Stereodirecting Effect of a Substrate Methoxy Substituent on the Addition of Singlet Methylene to a Double Bond

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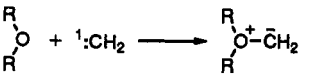
The stereodirecting effects of substrate methoxy, hydroxy, methylthio, and methyl substituents were examined in the addition of ^{1}:CH_2 to the double bonds of substrates **1a–d**. The carbene, generated by photolysis of CH_2N_2, inserted into the C–H bonds of solvent and substrate, added to the substrate double bond to give products **2a–d**, and attacked the oxygen or sulfur atom of substrates **1a–c** to produce ylide intermediates which underwent 2,3-sigmatropic rearrangement to give products **3a–c**. A preference for addition syn to the methoxy group of substrate **1a** was observed when the reaction was run in pentane solution (*syn*-**2a**/*anti*-**2a**, 1.14 ± 0.02), while a preference for formation of *anti*-**2a** was observed in diethyl ether solution (*syn*-**2a**/*anti*-**2a**, 0.92 ± 0.03). A preference for ^{1}:CH_2 addition anti to the substrate substituent was observed for substrates **1b–d** in both pentane and ether solution. The effect of the methoxy substituent was also examined in the addition of ^{1}:CH_2 to *syn*-7-methoxynorbornene (**5b**). Explanations for the substituent effects are offered based on both steric hindrance and interaction between ^{1}:CH_2 and the substituent, including formation and subsequent reaction of the ylide intermediates.

Several investigations of the directing effect of a substrate alkoxy or hydroxy group on the addition of a carbene to a double bond have been carried out with the expectation that reversible formation of a complex between the carbene and the substrate substituent might control the regio- and stereoselectivity of the reaction.[1] Dichlorocarbene (:CCl_2) generated by treatment of $CHCl_3$ with base,[1a] or by thermolysis of $Ph(BrCl_2C)Hg$,[1b] added predominantly anti to an alkoxy substituent on a cyclohexene ring. In contrast, :CCl_2 added predominantly syn to a substrate hydroxy group under phase transfer conditions.[1c] A substrate hydroxy group did not have a positive directing influence on the regioselectivity of :CCl_2 addition to a diene,[1d] but in other experiments a substrate hydroxy group had a positive regiodirecting effect on the addition of $(CH_3)_2C{=}C{=}C$: to a diene.[1e-g] The effect of the substrate substituent apparently depends on reaction conditions, including the carbene used and the method of its generation.

Formation of oxonium ylides in reactions of singlet carbenes with ethers and alcohols has been clearly demonstrated,[2,3] and ylides have been considered as potential intermediates in alkoxy-directed attack of a carbene on a double bond.[4] The intervention of an oxonium ylide in a directed attack would require that either: (1) the ylide behaves as a carbenoid species, or (2) the formation of the ylide be reversible, with capture of the carbene by the proximate face of the double bond following its release from the directing group. Some support for either possibility can be found in the literature. Carbene–ether adducts with carbene-like reactivity have been invoked by Tomioka and co-workers to explain the effect of 1,4-dioxane solvent on reactions of arylcarbenes.[5] Ab initio calculations (3–21G level) performed by Moreno and co-workers in which singlet methylene (^{1}:CH_2) was allowed to interact with H_2O, but was constrained from O–H insertion, predict formation of an ylide-like adduct capable of addition to the double bond of ethene.[6] Reports of reversible ylide formation in reactions of carbenes with alcohols have also appeared,[7] but remain controversial.[8]



Here we report the results of experiments involving the stereochemical influence of several substrate substituents on the addition of ^{1}:CH_2 to a double bond. We chose :CH_2 for study, despite its great reactivity and low selectivity, because it can be reliably and cleanly produced under a variety of conditions, in the singlet state, by the photolysis of CH_2N_2.[2] The use of pentane as solvent ensured that there would be no competition between the substrate substituent and a similar functional group of the solvent. Reactions of ^{1}:CH_2 with methoxy- and hydroxy-substituted substrates were examined. Reactions were also carried out with substrates bearing methyl and methylthio substituents for comparison. We anticipated that the methyl substituent would affect the stereochemical outcome of the reaction through steric hindrance alone, while the

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Table I. Composition of Product Mixtures from Reaction of ^{1}:CH_2 with 1a–d in Pentane Solution

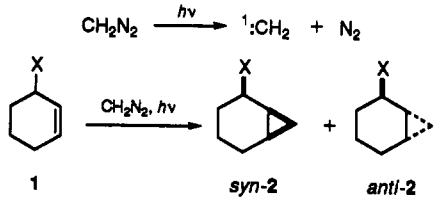
substrate	products (%)[a] 1a	2	3	C–H insertion
1a	–	28 ± 1	21 ± 2	51 ± 2
1b	25 ± 2	25 ± 1	3 ± 0	46 ± 3
1c	–	18 ± 1	38 ± 3	44 ± 4
1d	–	33 ± 1	–	67 ± 1

[a] Mean value from three reactions (GC analysis). Errors are reported as the standard deviation.

methylthio substituent would intercept ^{1}:CH_2 through formation of a relatively stable ylide intermediate.[3]

Results

The stereochemistry of ^{1}:CH_2 addition to the double bond was determined for substrates **1a–d**. The carbene was generated in situ by photolysis of CH_2N_2 (Hanovia 450-W mercury lamp, pyrex), prepared by reaction of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) with KOH in aqueous 2-methoxyethyl ether. The CH_2N_2 was trapped in decalin and the decalin solution was dried over KOH pellets. The CH_2N_2 was subsequently transferred in a stream of N_2 from the decalin solution to a 3% solution of the substrate. The reaction of each substrate with ^{1}:CH_2 was carried out in both pentane and diethyl ether solutions. A deficient amount of CH_2N_2 was used; typically 1–5% of the substrate underwent reaction. The carbene reacted by insertion into C–H bonds of the substrates and solvents, as well as by addition to substrate heteroatoms and double bonds, leading to complex reaction mixtures which were analyzed by capillary GC. Table I gives data concerning the composition of the reaction mixtures.



1, 2 **a**: X = OCH_3 **c**: X = SCH_3
b: X = OH **d**: X = CH_3

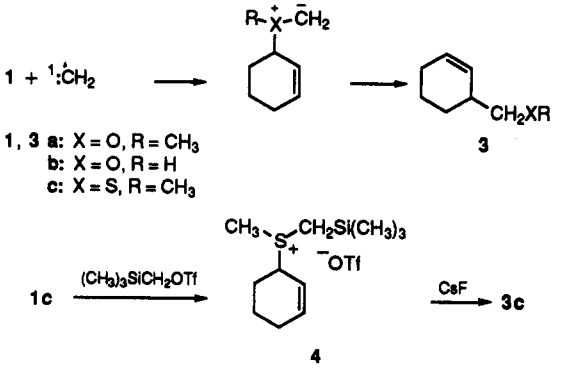
Products **3a–c**, most reasonably resulting from 2,3-sigmatropic rearrangement of ylide intermediates,were identified in the mixtures produced by reaction of ^{1}:CH_2 with ether **1a**, alcohol **1b**, and thioether **1c** by comparison (GC coinjection and GC/MS) with authentic samples. Authentic samples of compounds **3a** and **3b** were prepared by literature methods.[9] Thioether **3c** was obtained by reaction of thioether **1c** with (trimethylsilyl)methyl triflate to give sulfonium salt **4**, followed by treatment with CsF to give the ylide intermediate which rearranged to **3c** in 47% yield (based on **1c**).

The stereoisomeric products of ^{1}:CH_2 addition to the double bonds of substrates **1a–d** were identified in the reaction mixtures by comparison with authentic samples. Cyclopropanated ethers *syn*- and *anti*-**2a** and alcohols *syn*- and *anti*-**2b** were prepared by the method of Dauben and Berezin.[10] Thioethers *syn*- and *anti*-**2c** were prepared by conversion of alcohol *syn*-**2b** to a mixture of *syn*- and *anti*-thioacetate by a variation of the Mitsunobu procedure.[11] The thioacetates were reduced with $LiAlH_4$, then converted to thioethers *syn*- and *anti*-**3c** by treatment with CH_3I and DBU. Assignment of stereochemistry was based on the ^{1}H NMR chemical shift for the proton adjacent to the methylthio group and follows the argument of Seyferth and Mai.[1b] A mixture of *syn*- and *anti*-**2d** (syn/anti, 1.0:2.8) was prepared by Simmons–Smith cyclopropanation of **1d**.[12] The ratios of syn to anti isomer produced in the reaction of each substrate with ^{1}:CH_2, in both pentane solution and diethyl ether solution, are reported in Table II. GC response factors were not measured, but assumed to be equal for pairs of stereoisomers. (This assumption is supported by the equivalence of the stereoisomer ratios determined independently by GC and by ^{1}H NMR for mixtures of *syn*- and *anti*-**1b**.)

Table II. Effect of Substrate Substituent on Stereochemistry of ^{1}:CH_2 Addition to the Double Bonds of 1a–d

substrate	*syn*-2/*anti*-2[a] pentane	ether	substituent *A* value,[b] kcal/mol
1a	1.14 ± 0.02	0.92 ± 0.03	0.60
1b	0.82 ± 0.01	0.85 ± 0.03	0.52
1c	0.82 ± 0.02	0.74 ± 0.04	1.1
1d	0.95 ± 0.02	0.95 ± 0.01	1.8

[a] Mean value from three reactions (GC analysis). Errors are reported as the standard deviation. [b] Conformational free energy difference between axial and equatorial conformation of monosubstituted cyclohexanes, ref 17.



Reactions were also carried out with norbornene (**5a**) and *syn*-7-methoxynorbornene (**5b**)[13] as substrates. The products of addition of ^{1}:CH_2 to the exo and endo faces of the double bonds of **5a** and **5b** (*exo*- and *endo*-**6a** and *exo*- and *endo*-**6b**, respectively) were identified by comparison with authentic samples prepared by literature methods. Samples of *exo*- and *endo*-**6a** were prepared by Simmons–Smith cyclopropanation of **5a** and by cyclopropanation of norbornadiene followed by hydrogena-

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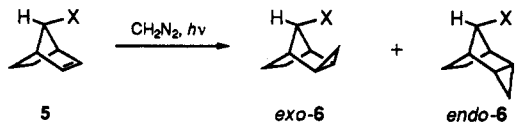
tion.[14] The directing effect of the methoxy group led to the formation of *exo*-**6b** in the Simmons–Smith reaction of **5b**.[15] An authentic sample of *endo*-**6b** was prepared by the procedure reported by Haywood-Farmer and Pincock.[16] Products of C–H insertion were also observed in the reactions of **5a** and **5b** with ^{1}:CH_2, but were not fully characterized.



5 *exo*-6 *endo*-6

5, 6 a: X = H
b: X = OCH_3

	exo-6/*endo*-6	
	pentane	ether
5a	3.16 ± 0.09	2.74 ± 0.01
5b	3.12 ± 0.08	2.28 ± 0.08

Discussion

The substrate substituent influences the stereochemistry of ^{1}:CH_2 addition to the double bond of substrates **1a–d**. The influence of the substituent is admittedly small, but ^{1}:CH_2 is a notoriously indiscriminate reagent, reacting at nearly diffusion controlled rates.[2] Any selectivity is expected to be small. A preference is observed for addition of ^{1}:CH_2 anti to the methyl group of substrate **1d** and can be explained as the result of steric hindrance by the methyl group to carbene attack. The hydroxy and methylthio groups of substrates **1b** and **1c**, respectively, hinder addition of ^{1}:CH_2 to the proximate face of the double bond to a slightly larger extent. In contrast, a small preference for formation of *syn*-**2a** is observed in the reaction with methoxy-substituted substrate **1a**. Notably, this stereochemical preference is solvent-dependent; a small preference for formation of *anti*-**2a** is observed when the reaction is run in ether solution.

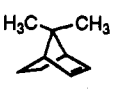
There is no correlation between the size of the substituent, as measured by the free energy difference between the axial and equatorial conformations of the monosubstituted cyclohexane (A value)[17] (see Table II) and the magnitude of its effect in this reaction. Explanations for the influence of the substrate substituents on the stereochemical outcome of the addition of ^{1}:CH_2 to the double bond must lie elsewhere. The formation of products **3a–c** in the reactions of substrates **1a–c**, respectively, is compelling evidence for the formation of ylide intermediates by attack of ^{1}:CH_2 on the nucleophilic atoms of these substrate substituents. Chemical interaction of the carbene with the substrate substituents, including formation and subsequent reactions of the ylides, may indeed be linked to the substituent effects.

For example, ^{1}:CH_2 is known to react irreversibly at the sulfur atoms of thioethers to give sulfonium ylides, species which do not cyclopropanate unactivated double bonds.[18] In the reaction of ^{1}:CH_2 with thioether **1c**, the product arising from rearrangement of the ylide **3c** is produced in twice the combined yield of cyclopropanated products *syn*- and *anti*-**2c** (see Table I). The methylthio group may trap the carbene as it approaches the syn face of the double bond, more effectively preventing formation of syn product than the less reactive methyl group. As expected, no evidence for formation of cyclopropanated product **2c** is seen when the sulfonium ylide is formed by fluoride-induced desilylation of [(trimethylsilyl)methyl]sulfonium salt **4**.

Incoming ^{1}:CH_2 is also intercepted by the hydroxy group of **1b** via reactions not available to the methyl group of **1d**. Alcohol **3b**, a product most reasonably resulting from rearrangement of an ylide intermediate, and ether **1a**, the product of ^{1}:CH_2 insertion into the O–H bond, are both formed. (To our knowlege, this is the first reported evidence of ylide formation in the reaction of ^{1}:CH_2 with an alcohol and will be the subject of a future communication.[19]) The combined yield of products **1a** and **3b** is approximately the same as the combined yield of cyclopropanated products *syn*- and *anti*-**2b**.

The methoxy substituent of **1a** also intercepts ^{1}:CH_2 through reaction at oxygen as evidenced by formation of **3a**. The ratio of products formed by attack at the oxygen atom vs products formed by addition to the double bond (1:1.3) is smaller than the comparable ratio for substrate **1b**, indicating a slightly smaller selectivity of the carbene for reaction at this site. Although this would explain a syn/anti ratio closer to unity for addition of ^{1}:CH_2 to the double bond of **1a**, it does not adequately explain the preference for attack at the more hindered face of the double bond. The methoxy substituent appears to exert a positive directing influence.

The effect of a substrate methoxy substituent on ^{1}:CH_2 addition to a double bond was also examined by comparing results of reactions with substrates **5a** and **5b**. A strong preference for electrophilic addition to the exo face of the double bond is the rule in reactions of **5a**,[20] but in most cases an apical substituent syn to the double bond severely hinders addition reactions. For example, $:CCl_2$ readily undergoes addition exclusively to the exo face of the double bond of **5a**, but does not react at all with 7,7-dimethylnorbornene (**7**) under comparable conditions.[20] We have found that the ratios of exo to endo addition of ^{1}:CH_2 to the double bonds of **5a** and **5b** (3.16 ± 0.09 and 3.12 ± 0.08, respectively) are remarkably similar when the reaction is carried out in pentane solution. We suggest that this is due to a fortuitous cancelation of a positive directing effect of, and steric hindrance by, the methoxy substituent of **5b**. Because the methoxy substituent of **5b** is no longer in an allylic position, this result points to a through-space rather than an exclusively through-bond mechanism for the directing effect.



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We speculated that competition between substrate methoxy groups and solvent molecules might block or at least reduce the directing effect if reactions were run in ether solution, especially if intramolecular solvation of the carbene was responsible for the directing effect. In fact, when the experiments were carried out, we found the

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stereochemistry of ^{1}:CH_2 addition to the double bonds of both **1a** and **5b** to be solvent-dependent, with relatively less addition to the proximate face of the double bond observed in diethyl ether solution. The stereochemistry of addition to the double bonds of substrates **1b–d** was unaltered (within experimental error) by replacing pentane with ether solvent. A solvent effect was observed, however, in the reaction of unsubstituted substrate **5a**. Like substrate **5b**, relatively less addition to the exo face of the double bond occurs in ether solution.

Although our original hypothesis might be correct, other explanations for the solvent effect are certainly plausible. For example, the stability and structure of an ylide or ylide-like adduct involved as an intermediate in a directed attack of the carbene on the double bond would be susceptible to changes in polarity of the reaction medium. Alternatively, a solvent-induced change in the conformation or change in conformational equilibrium for substrate **1a** could result in a change in the stereochemistry of the addition reaction. (The observation of a similar solvent effect in the reaction of **5b**, in which the conformation of the ring system is fixed, indicates that this is probably not the only source of the solvent effect.) Indeed, any solvent-related change in the relative stability of the transition states leading to the two addition products would lead to a solvent effect.

In conclusion, a preference for addition of ^{1}:CH_2 to the face of a double bond proximate to a substrate methoxy group has been observed in reactions of substrates **1a** and **5b**. In comparison, methyl, methylthio, and hydroxy substituents were found to hinder addition to the proximate face of the double bond in reactions of substrates **1b–d**. The positive directing effect of the methoxy substituent is attributed, at least in part, to a through-space interaction between the carbene and the substituent oxygen.

Experimental Section

General Remarks. Infrared spectra were obtained with a Perkin-Elmer 1600 Series FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded on a Varian Gemini spectrometer operating at 300 and 75.5 MHz, respectively, and referenced to the solvent peak. Low-resolution mass spectra were obtained on a Hewlett-Packard 5970 Series quadrupole mass detector connected to a Hewlett-Packard 5890 GC fitted with an Alltech RSL-150 column (30 m × 0.25 mm, 0.25-μm film thickness). High-resolution mass spectral determinations were made at the Midwest Center for Mass Spectrometry. Preparative GC was carried out with a Gow-Mac Series 580 GC fitted with a 20% DC-710 on Chromasorb P column (2 m × 3mm). Capillary GC analyses were performed on a Hewlett-Packard 5890 GC with FID. The following columns were used: Supelco SPB-1, 30 m × 0.25 mm, 0.25-μm film thickness (analysis of reactions with substrates **1c**, **5a**, **5b**); Supelcowax 10, 30 m × 0.20 mm, 0.20-μm film thickness (analysis of reactions with substrate **1b**); Supelco SPB-1701, 30 m × 0.25 mm, 0.25-μm film thickness (analysis of reactions with substrate **1a** and **1d**). GC response factors for stereoisomers were assumed identical. Products of reactions involving the photolysis of CH_2N_2 were identified by comparison of GC retention times (coinjection) and by matching either mass spectra or IR spectra with those of authentic samples.

Preparation of Decalin Solutions of CH_2N_2. (*Warning!* All operations involving CH_2N_2 should be carried out in an efficient fume hood and behind a safety shield.) Diazald (Aldrich) (2–8 g) was dissolved in the minimum amount of 2-methoxyethyl ether. The filtered solution was added dropwise with vigorous stirring to 50% aqueous KOH (100 mL) heated to 75–85 °C. During the addition, a slow stream of N_2 was bubbled through the reaction mixture, passed through a water-cooled condenser, and then bubbled through a dry ice-cooled trap containing decalin (30 mL) and several KOH pellets. The N_2 flow was continued for 15 min after the addition of Diazald was complete. The yellow solution of CH_2N_2 in decalin was dried over the KOH pellets at room temperature prior to use.

Photolysis of CH_2N_2 Solutions. The CH_2N_2 was transferred in a stream of N_2 from a decalin solution to a N_2-purged solution of substrate (0.5 g) in dry solvent (15 mL) in a Pyrex vessel. The solution was cooled by contact with a tap water-cooled cold finger and irradiated 45 min with a Hanovia 450-W mercury lamp held in a water-cooled Pyrex sleeve.

Bicyclo[4.1.0]heptane-2-thioacetate. Diisopropyl azodicarboxylate (6.7 g, 33 mmol) was added to a stirred solution of triphenylphosphine (8.6 g, 33 mmol) in dry THF (75 mL) under N_2 at 0 °C and stirring was continued for 30 min. A solution of *syn*-**2b** (1.8 g, 16 mmol) and thioacetic acid (2.5 g, 33 mmol) in dry THF (35 mL) was added dropwise at 0 °C and the mixture was stirred 30 min at 0° and then 20 h at room temperature. The mixture was filtered and the filtrate concentrated under reduced pressure. The crude product mixture was extracted with four 100-mL portions of pentane. The combined pentane extracts were filtered through silica gel and concentrated at reduced pressure. The resulting oil was distilled under vacuum to give 2.2 g (81% of theory) of a mixture of *syn*- and *anti*-**2c** as a slightly yellow oil (bp 45–55 °C, 0.2 mmHg). Spectroscopic data for major isomer: IR (thin film) 2998, 2933, 2860, 1689, 1456, 1353, 1270, 1109 cm^{-1}; ^{1}H NMR δ 0.17 (q, 1H), 0.68 (m, 1H), 0.8–1.9 (m, 8H), 2.30 (s, 3H), 3.81 (m, 1H); MS, *m/e* (rel inten) 128 (20), 95 (57), 67 (33), 43 (100), 41 (33), 39 (34), 15 (31).

Bicyclo[4.1.0]heptane-2-thiol. A mixture of *syn*- and *anti*-bicyclo[4.1.0]heptane-2-thioacetate (1.5 g, 8.8 mmol) was dissolved in dry ether (15 mL) and added dropwise to a stirred suspension of $LiAlH_4$ (0.36 g, 9.5 mmol) in dry ether (9 mL) under N_2. The mixture was stirred 30 min and then 1.2 M HCl (9 mL) was added dropwise. The ether supernatant was decanted and the remaining solid was washed with two 20-mL portions of ether. The combined ether solutions were dried ($MgSO_4$) and concentrated under reduced pressure to give a mixture of the *syn*- and *anti*-thiols as a slightly yellow oil (0.80 g, 71% of theory). The crude thiol mixture was used in the preparation of the thioethers without further purification. Spectroscopic data for major isomer: ^{1}H NMR δ 0.09 (q, 1H), 0.63 (m, 1H), 1.0–1.7 (m, 8 H), 1.8 (d, 1H), 3.17 (m, 1H); MS, *m/e* (rel inten) 128 (8, M$^+$), 95 (100), 79 (42), 77 (21), 67 (63), 55 (20), 53 (21), 45 (31), 41 (53), 39 (66), 27 (47).

***syn*-and *anti*-2-(Methylthio)bicyclo[4.1.0]heptane (*syn*-and *anti*-2c).** A mixture of *syn*- and *anti*-bicyclo[4.1.0]heptane-2-thiol (0.80 g, 6.2 mmol), iodomethane (0.35 mL, 5.6 mmol), and DBU (0.84 mL, 5.6 mmol) were added to benzene (20 mL) and stirred 3 h. The white precipitate was removed by filtration and washed with benzene (20 mL). The combined filtrates were washed with two 25-mL portions of H_2O, dried ($MgSO_4$), and concentrated under reduced pressure to give a mixture of *syn*- and *anti*-**2c** (15:85, GC) as a slightly yellow oil (0.89 g, 93% of theory). The stereoisomers can be separated by preparative GC (140 °C).

Data for *syn*-**2c**: shown by analytical GC to be 85% of purity (15% *anti*-**2c** as contaminant); IR (thin film) 2929, 2861, 1461 cm^{-1}; ^{1}H NMR δ 0.27 (q, 1H), 0.63 (d of t, 1H), 1.1 (m, 4 H), 1.5 (m, 2H), 1.72 (m, 1H), 1.92 (m, 1H), 2.14 (s, 3H), 3.19 (m, 1H, *H*CSMe); ^{13}C NMR 9.03, 12.15, 13.70, 15.03, 21.77, 23.47, 27.30, 42.65 ppm; MS, *m/e* (rel inten) 142 (21, M$^+$), 95 (100), 79 (33), 77 (16), 67 (58), 55 (17); HRMS calcd for $C_8H_{14}S$ 142.0817, found 142.0816.

Data for *anti*-**2c**: shown by analytical GC to be 93% of purity (6% *syn*-**2c** as contaminant); IR (thin film) 3063, 2997, 2931, 2857, 1450, 1227, 1018 cm^{-1}; ^{1}H NMR δ 0.09 (q, 1H), 0.64 (d of t, 1H), 1.0 (m, 3H), 1.23 (q, 1H), 1.53 (m, 1H), 1.7 (m, 3H), 2.15 (s, 3H), 2.81 (m, 1H, *H*CSMe); ^{13}C NMR 10.57, 10.69, 14.14, 16.14, 18.67, 22.93, 28.50, 42.91 ppm; MS, *m/e* (rel inten) 142 (20, M$^+$), 95 (100), 79 (27), 77 (16), 67 (66), 55 (18); HRMS calcd for $C_8H_{14}S$ 142.0817, found 142.0814.

3-[(Methylthio)methyl]cyclohexene (3c). A solution of (trimethylsilyl)methyl triflate (1.0 g, 4.5 mmol) in benzene (5 mL) was added dropwise to a stirred solution of **1c** (0.50 g, 3.9

mmol) in benzene (5 mL). The solution was stirred 20 h and then concentrated under reduced pressure to a tan oil. A solution of CsF (1.3 g, 7.7 mmol) in anhydrous dimethoxyethane (20 mL) was added and the solution was stirred 20 h at 50 °C. The reaction mixture was poured into H_2O (150 mL) and the aqueous mixture was extracted with three 30-mL portions of CH_2Cl_2. The combined CH_2Cl_2 extracts were dried ($MgSO_4$) and concentrated under reduced pressure to a tan oil (0.26 g, 47% of theory). A portion of this oil was purified by preparative GC (120 °C) and shown by analytical GC to be 99.6% of purity: IR (thin film) 3017, 2921, 2858, 1433, 1033, 911, 723 cm^{-1}; ^1H NMR δ 1.31 (m, 2H), 1.72 (m, 1H), 1.87 (m, 1H), 2.00 (m, 2H), 2.12 (s, 3H), 2.33 (m, 1H), 2.48 (d of d, 1H), 5.70 (m, 2H); ^{13}C NMR 16.1, 21.07, 25.30, 28.51, 34.80, 40.86, 128.19, 130.20 ppm; MS, *m/e* (rel inten) 142 (17, M^+), 127 (18), 94 (45), 81 (75), 80 (30), 79 (96), 77 (23), 61 (100), 53 (33), 45 (36), 41 (53), 39 (71); HRMS calcd for $C_8H_{14}S$ 142.0817, found 142.0821.

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Supplementary Material Available: NMR spectra for *syn*-**2c**, *anti*-**2c**, and **3c** (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.