-73 °C (44 mm); IR (neat) 1664 ($\text{C}=\text{C}$), 1253, 1179, 879, 843 cm^{-1} ; ^1H NMR (neat, external Me_4Si) (*E* isomer) δ 0.34 (s, 9, SiMe_3), 1.21 (d, 6, J = 6.8 Hz, Me_2C), 1.73 (d, 3, J = 1.5 Hz, $\text{CH}_3\text{C}=\text{C}$), 2.42 (m, 1, *i*-PrCH), 6.27 (m, 1, $\text{HC}=\text{C}$), (*Z* isomer) δ 0.34 (s, 9, SiMe_3), 1.17 (d, 6, J = 7.0 Hz, Me_2C), 1.63 (d, 3, J = 1.5 Hz, $\text{CH}_3\text{C}=\text{C}$), 3.28 (m, 1, *i*-PrCH), 6.10 (m, 1, $\text{HC}=\text{C}$).

Silyl Enol Ether from 2,3,3-Trimethylbutanal. 2,3,3-Trimethylbutanal was prepared by a previously described procedure.¹⁴ From this procedure, a 4:1 mixture of 2,3,3-trimethylbutanal and 2,3,3-trimethyl-2-butanol was obtained in 18% yield. Treatment of 19 g of this mixture (0.133 mol of aldehyde, 0.033 mol of alcohol) by the general method produced after 4.5 days of reflux (disappearance of aldehyde monitored on column A at 95 °C) and standard workup 24.4 g of products: bp 78-83 °C (45 mm). Two main components were found in a 1:3 ratio and were separated on column A at 105 °C. The faster eluting minor compound was trimethyl(2,3,3-trimethyl-2-butoxy)silane, $\text{Me}_2\text{C}(\text{i-Bu})\text{C}=\text{C}(\text{H})\text{OSiMe}_3$ (6.2 g): IR (neat) 2960, 1252, 1160, 1042, 838 cm^{-1} ; ^1H NMR (CCl_4 , external Me_4Si) δ 0.03 (s, 9, SiMe_3), 0.84 (s, 9, *i*-Bu), 1.14 (s, 6, Me_2C). The slower eluting major fraction was an 89:11 mixture (NMR) of (*E*)- and (*Z*)-trimethyl[(2,3,3-trimethyl-1-butenyl)oxy]silanes, $\text{Me}(\text{i-Bu})\text{C}=\text{C}(\text{H})\text{OSiMe}_3$ (18.2 g, 75%): IR (neat) 1653 ($\text{C}=\text{C}$), 1253, 1162, 1123, 882, 842 cm^{-1} ; ^1H NMR (CCl_4 , external Me_4Si) (*E* isomer) δ 0.08 (s, 9, SiMe_3), 0.96 (s, 9, *i*-Bu), 1.49 (d, 3, J = 1.4 Hz, $\text{CH}_3\text{C}=\text{C}$), 5.97 (m, 1, J = 1.4 Hz, $\text{HC}=\text{C}$), (*Z* isomer) δ 0.08 (s, 9, SiMe_3), 1.06 (s, 9, *i*-Bu), 1.42 (d, 3, J = 1.5 Hz, $\text{CH}_3\text{C}=\text{C}$), 5.78 (m, 1, J = 1.5 Hz, $\text{HC}=\text{C}$).

Triflates 8E and 8Z. A 63:37 mixture (NMR) of (*E*)- and (*Z*)- $\text{Me}(\text{i-Pr})\text{C}=\text{C}(\text{H})\text{OSiMe}_3$ (31.0 g, 0.18 mol) gave after standard procedure¹¹ a 79:21 mixture (NMR) of (*E*)- and (*Z*)-2,3-dimethyl-1-butenyl triflates (8E and 8Z, 22.3 g, 53%) and 2-((trifluoromethyl)sulfonyl)-2,3-dimethylbutanal (C-triflated product, α -sulfonylaldehyde, 5.9 g, 14%); the boiling point of the 79:21 mixture was 69-71 °C (29 mm). As the α -sulfonylaldehyde was not removed by the standard NaHSO_3 wash, the following procedure was employed to remove it. The triflate/ α -sulfonylaldehyde mixture was added to 140 mL of slightly basic methanol. To the stirred methanol solution was added 1.1 g (0.028 mol) of NaBH_4 over a 10-min period. After addition was complete, the mixture was stirred for 0.5 h and then 250 mL of cold water was added to it. The two-phase system was extracted with four 250-mL portions of pentane. Following drying of the organic layer by CaCl_2 , the pentane was removed with a rotary evaporator. The light yellow residue was vacuum distilled through a short Vigreux column. After a small forecut containing some 2,3-dimethylbutanal, 20.7 g (93% recovery) of >99% pure (column A, 100 °C) 8E and 8Z distilling from 71 to 73 °C (30 mm) was obtained. The isomers were found to be in a 70:30 *E*:*Z* ratio (NMR)⁵³ and were separated by preparative GC on column E at 95 °C. For 8E: IR (neat) 3114 ($\text{HC}=\text{C}$), 1674 ($\text{C}=\text{C}$), 1426, 1250, 1212, 1148, 1020, 980 cm^{-1} ; ^1H NMR (neat) δ 1.05 (d, 6, J = 6.8 Hz, Me_2C), 1.70 (d, 3, J = 1.6 Hz, $\text{CH}_3\text{C}=\text{C}$), 2.22 (m, 1, Me_2CH), 6.46 (br s, 1, $\text{HC}=\text{C}$); mass spectrum, 232 (M^+ , 8), 86 (10), 84 (12), 83 (15), 82 (46), 81 (29), 71 (15), 69 (90), 67 (57), 65 (13), 59 (33), 55 (100), 53 (25), 51 (11), 49 (25). For 8Z: IR (neat) 3098 ($\text{HC}=\text{C}$), 1673 ($\text{C}=\text{C}$), 1425, 1252, 1213, 1150, 1027, 983, 868 cm^{-1} ; ^1H NMR (neat) δ 1.02 (d, 6, J = 7.0 Hz, Me_2C), 1.58 (d, 3, J = 1.6 Hz, $\text{CH}_3\text{C}=\text{C}$), 3.02 (m, 1, Me_2CH), 6.31 (br s, 1, $\text{HC}=\text{C}$); mass spectrum, 232 (M^+ , 2), 83 (13), 82 (33), 81 (22), 71 (12), 69 (83), 67 (42), 65 (10), 59 (25), 55 (100), 53 (26), 49 (13).

Triflates 9E and 9Z. A 3:1 mixture of $\text{Me}(\text{i-Bu})\text{C}=\text{C}(\text{H})\text{OSiMe}_3$ (18.2 g, 0.10 mol) and $\text{Me}_2\text{C}(\text{i-Bu})\text{OSiMe}_3$ (6.2 g, 0.033 mol) gave after standard workup an 85:15 mixture (NMR) of (*E*)- and (*Z*)-2,3-trimethyl-1-butenyl triflates (9E and 9Z, 10.6 g, 44%) and 2-((trifluoromethyl)sulfonyl)-2,3,3-trimethylbutanal (α -sulfonylaldehyde, 1.9 g, 8%); the boiling point of the 85:15 mixture was 68-70 °C (17 mm). (The $\text{Me}_2\text{C}(\text{i-Bu})\text{OSiMe}_3$ did not react and was removed together with some 9 by fractional distillation.) The triflate was freed of α -sulfonylaldehyde in the same manner as was triflate 8. After isolation by distillation at 66-68 °C (14 mm), an 82% recovery of 9 resulted. Through NMR analysis the *E*:*Z* ratio was determined to be 89:11. For 9E and 9Z: IR (neat) 3145 ($\text{HC}=\text{C}$), 1661 ($\text{C}=\text{C}$), 1424, 1248, 1209, 1147, 1049, 1007, 973, 868 cm^{-1} ; ^1H NMR (CCl_4) (9E) δ 1.15 (s, 9, *i*-Bu), 1.80 (d, 3, $\text{CH}_3\text{C}=\text{C}$), 6.65 (br s, 1, $\text{HC}=\text{C}$), (9Z) δ 1.23 (s, 9, *i*-Bu), 1.72 (d, 3, $\text{CH}_3\text{C}=\text{C}$), 6.52 (br s, 1, $\text{HC}=\text{C}$); mass spectrum, 9E 246 (M^+ , 3), 231 (18), 113 (12), 98 (17), 97 (52), 96 (31), 81 (56), 79 (36), 73 (25), 69 (91), 67 (15), 61 (37), 57 (85), 55 (100), 53 (58), 49 (17); 9Z 246 (M^+ , 4), 231 (19), 113 (16), 98 (15), 97 (71), 96 (40), 81 (52), 79 (40), 73 (21), 69 (84), 67 (13), 61 (36), 57 (100), 56 (12), 55 (94), 53 (50), 49 (11). For mass spectra, 9E and 9Z were separated by preparative GC on column E at 100 °C.

General Procedure for the Reaction of Triflates 7-9 with KO-*t*-Bu. Into an appropriate round-bottom flask equipped with a stirring bar and either a serum cap or a vacuum stopcock were added KO-*t*-Bu (50% excess) and either *tert*-butylethylene or isobutylene as solvent. When isobutylene or only a small amount of *tert*-butylethylene was used as solvent, a wired-on vacuum stopcock was employed instead of a serum cap to prevent solvent loss. Isobutylene was condensed into the reaction flask by means of a dry ice-isopropyl alcohol condenser. The base-olefin mixture was cooled to the indicated reaction temperature for reactions in *tert*-butylethylene and to -78 °C for those in isobutylene, and triflate was either added via a syringe or was rinsed through the vacuum stopcock with a small amount of the appropriate olefin. Reactions were monitored by GC for disappearance of triflate. For isobutylene reactions, trial reactions were utilized to determine the time required for complete re-

(51) Trimethylsilyl enol ethers are known to give thermodynamic product ratios when prepared in the indicated fashion.⁵²

(52) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. J. Org. Chem. 1969, 34, 2324.

(53) The isomers were assigned on the basis of expected van der Waals deshielding^{16,17} of the β -methyl and the vinylic proton in the *E* isomer relative to those in the *Z* isomer. Similar deshielding was observed in the corresponding trimethylsilyl enol ethers.

action. As the reaction proceeded, reaction mixtures generally turned yellow. Small-scale analytical reactions were analyzed directly by GC whereas preparative reactions were first extracted with small portions of water and then dried with MgSO_4 . The aqueous layer was back extracted with either pentane or ether. Solvents were removed by distillation, and products were isolated through preparative GC. In isobutylene reactions, the isobutylene was distilled from the reaction mixture at 5 °C and an equal volume of pentane or ether was added before GC analysis or water extraction.

Reaction of Triflates 7E and 7Z in Isobutylene. A mixture of triflates 7E and 7Z (5.0 mmol, 62% E:38% Z) was treated with 7.5 mmol of base in 20 mL of isobutylene for 3 days at -20 °C. After workup and removal of solvents, analysis of the residue on column F at 90 °C showed it to contain 15% vinyl ether 12Z, 34% vinyl ether 12E, 21% adduct 11Z, and 30% adduct 11E. The four products were each obtained pure from column F at 90 °C. For (Z)-1-tert-butoxy-2-methyl-1-butene (12Z): IR (CCl_4) 1678 ($\text{C}=\text{C}$), 1460, 1393, 1368, 1195, 1149 ($\text{C}-\text{O}$), 896 cm^{-1} ; ^1H NMR (CCl_4) δ 0.93 (t, 3, $J = 7.3$ Hz, CH_3), 1.22 (s, 9, *t*-Bu), 1.53 (d, 3, $J = 1.4$ Hz, $\text{CH}_3\text{C}=\text{C}$), 2.05 (m, 2, $J = 7.3$ Hz, CH_2), 5.92 (br s, 1, $\text{HC}=\text{C}$); mass spectrum, 142 (M^+ , 21), 86 (89), 71 (100), 68 (16), 59 (15), 58 (15), 57 (88), 56 (14), 55 (11), 43 (22), 41 (65). For (E)-1-tert-butoxy-2-methyl-1-butene (12E): IR (CCl_4) 1672 ($\text{C}=\text{C}$), 1458, 1391, 1366, 1193, 1152 ($\text{C}-\text{O}$), 898 cm^{-1} ; ^1H NMR (CCl_4) δ 0.98 (m, 3, CH_3), 1.22 (s, 9, *t*-Bu), 1.55 (m, 3, $\text{CH}_3\text{C}=\text{C}$), 1.93 (m, 2, CH_2), 6.02 (m, 1, $\text{HC}=\text{C}$); mass spectrum, 142 (M^+ , 19), 86 (86), 71 (100), 68 (15), 59 (25), 58 (16), 57 (82), 56 (15), 55 (13), 44 (11), 43 (21), 41 (69). For (Z)-1,1-dimethyl-2-(2-butyldiene)cyclopropane (11Z): IR (CCl_4) 3020 (cyclopropyl H), 2983, 2875, 1775 ($\text{C}=\text{C}$), 1462, 1452, 1372, 1128 cm^{-1} ; ^1H NMR (CCl_4) δ 0.75 (m, 2, cyclopropyl), 1.05 (m, 3, CH_3), 1.16 (s, 6, Me_2C), 1.76 (m, 3, $^5J = 1.5$ Hz, $^4J = 0.5$ Hz, $\text{CH}_3\text{C}=\text{C}$), 2.12 (m, 2, CH_2); mass spectrum, 124 (M^+ , 5), 109 (15), 86 (16), 68 (12), 67 (48), 57 (100), 56 (67), 55 (23), 53 (13), 43 (86), 42 (49). For (E)-1,1-dimethyl-2-(2-butyldiene)cyclopropane (11E): IR (CCl_4) 3020 (cyclopropyl H), 2962, 2938, 2906, 2875, 2856, 1776 ($\text{C}=\text{C}$), 1455, 1374 cm^{-1} ; ^1H NMR (CCl_4) δ 0.87 (m, 2, cyclopropyl), 1.06 (m, 3, CH_3), 1.15 (s, 6, Me_2C), 1.77 (m, 3, $^5J = 1.8$ Hz, $^4J = 0.5$ Hz, $\text{CH}_3\text{C}=\text{C}$), 2.13 (m, 2, CH_2); mass spectrum, 124 (M^+ , 8), 109 (22), 95 (13), 86 (16), 81 (12), 69 (10), 68 (19), 67 (72), 57 (100), 56 (69), 55 (33), 53 (20), 44 (14), 43 (90), 42 (50).

Analytical Reactions of Triflates 7E and 7Z in Isobutylene. As reported in a prior investigation,¹¹ individual small-scale reactions (0.30 mmol) of both pure 7E and pure 7Z in isobutylene led within experimental error to the same product distribution: 7.5% 12Z, 18.8% 12E, 31.9% 11Z, and 41.8% 11E. An additional product found through GC analysis was later identified as 2-pentyne through coinjection with authentic material on both columns J and K. The alkyne was formed to the extent of an average value for the two reactions of $10.5 \pm 0.6\%$ of total products.

Reaction of Triflates 8E and 8Z in Isobutylene. A mixture of triflates 8E and 8Z (10 mmol, 70% E:30% Z) was treated with 15 mmol of base in 75 mL of isobutylene for 4 days at -20 °C. Analysis of the mixture on column G at 45 °C showed it to contain 3% 4-methyl-2-pentyne, 23% vinyl ethers 14E and 14Z, 30% adduct 13Z, and 44% adduct 13E. The five products were obtained from column B at 70 °C. Vinyl ethers 14E and 14Z were obtained together (77% 14E:23% 14Z determined by NMR) and were later separated on column E at 85 °C. The collected alkyne was identified by spectral comparison with authentic material. For (Z)-1-tert-butoxy-2,3-dimethyl-1-butene (14Z): IR (neat) 1673 ($\text{C}=\text{C}$), 1392, 1367, 1262, 1194, 1146 ($\text{C}-\text{O}$) cm^{-1} ; ^1H NMR (CCl_4) δ 0.92 (d, 6, Me_2CH), 1.20 (s, 9, *t*-Bu), 1.43 (d, 3, $J = 1.5$ Hz, $\text{CH}_3\text{C}=\text{C}$), 2.69 (m, 1, HCMe_2), 5.78 (m, 1, $\text{HC}=\text{C}$); mass spectrum, 156 (M^+ , 2), 100 (20), 85 (100), 82 (15), 57 (66), 55 (15). For (E)-1-tert-butoxy-2,3-dimethyl-1-butene (14E): IR (neat) 1673 ($\text{C}=\text{C}$), 1464, 1393, 1368, 1260, 1238, 1198, 1168 ($\text{C}-\text{O}$), 1126, 1073, 904 cm^{-1} ; ^1H NMR (CCl_4) δ 0.98 (d, 6, Me_2CH), 1.20 (s, 9, *t*-Bu), 1.49 (d, 3, $J = 1.4$ Hz, $\text{CH}_3\text{C}=\text{C}$), 2.17 (m, 1, HCMe_2), 5.96 (m, 1, $\text{HC}=\text{C}$); mass spectrum, 156 (M^+ , 3), 100 (23), 85 (100), 82 (13), 57 (39). For (Z)-1,1-dimethyl-2-(3-methyl-2-butyldiene)cyclopropane (13Z): IR (neat) 1764 ($\text{C}=\text{C}$), 1466, 1451, 1368, 1124, 1102, 1050, 978 cm^{-1} ; ^1H NMR (CCl_4) δ 0.68 (m, 2, CH_2), 1.02 (d, 6, $J = 6.8$ Hz, Me_2CH), 1.13 (s, 6, Me_2C), 1.68 (t, 3, $^5J = 1.5$ Hz, $\text{CH}_3\text{C}=\text{C}$), 2.30 (m, 1, HCMe_2); 75-MHz ^{13}C NMR ($\text{CDCl}_3/\text{CCl}_4$, 2:1) δ 15.9, 17.4, 18.6, 21.7, 25.1, 34.4, 126.7, 129.9; mass spectrum, 138 (M^+ , 27), 123 (64), 109 (25), 95 (31), 91 (12), 82 (64), 81 (50), 79 (23), 77 (10), 70 (94), 69 (21), 68 (33), 67 (100), 55 (83), 53 (31). For (E)-1,1-dimethyl-2-(3-methyl-2-butyldiene)cyclopropane (13E): IR (neat) 1767 ($\text{C}=\text{C}$), 1449, 1370, 1115, 982 cm^{-1} ; ^1H NMR (CCl_4) δ 0.87 (m, 2, CH_2), 1.02 (d, 6, $J = 6.5$ Hz, Me_2CH), 1.13 (s, 6, Me_2C), 1.68 (t, 3, $^5J = 1.9$ Hz, $\text{CH}_3\text{C}=\text{C}$), 2.34 (m, 1, HCMe_2); 75-MHz ^{13}C NMR ($\text{CDCl}_3/\text{CCl}_4$, 2:1) δ 13.8, 17.7, 18.2, 21.3, 24.0, 34.4, 126.2, 128.9; mass spectrum, 138 (M^+ , 26), 123

(45), 109 (24), 96 (24), 95 (28), 84 (21), 83 (10), 82 (50), 81 (51), 79 (15), 77 (12), 70 (74), 69 (34), 68 (26), 67 (100), 57 (16), 56 (12), 55 (70), 53 (29).

Reaction of Triflates 9E and 9Z in Isobutylene. A mixture of triflates 9E and 9Z (9.2 mmol, 89% E:11% Z) was treated with 13.7 mmol of base in 55 mL of isobutylene for 60 h at -20 °C. Analysis of the mixture on column A at 82 °C showed it to contain 38% 4,4-dimethyl-2-pentyne, 47% vinyl ether 16E, 5% adduct 15Z, and 10% adduct 15E. The four products were obtained from column A at 80 °C. The collected alkyne was identified by spectral comparison with authentic material. For (E)-1-tert-butoxy-2,3,3-trimethyl-1-butene (16E): IR (neat) 1658 ($\text{C}=\text{C}$), 1366, 1256, 1193, 1155, 1120 ($\text{C}-\text{O}$) cm^{-1} ; ^1H NMR (CCl_4) δ 1.01 (s, 9, *t*-Bu), 1.20 (s, 9, *t*-BuO), 1.52 (d, 3, $J = 1.3$ Hz, $\text{CH}_3\text{C}=\text{C}$), 5.98 (m, 1, $J = 1.3$ Hz, $\text{HC}=\text{C}$); mass spectrum, 170 (M^+ , 12), 114 (30), 100 (12), 99 (100), 58 (19), 57 (69), 56 (13), 55 (17), 43 (45), 41 (55). For (Z)-1,1-dimethyl-2-(3,3-dimethyl-2-butyldiene)cyclopropane (15Z): IR (neat) 1734 ($\text{C}=\text{C}$), 1483, 1461, 1372, 1362, 1218, 1152, 1129, 1102 cm^{-1} ; ^1H NMR (CCl_4) δ 0.64 (m, 2, $^5J = 1.5$ Hz, CH_2), 1.06 (s, 9, *t*-Bu), 1.13 (s, 6, Me_2C), 1.73 (t, 3, $^5J = 1.5$ Hz, $\text{CH}_3\text{C}=\text{C}$); mass spectrum, 152 (M^+ , 32), 137 (17), 109 (32), 97 (18), 96 (88), 95 (20), 84 (96), 81 (97), 79 (11), 69 (100), 67 (32), 57 (38), 56 (14), 55 (39), 53 (19), 43 (70), 41 (65). For (E)-1,1-dimethyl-2-(3,3-dimethyl-2-butyldiene)cyclopropane (15E): IR (neat) 1762 ($\text{C}=\text{C}$), 1479, 1461, 1452, 1372, 1362, 1140, 1107 cm^{-1} ; ^1H NMR (CCl_4) δ 0.98 (m, 2, CH_2), 1.06 (s, 9, *t*-Bu), 1.11 (s, 6, Me_2C), 1.73 (t, 3, $^5J = 1.9$ Hz, $\text{CH}_3\text{C}=\text{C}$); mass spectrum, 152 (M^+ , 43), 137 (19), 109 (33), 97 (12), 96 (94), 95 (22), 84 (97), 81 (98), 79 (11), 77 (12), 69 (100), 67 (31), 57 (29), 56 (13), 55 (27), 53 (18), 43 (18), 41 (59).

Reaction of Triflates 7E and 7Z in *tert*-Butylethylene. A mixture of triflates 7E and 7Z (7.5 mmol, 62% E:38% Z) was treated with 11.3 mmol of base in 80 mL of *tert*-butylethylene for 36 h at -20 °C. Analysis of the mixture on column G at 90 °C showed it to contain 37% vinyl ethers 12E and 12Z and 63% adducts 17E and 17Z. After removal of most of the *tert*-butylethylene, adducts 17E and 17Z were separated and obtained with column D at 120 °C. A ratio of 67% 17E:33% 17Z was observed. For (Z)-1-tert-butyl-2-(2-butyldiene)cyclopropane (17Z): IR (neat) 1776 ($\text{C}=\text{C}$), 1462, 1443, 1362, 1256, 1195, 1183, 955 cm^{-1} ; ^1H NMR (CCl_4) δ 0.73 (m, 2, cyclopropyl CH_2), 0.87 (s, 9, *t*-Bu), 1.04 (t, 3, CH_3), 1.36 (m, 1, HC), 1.78 (m, 3, $\text{CH}_3\text{C}=\text{C}$), 2.18 (m, 2, CH_2); mass spectrum, 152 (M^+ , 7), 137 (16), 123 (24), 110 (12), 96 (20), 95 (32), 86 (51), 82 (13), 81 (100), 79 (14). For (E)-1-tert-butyl-2-(2-butyldiene)cyclopropane (17E): IR (neat) 1773 ($\text{C}=\text{C}$), 1462, 1441, 1387, 1360, 1259, 1195, 1185, 988, 980 cm^{-1} ; ^1H NMR (CCl_4) δ 0.78 (m, 2, cyclopropyl CH_2), 0.88 (s, 9, *t*-Bu), 1.05 (t, 3, CH_3), 1.33 (m, 1, CH), 1.78 (m, 3, $\text{CH}_3\text{C}=\text{C}$), 2.17 (m, 2, CH_2); mass spectrum, 152 (M^+ , 8), 137 (19), 123 (27), 110 (15), 109 (10), 96 (21), 95 (39), 86 (37), 82 (11), 81 (100), 79 (19), 77 (13).

Analytical Reaction of Triflates 7E and 7Z in *tert*-Butylethylene. A mixture of triflates 7E and 7Z (0.2 mmol, 62% E:38% Z) in 2 mL of *tert*-butylethylene was degassed⁵⁴ by two freeze-thaw cycles and vacuum transferred to a flask that contained 0.3 mmol of base. After 14 h of reaction at -15 °C, the reaction mixture was analyzed on column J at 25-130 °C and found to contain 30% 2-pentyne, 6% vinyl ether 12Z, 16% vinyl ether 12E, 16% adduct 17Z, and 32% adduct 17E. The presence of 2-pentyne was confirmed by coinjection of the reaction mixture with an authentic sample on both column J and column K.

Reaction of Triflates 8E and 8Z in *tert*-Butylethylene. A mixture of triflates 8E and 8Z (8 mmol, 70% E:30% Z) was treated with 12 mmol of base in 85 mL of *tert*-butylethylene for 48 h at -20 °C. Analysis of the mixture on column G at 80 °C showed it to contain 41% vinyl ethers 14E and 14Z and 59% adducts 18E and 18Z. The vinyl ethers were found to be in a 78% E:22% Z ratio on column I at 90 °C. Separation and isolation of adducts 18E and 18Z were achieved on column D at 120 °C where they were found in a 75% E:25% Z ratio. The presence of 4-methyl-2-pentyne in the reaction mixture was confirmed by coinjection with authentic material on column J at 80 °C and on column K at 100 °C. For (Z)-1-tert-butyl-2-(3-methyl-2-butyldiene)cyclopropane (18Z): IR (neat) 1760 ($\text{C}=\text{C}$), 1464, 1360, 1256, 1195, 1142, 1000 cm^{-1} ; 300-MHz ^1H NMR ($\text{CDCl}_3/\text{CCl}_4$, 2:1) δ 0.68 (m, 1, cyclopropyl), 0.84 (m, 1, cyclopropyl), 0.88 (s, 9, *t*-Bu), 1.008 (d, 3, $J = 7.0$ Hz, *i*-Pr Me), 1.034 (d, 3, $J = 7.0$ Hz, *i*-Pr Me), 1.40 (m, 1, $\text{HC}-t\text{-Bu}$), 1.70 (m, 3, $\text{CH}_3\text{C}=\text{C}$), 2.68 (m, 1, $J = 7.0$ Hz, HCMe_2); 75-MHz ^{13}C NMR ($\text{CDCl}_3/\text{CCl}_4$, 2:1) δ 3.7, 15.0, 20.96, 21.13, 28.5, 28.7, 30.6, 35.0, 118.7, 130.1; mass spectrum, 166 (M^+ , 7), 151 (24), 137 (13), 123 (26), 110 (15), 109 (21), 96 (13), 95 (73), 81 (100), 79 (12), 77 (10), 70 (83), 69 (15), 68 (10), 67 (32), 57 (46), 55 (53), 53 (17). For (E)-1-tert-bu-

(54) Degassing increased the amount of 2-pentyne formed by 40% over that formed in an identical reaction that was not degassed. Isomer ratios and the ratio of adducts to vinyl ethers were not affected by degassing.

tyl-2-(3-methyl-2-butyldiene)cyclopropane (**18E**): IR (neat) 1760 (C=C), 1464, 1362, 1259, 1193, 1138, 999 cm^{-1} ; 300-MHz ^1H NMR ($\text{CDCl}_3/\text{CCl}_4$, 2:1) δ 0.78 (m, 1, cyclopropyl), 0.87 (s, 9, *t*-Bu), 0.95 (m, 1, cyclopropyl), 1.042 (d, 3, $J = 6.9$ Hz, *i*-Pr Me), 1.050 (d, 3, $J = 6.9$ Hz, *i*-Pr Me), 1.28 (m, 1, HC-*t*-Bu), 1.76 (m, 3, $\text{CH}_3\text{C}=\text{C}$), 2.50 (m, 1, $J = 6.9$ Hz, HCMe₂); 75-MHz ^{13}C NMR ($\text{CDCl}_3/\text{CCl}_4$, 2:1) δ 5.0, 18.6, 21.28, 21.39, 25.8, 28.6, 30.6, 35.0, 118.1, 130.0; mass spectrum, 166 (M^+ , 6), 151 (23), 123 (15), 110 (11), 109 (19), 96 (17), 95 (58), 91 (12), 82 (11), 81 (96), 79 (14), 77 (14), 70 (100), 69 (16), 68 (10), 67 (34), 65 (14), 57 (48), 56 (15), 55 (73), 54 (13), 53 (22), 52 (31).

Reaction of Triflates **9E and **9Z** in *tert*-Butylethylene.** A mixture of triflates **9E** and **9Z** (10 mmol, 89% *E*:11% *Z*) was treated with 15 mmol of base in 150 mL of *tert*-butylethylene for 60 h at -20°C and then 24 h at 5°C . Analysis of the mixture on column G at 90°C showed it to contain 39% 4,4-dimethyl-2-pentyne, 17% vinyl ether **16E**, 41% adduct **19E**, and 3% adduct **19Z**. Identity of the alkyne was established through coinjection with authentic material on column G at 25°C and on column K at 110°C . Separation and isolation of the other products were achieved with column D at 120°C . For (*E*)-1-*tert*-butyl-2-(3,3-dimethyl-2-butyldiene)cyclopropane (**19E**): IR (neat) 3025 (cyclopropyl H), 1758 (C=C), 1478, 1467, 1453, 1393, 1374, 1365, 1262, 1158, 1142 cm^{-1} ; ^1H NMR (CCl_4) δ 0.75–1.25 (m, 3, CH_2 and CH), 0.88 (s, 9, *t*-Bu), 1.10 (s, 9, *t*-BuC=C), 1.80 (m, 3, $\text{CH}_3\text{C}=\text{C}$); mass spectrum, 180 (M^+ , 7), 165 (24), 137 (21), 124 (32), 123 (24), 110 (13), 109 (85), 95 (46), 84 (100), 81 (29), 70 (17), 69 (65), 68 (14), 67 (21), 57 (100), 55 (15), 53 (10). For (*Z*)-1-*tert*-butyl-2-(3,3-dimethyl-2-butyldiene)cyclopropane (**19Z**): IR (CCl_4) 3025 (cyclopropyl H), 1746 (C=C), 1478, 1467, 1397, 1375, 1367, 1262, 1200, 1156, 1052 cm^{-1} ; ^1H NMR (CCl_4) δ 0.59 (m, 2, CH_2), 0.91 (s, 9, *t*-Bu), 1.11 (s, 9, *t*-BuC=C), 1.47 (m, 1, CH), 1.80 (m, 3, $\text{CH}_3\text{C}=\text{C}$); mass spectrum, 180 (M^+ , 4), 165 (19), 137 (18), 124 (25), 123 (22), 110 (10), 109 (70), 95 (36), 84 (100), 81 (27), 70 (18), 69 (66), 68 (11), 67 (19), 57 (87), 55 (20).

Analytical Reaction of Triflates **9E and **9Z** in *tert*-Butylethylene.** A mixture of triflates **9E** and **9Z** (0.2 mmol, 89% *E*:11% *Z*) in 2 mL of *tert*-butylethylene was degassed by three freeze-thaw cycles and vacuum transferred into a flask that contained 0.3 mmol of base. After 120 h of reaction at -15°C , the reaction mixture was analyzed on column G at 25 – 100°C and found to contain 56% 4,4-dimethyl-2-pentyne, 16% vinyl ether **16E**, 25.2% adduct **19E**, and 2.8% adduct **19Z**.

Synthesis of Alkylidenecyclopropanes **23, **24**, and **25**.** The cyclopropanes were prepared by the general route for alkylidenecyclopropane synthesis from allenes developed by Rahman and Kuivila.²² A 64:36 mixture of 2,4,5-trimethyl-2,3-hexadiene (**22**) and 4,5,5-trimethyl-2-hexyne²⁰ (0.64 g of allene, 5.2 mmol) was utilized in this preparation. The presence of the alkyne did not interfere to any noticeable extent in the synthesis. After workup, 0.8 g (52%) of a mixture of **23**, **24**, and **25** distilling from 29 to 31°C at approximately 0.005 mm was obtained. Analysis on column H at 110°C showed the mixture to be 66% **23**, 5% **24**, and 29% **25**. The individual isomers were separated by preparative GC on column C at 115°C . For (*E*)-1,1-dibromo-2,2-dimethyl-3-(3-methyl-2-butyldiene)cyclopropane (**23**): IR (neat) 2965, 2930, 2875, 1755 (C=C), 1462, 1441, 1375, 1369, 757 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.06 (d, 6, Me_2CH), 1.44 (s, 6, Me_2C), 1.94 (s, 3, $\text{CH}_3\text{C}=\text{C}$), 2.36 (m, 1, HCMe₂); mass spectrum, 294, 296, 298 (M^+ , 3.6, 6.8, 4.0), 217 (35), 215 (31), 147 (13), 145 (16), 136 (82), 135 (64), 121 (64), 120 (11), 119 (19), 107 (27), 105 (27), 94 (16), 93 (37), 91 (55), 81 (12), 79 (36), 78 (17), 77 (59), 70 (100), 67 (17), 65 (36), 63 (12), 57 (11), 55 (45), 53 (39), 52 (12), 51 (31). For (*Z*)-1,1-dibromo-2,2-dimethyl-3-(3-methyl-2-butyldiene)cyclopropane (**24**): IR (CCl_4) 2966, 2930, 2875, 1757 (C=C), 1462, 1454, 1442, 1372, 1367 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.18 (d, 6, Me_2CH), 1.45 (s, 6, Me_2C), 1.76 (s, 3, $\text{CH}_3\text{C}=\text{C}$), 2.80 (m, 1, HCMe₂); mass spectrum, 294, 296, 298 (M^+ , 0.5, 1.1, 0.5), 136 (31), 135 (23), 121 (31), 107 (15), 105 (17), 93 (27), 91 (45), 81 (14), 79 (30), 78 (12), 77 (57), 70 (100), 67 (14), 65 (35), 63 (11), 57 (15), 55 (56), 53 (42), 52 (11), 51 (27). For 1,1-dibromo-2-isopropyl-2-methyl-3-isopropylidenecyclopropane (**25**): IR (neat) 2967, 2935, 2875, 1755 (C=C), 1465, 1443, 1372, 1020, 762 cm^{-1} ; ^1H NMR (CCl_4) δ 1.07 (d, 6, Me_2CH), 1.24 (s, 3, $\text{CH}_3\text{C}-i\text{Pr}$), 1.5–2.0 (m, 1, HCMe₂), 1.83 (s, 3, $\text{CH}_3\text{C}=\text{C}$), 1.92 (s, 3, $\text{CH}_3\text{C}=\text{C}$); mass spectrum, 294, 296, 298 (M^+ , 5, 13, 7), 217 (37), 215 (37), 147 (13), 145 (13), 137 (12), 136 (100), 135 (87), 134 (36), 122 (11), 121 (74), 120 (22), 119 (49), 117 (12), 107 (37), 106 (12), 105 (43), 103 (12), 95 (14), 94 (17), 93 (72), 92 (21), 91 (98), 81 (17), 79 (44), 78 (16), 77 (61), 70 (74), 69 (10), 67 (22), 66 (11), 65 (39), 63 (12), 57 (24), 55 (46), 53 (32), 52 (14), 51 (29).

Synthesis of Alkylidenecyclopropane **13Z from **23**.** This procedure was adapted from the work of Rahman and Kuivila²² and of Seyferth, Ya-

mazaki, and Alleston.²⁴ Into a 5-mL ampule equipped with a rubber serum cap and N_2 outlet and inlet were added 1 mL of pentane and 0.1189 g (0.4 mmol) of **23** (98% **23**, 2% **24**; column H, 110°C). The ampule was cooled in an ice bath and tri-*n*-butyltin hydride (0.2322 g, 0.8 mmol) was added dropwise with a syringe over a 0.5-h period. The reaction mixture was stirred for 0.5 h at 0°C , sealed off under N_2 , and allowed to stir at room temperature for 40 h. The pentane was then removed from the reaction mixture with a stream of N_2 and a 35°C oil bath into a receiving flask cooled by a dry ice-isopropyl alcohol bath. Only pentane was observed in the distillate through GC analysis. The reaction mixture was again sealed in an ampule and stirred at 35°C for 60 h. Following addition of 1.5 mL of pentane to the colorless reaction mixture, a vacuum transfer into a receiver cooled by liquid N_2 was done at room temperature and 0.025 mm to remove the volatiles from the tri-*n*-butyltin bromide formed in the reaction. Analysis of the transferred material on column G at 60 – 130°C revealed two low-boiling components in an 89:11 ratio and one high-boiling component. No **23** was seen. Preparative GC on column B at 80 – 140°C was utilized to isolate both alkylidenecyclopropane **13Z**, the major low-boiling component, and the high-boiling component. Spectral data obtained for **13Z** synthesized here exactly matched that of the minor carbene adduct isolated from the carbene reaction of triflate **8** in isobutylene (see previous section for reaction and spectral information). The minor low-boiling product was determined to be alkylidenecyclopropane **13E** through coinjection on both column G at 70°C and column K at 95°C with the major adduct obtained in the reaction of triflate **8** in isobutylene. The high-boiling component (37% of total products by GC integration) had spectral data consistent with those expected for the singly reduced monobromide, (*E*)-1-bromo-2,2-dimethyl-3-(3-methyl-2-butyldiene)cyclopropane: IR (neat) 2957, 2860, 1756 (C=C), 1461, 1447, 1370, 1184, 690 cm^{-1} ; ^1H NMR (CCl_4) δ 1.06 (d, 6, Me_2CH), 1.22 (s, 3, CH_3), 1.28 (s, 3, CH_3), 1.79 (m, 3, $\text{CH}_3\text{C}=\text{C}$), 2.32 (m, 1, HCMe₂), 3.24 (m, 1, HCB₂).

Synthesis of Alkylidenecyclopropane **13E from **24**.** Into a 2-mL glass tube was added a solution of **24** (0.4 mg, 1.4 μmol , >99.5% pure; column H, 110°C) in 20 μL of pentane. The glass tube was cooled in an ice bath and tri-*n*-butyltin hydride (0.8 mg, 2.7 μmol) in 20 μL of pentane was added. After the pentane was removed by a gentle stream of argon, the tube was sealed and placed in a 35°C oil bath for 60 h. To the colorless liquid was then added 50 μL of pentane, and GC analysis of the solution was carried out. Alkylidenecyclopropanes **13E** and **13Z** in a ratio of 95:5 were found to be present through double coinjection with isolated carbene adducts as described above. A small amount of presumed monobromide was also seen.

Stability of Alkylidenecyclopropanes **18E and **18Z** to Isomerization.** Into a 5-mL round-bottom flask equipped with a vacuum stopcock and a stirring bar were added 17 mg (0.15 mmol) of KO-*t*-Bu and a solution of 7 mg (0.05 mmol) of pure **18E** in 1 mL of *tert*-butylethylene. The mixture was allowed to stir at -15°C for 60 h. Analysis of the mixture on column J at 140°C showed that no isomerization of **18E** to **18Z** had occurred. A stock solution of pure **18Z** was also analyzed on column J at 140°C and only **18Z** was observed.

Stability of Vinyl Ether **12E to Isomerization.** Into a 5-mL round-bottom flask equipped with a vacuum stopcock and a stirring bar were added 17 mg (0.15 mmol) of KO-*t*-Bu and a solution of 3 mg (0.02 mmol) of pure **12E** in 1 mL of *tert*-butylethylene. The mixture was allowed to stir for 19 h at -15°C . Analysis of the mixture on column K at 80°C showed only **12E**; no **12Z** was observed.

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Registry No. **7E**, 53282-37-4; **7Z**, 53282-38-5; **8E**, 85851-23-6; **8Z**, 85851-24-7; **9E**, 85851-25-8; **9Z**, 85851-26-9; **10** ($R = \text{H}$), 70277-78-0; **10** ($R = \text{Et}$), 85851-29-2; **11Z**, 53282-44-3; **11E**, 53282-43-2; **12Z**, 53282-42-1; **12E**, 53282-41-0; **13Z**, 85851-36-1; **13E**, 85851-37-2; **14Z**, 85851-34-9; **14E**, 85851-35-0; **15Z**, 85851-39-4; **15E**, 85851-40-7; **16E**, 85851-38-3; **17Z**, 85851-41-8; **17E**, 85851-42-9; **18Z**, 85851-43-0; **18E**, 85882-50-4; **19E**, 85851-44-1; **19Z**, 85851-45-2; **23**, 85851-46-3; **24**, 85851-47-4; **25**, 85851-48-5; *i*-PCH=C, 85851-27-0; *t*-BuCH=C, 85851-28-1; $\text{H}_2\text{C}=\text{CH}_2$, 74-85-1; $\text{CH}_3\text{CH}=\text{CH}_2$, 115-07-1; (*E*)-Me(*i*-Pr)C=CHOSiMe₃, 85851-30-5; (*Z*)-Me(*i*-Pr)C=CHOSiMe₃, 85851-31-6; (*E*)-Me(*t*-Bu)C=CHOSiMe₃, 85851-32-7; (*Z*)-Me(*t*-Bu)C=CHOSiMe₃, 85851-33-8; $\text{H}_2\text{C}=\text{C}$, 2143-69-3; isobutylene, 115-11-7; *tert*-butylethylene, 558-37-2.