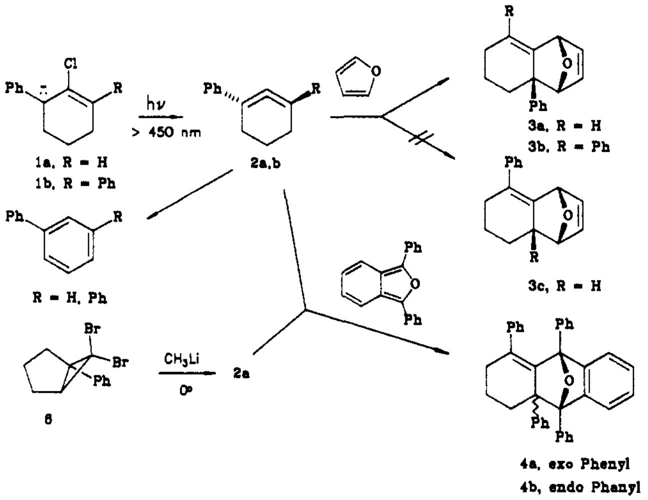
isobenzofuran afforded adducts **4a** and **4b** in a 4:1 ratio.[7] 1,3-Diphenyl-1,2-cyclohexadiene was also generated and trapped by furan to yield adduct **3b**, mp 124–125 °C, in similar fashion.[8]

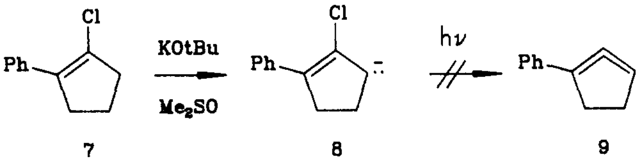


Confirmation of intermediate allene **2a** was obtained by a second route. Dibromocarbene addition to 1-phenylcyclopentene afforded thermally unstable adduct **6** in 20% yield. Treatment of **6** with CH_3Li in the presence of diphenylisobenzofuran gave adducts **4a** and **4b** in the same ratio as from **1a** photolysis. This route to 1,2-cyclohexadienes is well precedented[3] and confirms the intermediacy of **2a** from anion photolysis. Attempted reaction of **6** with CH_3Li in the presence of furan gave only products of furan lithiation.

Thermolysis of anion **1a** or **1b** and furan in THF at 50 °C for 20 h gave the same cycloadducts **3a** and **3b** in good yield. In the absence of furan, biphenyl became the major product from photolysis or thermolysis of anion **1a**, while *m*-terphenyl was formed from **1b**. One logical mechanism includes base-catalyzed rearrangement of the allene to a 1,3-cyclohexadiene, which aromatizes upon workup.

The cycloadditions of allene **2a** are regiospecific and display high stereoselectivity, despite the high reactivity and expectation of a highly nonsynchronous mechanism.[9] Initial bonding at the central allene carbon relieves ca. 30 kcal/mol of strain;[10] this is followed by closure at the sites of higher odd electron density. AM1 calculations on **2a** predict a chiral allenic structure, with a C1–C2–C3 angle of 134°. Frontier MO coefficients are greater at the styryl centers, which also is consistent with the observed regiospecificity.

Surprisingly, there was no evidence that irradiation of **8** provided 1-phenyl-1,2-cyclopentadiene (**9**); precursor **7** was recovered unchanged, along with a minor amount of dehalogenation product 1-phenylcyclopentene. It is possible that the anion does not undergo elimination because of the increased strain in **9**, or anion **8** may undergo a spontaneously *reversible* electron ejection[1] or electrocyclic opening.



Photodehalogenation of chlorocarbanions continues to provide an excellent route to novel reactive intermediates. The ready formation and efficient cycloaddition of 1,2-cyclohexadienes suggest more general applications in synthesis as well as routes to other reactive intermediates.

Acknowledgment. We thank the National Science Foundation for support of this research through Grants CHE-8805577 and CHE-8722079.

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[7] Adducts **4a** and **4b** were isolated by preparative TLC. Data include the following. **4a**: ^1H NMR ($CDCl_3$, 360 MHz) δ 7.84–7.86 (2 H, br d, 7.10 Hz), 7.74–7.75 (2 H, br d, 7.19 Hz), 7.56–7.60 (2 H, br t, 7.48 Hz), 7.47–7.51 (2 H, br t, 7.88 Hz), 7.35–7.45 (5 H, m), 7.05–7.12 (3 H, m), 6.83–6.90 (3 H, m), 1.84–1.98 (2 H, m), 1.36–1.61 (3 H, m), 1.17–1.31 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 148.76, 146.38, 144.71, 141.22, 137.48, 136.43, 129.16, 128.48, 127.95, 127.45, 127.34, 126.92, 126.61, 126.35, 126.26, 125.92, 125.85, 120.73, 119.57, 119.07, 91.92, 89.81, 56.16, 30.36, 21.15, 17.49. Anal. C, H. **4b**: ^1H NMR δ 7.99–8.02 (2 H, m), 7.48–7.59 (4 H, m), 7.42–7.44 (m, 2 H), 7.12–7.31 (6 H, m), 6.92–6.98 (m, 5 H), 5.93–5.95 (1 H, dd, 4.67, 2.94 Hz), 2.64–2.69 (1 H, td, 11.64, 3.42 Hz), 1.81–1.99 (2 H, m), 1.46–1.55 (1 H, m), 1.21–1.32 (1 H; m), 0.91–0.99 (1 H, dt, 11.98, 4.16); ^{13}C NMR δ 150.0, 147.6, 145.1, 142.1, 137.9, 135.1, 129.6, 128.7, 128.6, 128.4, 127.8, 127.3, 126.9, 126.7, 125.6, 125.5, 125.3, 123.3, 121.9, 117.4, 93.6, 89.2, 56.9, 32.1, 24.1, 18.7. Anal. C, H.

[8] Adduct **3c** is assigned the exo stereochemistry by analogy with **3a** and by its similar spectral properties: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.19–7.44 (10 H, m), 6.37 (2 H, m), 5.40 (1 H, br s), 5.06 (1 H, br s), 2.28–2.35 (3 H, m), 1.63–1.66 (1 H, m), 1.29–1.36 (1 H, m), 0.92–1.01 (1 H, m); MS (70 eV) 300 (M^+, 69.2), 271 (100.0), 228 (61.0), 215 (33.0), 202 (35.1), 165 (55.0), 128 (31.0), 115 (68.1), 91 (88.0), 77 (39.3). Anal. C, H.

[9] (a) Houk, K. N.; Lin, Y.-T.; Brown, F. K. *J. Am. Chem. Soc.* **1986**, *108*, 554. (b) Dewar, M. J. S.; Pierini, A. B. *J. Am. Chem. Soc.* **1984**, *106*, 203. (c) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209. (d) Dewar, M. J. S.; Olivella, S.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1986**, *108*, 5771. (e) Tolbert, L. M.; Ali, M. B. *J. Am. Chem. Soc.* **1984**, *106*, 3806. (f) Tolbert, L. M.; Ali, M. B. *J. Am. Chem. Soc.* **1981**, *103*, 2104.

[10] Angus, R. O., Jr.; Schmidt, M. W.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 532.

Geminal Selectivity of Singlet Oxygen Ene Reactions. The Nonbonding Large Group Effect

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The mechanism of the ene reaction of singlet oxygen with olefins has received extensive experimental and theoretical attention over the last several years.[1] Although recent theoretical calculations[2] support an earlier proposed concerted mechanism,[3] it is generally accepted that the ene reaction proceeds through an intermediate.[1] The regioselective addition of singlet oxygen to alkenes has received less attention. In the last few years it has been shown that $^1O_2$ adds to trisubstituted alkenes with syn selectivity[4] and to unsymmetrical *cis*-alkenes with regioselective double-bond formation in the larger group.[5]

Recently geminal selectivity has been found to favor the alkyl group on the double-bond carbon that bears an electron-withdrawing group in either a vinylic or allylic relationship, as shown in Scheme I.

To date, these results have been rationalized by invoking (a) the formation of trioxenes[6a,7] and [4 + 2] adducts;[11] (b) polar

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[1] (a) *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979. (b) Stephenson, L. M.; Grdina, M. J.; Orfanopoulos, M. *Acc. Chem. Res.* **1980**, *13*, 419–425. (c) Frimer, A. A.; Stephenson, L. M. In *Singlet Oxygen*; Frimer, A. A., Ed.; CRC Press, Inc.: Boca Raton, FL, 1985; Vol, II, Chapter 3, pp 68–87.

[2] Davies, G. A.; Schiesser, C. H. *Tetrahedron Lett.* **1989**, 7099–7102.

[3] (a) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359–387. (b) Gollnick, K.; Kuhn, H. J. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; pp 287–429. (c) Gollnick, K.; Hartmann, H.; Paur, H. In *Oxygen and Oxy-Radicals in Chemistry and Biology*; Powers, E. L., Rodgers, M. A. J., Eds.; Academic Press: New York, 1981; pp 379–395.

[4] (a) Orfanopoulos, M.; Grdina, M. B.; Stephenson, L. M. *J. Am. Chem. Soc.* **1979**, *101*, 275–276. (b) Schulte-Elte, K. H.; Muller, B. L.; Rautenstrauch, V. *Helv. Chim. Acta* **1978**, *61*, 2777–2783.

[5] Orfanopoulos, M.; Stratakis, M.; Elemes, Y. *Tetrahedron Lett.* **1989**, 6903–6906.

[6] (a) Ensley, H. E.; Carr, R. V. C.; Martin, R. S.; Pierce, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 2836–2838. (b) Kwon, B. M.; Kanner, R. C.; Foote, C. S. *Tetrahedron Lett.* **1989**, *903*–906.

[7] Organopoulos, M.; Foote, C. S. *Tetrahedron Lett.* **1985**, 5991–5994.

[8] (a) Adam, W.; Griesbeck, A. *Synthesis* **1986**, 1050–1051. (b) Adam, W.; Griesbeck, A. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1070–1071.

[9] Akasaka, T.; Misawa, Y.; Goto, M.; Ando, W. *Tetrahedron* **1989**, *45*, 6657–6666.

[10] Clennan, E. L.; Chen, X. *J. Org. Chem.* **1988**, *53*, 3124–3125.

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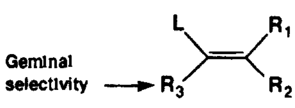
Scheme I



L = $-C(O)R^{6a,b}$, $-COOR^7$, $-COOH^8$, $-S(O)Ph^9$, $-CH_2SPh^{10}$, $-CH_2S(O)Ph^{10}$, $-CH_2X^{10}$, $-CH{=}N^tBu^{11}$.

intermediates,[6b,9] perepoxides or zwitterions; (c) electronic repulsions between the incoming oxygen and the heteroatom of the substituent, and rotational barrier differences within the alkyl groups of the double bond.[10]

We report here that the reaction of singlet oxygen with alkyl-substituted alkenes shows general preference for hydrogen abstraction from the group that is geminal to the larger substituent of the double bond. This geminal selectivity has not been previously recognized and may shed light on the factors controlling the formation of isomeric product.

As seen from Chart I, photooxygenation of a series of alkyl- and phenyl-substituted olefins[12] **1–10** shows a strong preference for hydrogen abstraction on the methyl group that is geminal to the larger alkyl or phenyl substituent of the alkene. Disubstituted olefin **1** impressively illustrates this point. Similarly, alkenes **2–4** give again as the major product the ene adduct with the double bond on the methyl that is geminal to the larger alkl group. This selectivity is demonstrated again in the symmetrical olefins **5–E** and **5-Z**, where only the methyl hydrogens react. The same trend is also noted in tri- and tetrasubstituted alkenes (**6** and **7**, taken from Frimer et al.[13]).

The presence of a phenyl substituent does not alter the geminal selectivity. This is demonstrated with substrate **10**, where the selectivity is insensitive to substitution on the para position of the phenyl ring.[14] This result indicates that nonbonding interactions play a more important role than electronic effects of the para-substituted phenyl ring in determining the stability of the transition state of the product-determining step of this reaction. The remarkable regioselectivity of the vinylsilane **9** might be attributed not only to nonbonded interactions but also to special electronic interactions involving the empty d orbitals of silicon.[15]

Examination of the possible transition states leading to the major and the minor product provides a new insight into the geminal selectivity. In transition state I, leading to the minor or absent product, the nonbonding interactions involving the large alkyl group L and the methyl group, which are placed in a cis configuration, are expected to be stronger than those in transition states II and III, where this steric interaction is absent. Furthermore, because of nonbonded interactions, transition state III leading to the major product is expected to have lower energy than II. On the basis of similar arguments, transition state IV is expected to have lower energy than V and thus account for the geminal selectivity of alkenes with the large L group in the vinylic position. Furthermore, this interpretation suffices to rationalize the geminal selectivity recently observed in systems where the L alkyl group has been replaced by a variety of functional groups.[6-11]

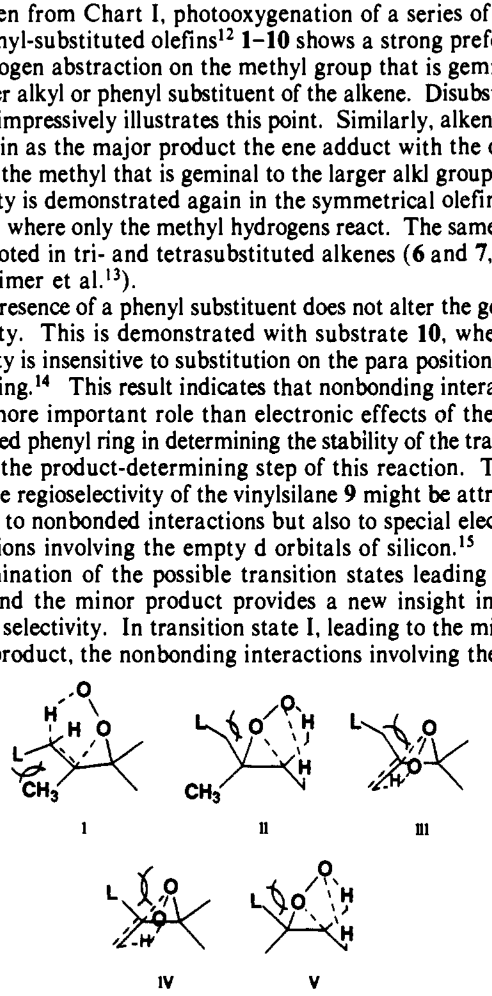
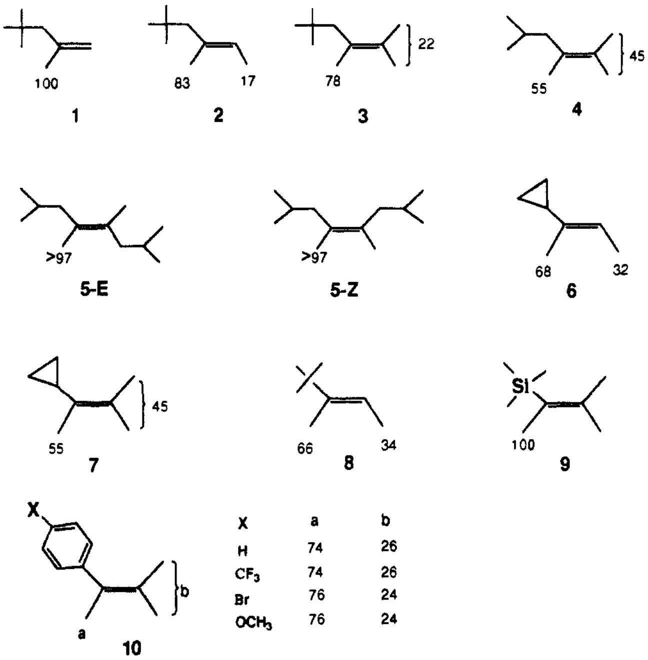


Chart I. Geminal Regioselectivity[a] in the Ene Reaction of Singlet Oxygen with Disubstiiuted, Trisubstituted, and Tetrasubstituted Alkenes[b]

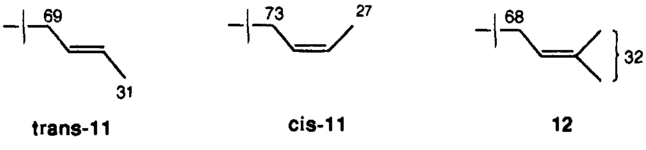


X	a	b
H	74	26
CF_3	74	26
Br	76	24
OCH_3	76	24

[a] The photooxygenations were carried out at 0 °C in carbon tetrachloride with 1.5×10^{-4} M tetraphenylporphine (TPP) as sensitizer. A 650-W tungsten–halogen lamp was used for these experiments. The product ratio was determined by NMR integration and by GC, where appropriate. [b] Numerical values represent percent of hydrogen abstraction.

Although it is difficult to separate the relative contribution of nonbonding interactions from those of other effects, such as electronic and neighboring-group participation, it is clearly demonstrated by the present results that an alkyl substituent in a geminal position activates a C–H bond roughly to the same extent as any of the functionalized substituents.[6-11] The results therefore are consonant with the interpretation that the relative stabilities of the isomeric transition states are controlled by nonbonding interactions.

It is instructive to note that unlike the present results, where the methylene hydrogens in olefins **1–5** are totally unreactive, the reactivity increases dramatically when the geminal methyl group is absent. This is illustrated with the disubstituted cis and trans olefins **11** and the trisubstituted olefin **12**. The ene adducts now are formed by preferential abstraction of methylene hydrogens next to the *tert*-butyl group. This type of regioselectivity, as well as the present results of geminal selectivity, was also rationalized in terms of steric interactions in the transition states.[5]



trans-11 **cis-11** **12**

Houk and co-workers[16] rationalized the greater reactivity of

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(11) Akasaka, T.; Takeuchi, K.; Ando, W. *Tetrahedron Lett.* **1987**, 6633–6636.

(12) Alkenes were prepared by the following methods: Dehydration of the corresponding Grignard carbinols gave alkenes **1–4**, **8**, **10**, and **12**. McMurry's coupling of the proper ketone (McMurry, E. J.; Fleming, M. P.; Kees, K. L.; Krepski, L. R. *J. Org. Chem.* **1978**, *43*, 3255–3266) gave olefins **5**; compound **9** was synthesized by the coupling of chlorotrimethylsilane and the corresponding vinylorganolithium intermediate and *trans*-**11** by complete reduction of the corresponding trans ester (Shen, Y.; Xin, Y.; Zhao, J. *Tetrahedron Lett.* **1988**, 6119–6120). Alkene isomers, where appropriate, were purified by preparative GC.

(13) Frimer, A. A.; Rot, D.; Sprecher, M. *Tetrahedron Lett.* **1977**, 1927–1930.

(14) Similar results on the photooxygenation of substrates **10** are reported in this reference: Foote, C. S.; Denny, W. R. *J. Am. Chem. Soc.* **1971**, *93*, 5162–5167.

(15) Fristard, E. W.; Baily, T. R.; Paquette, L. A.; Gleiter, R.; Bohm, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4420–4423.

cis-2-butene over *trans*-2-butene and syn selectivity in trisubstituted olefins in terms of barriers to rotation of the methyl groups. The lower the calculated barrier to rotation, the higher the reactivity. For example, they showed that the cis methyl group of 2-butene, which has a lower rotational barrier than the trans, is more reactive than the trans olefin. The geminal methyl groups of 2-methylpropene, which have a higher barrier to rotation, are rather deactivated. Similar trends hold with 2-methyl-2-butene. These useful arguments, which are valid for methylated di- and trisubstituted ethylenes, are insufficient to rationalize the present results. For example, the neopentyl group is expected to have an appreciably higher barrier to rotation than the methyl groups in olefins **11** and **12**, yet it is more reactive. We suggest that nonbonded interactions in the isomeric transition states are far better indicators of product distributions than barriers to rotation.

Further work to clarify the various types of regioselectivity on tri- and tetrasubstituted alkenes is in progress.[17]

Acknowledgment. We thank Professors G. J. Karabatsos and C. S. Foote for valuable comments and discussions. This work was supported by Greek General Secretariat of Research and Technology Grant No. ΠΣ 64. NATO Grant No. 880120 for travel expenses is also acknowledged.

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(16) Houk, K. N.; Williams, J. C., Jr.; Mitchell, P. M.; Yamaguchi, K. *J. Am. Chem. Soc.* **1981**, *103*, 949–951.

(17) After completion of this manuscript, we were informed by Prof. E. Clennan of some results similar to those reported here. We thank him for a prepublication copy of his manuscript: Clennan, E. L.; Chen, X.; Koola, J. J. *J. Am. Chem. Soc.*, in press.

Ene versus [2 + 2] Cycloaddition Reactions of Fischer Carbene Complexes: An Unusual Effect of Silicon on the Product Partition and the Stereospecificity

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The propensity of a triple bond to participate in a [2 + 2] cycloaddition with an enol ether is greatly facilitated if the triple bond is appended to a chromium or tungsten carbene complex[2] such as in complexes **1** or **2**.[3,4] Further investigations of reactions in this class led to the discovery of ene reactions mediated by a transition metal carbene complex and is the subject of this communication. Additionally, an unusual effect of silicon on the distribution between ene and [2 + 2] cycloaddition products and on the stereospecificity of the [2 + 2] cycloadditions was found which has not yet been observed in organic systems.

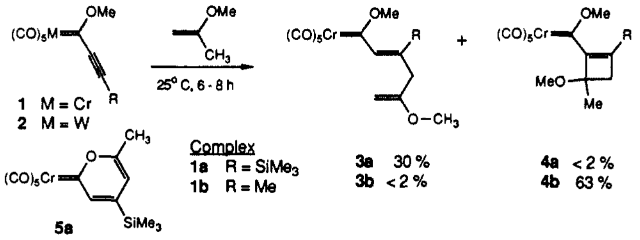
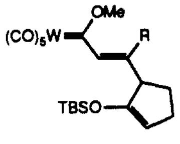
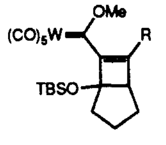
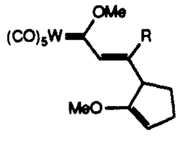
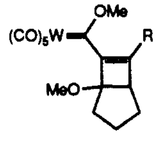
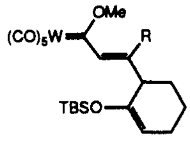
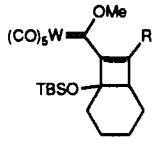
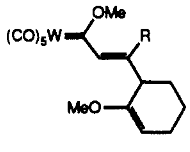
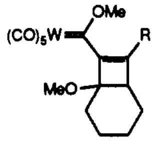


Table I. Ene versus [2 + 2] Cycloaddition Reactions of Carbene Complexes[a]

Time	Ene Product[b]		[2 + 2] Product	Ene/[2 + 2]
				
24 h	**10a** 39 %	R = SiMe$_3$	**11a** 12 %	3.25 [c]
12 h	**10b** 28 %	R = Me	**11b** 62 %	0.45 [c]
				
8 h	**13a** 10 %	R = SiMe$_3$	**14a** 64 %	0.16
1 h	**13b** 2 %	R = Me	**14b** 87 %	0.02
3 h	**13c** < 2 %	R = iPr	**14c** 90 %	< 0.02
9 h	**13d** < 2 %	R = tBu	**14d** 59 %	< 0.02
				
48 h	**16a** 42 %	R = SiMe$_3$	**17a** < 3 %	> 14.0
12 h	**16b** 86 %	R = Me	**17b** 10 %	8.8
				
48 h	**19a** 67 %	R = SiMe$_3$	**20a** < 2 %	> 33.0
4 h	**19b** 21 %	R = Me	**20b** 69 %	0.35
12 h	**19c** 24 %	R = iPr	**20c** 69 %	0.35

[a] All reactions were carried out in neat enol ether (10–20 equiv) at 25 °C under argon for the indicated time. All products were purified on silica gel. [b] A single double-bond isomer was obtained in each case which is assumed to be that resulting from syn addition since this was shown to be the case for **19a** by NOE experiments (see supplementary material). [c] Compounds **10b** and **11b** could not be separated by silica gel chromatogrpahy.

The first ene reaction of a transition metal carbene complex was encountered in the reaction of the chromium carbene complex **1a** with methyl isopropenyl ether. The ene product **3a** slowly cyclizes to the pyranylidene complex **5a**[5] upon hydrolysis on silica gel but can be isolated if eluted rapidly. The nature of the substituent R in the reaction of **1** was found to be crucial to the outcome; the trimethylsilyl complex **1a** gave only the ene product **3a** whereas the methyl complex **1b** led only to the [2 + 2] cycloadduct **4b**. The Lewis acid mediated reactions of acetylenic esters and alkenes are known to give mixtures of ene and [2 + 2] cycloadducts where the ratio of products has been shown to have a strong dependence on the olefin substitution pattern and on the conformations of the starting materials.[6,7] However, this

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(1) National Institutes of Health Predoctoral Fellow.

(2) For recent reviews, see: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. (b) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press Inc.: Greenwich, CT, 1989; Vol. 1. (d) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1990, Vol. 5. (e) *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic Publishers: Boston, MA, 1989. (f) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081.

(3) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1988**, *110*, 8727.

(4) For additional examples, see ref 5e and the following: (a) Camps, F.; Llebaria, M. G.; Moreto, J. M.; Ricart, S.; Vinas, J. M. *Tetrahedron Lett.* **1990**, *31*, 2479. (b) de Meijere, A.; Wessjohann, L. *Synlett.* **1990**, 20.

(5) (a) Gilchrist, T. L.; Livingston, R.; Rees, C. W.; Angerer, E. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2535. (b) Berke, H.; Narter, P.; Huttner, G.; Zsolnai, L. *Z. Naturforsch.* **1981**, *86b*, 929. (c) Aumann, R.; Heinen, H. *Chem. Ber.* **1987**, *120*, 537. (d) Juneau, K. N.; Hegedus, L. S.; Roepke, F. W. *J. Am. Chem. Soc.* **1989**, *111*, 4762. (e) Camps, F.; Moreta, J. M.; Ricart, S.; Vinas, J. M.; Molins, E.; Miravitles, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1560. (f) Wang, S. L. B.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 4550.

(6) (a) Snider, B. B.; Rodini, D. J.; Conn, R. S. E.; Sealfon, S. *J. Am. Chem. Soc.* **1979**, *101*, 5283. (b) Snider, B. B.; Roush, D. M.; Rodini, D. J.; Gonzalez, D.; Spindell, D. *J. Org. Chem.* **1980**, *45*, 2773. (c) Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426.