sulfate and the solvents were evaporated, the crude product was purified by PLC.

Data for the products 3–8 are as follows.

3a: ^{1}H NMR (CCl_4) 7.4–7.2 (m, 6 H), 6.40 (br s 1 H), 6.2 (m, 1 H), 6.0 (m, 1 H), 3.72 (br s, 2 H). ^{13}NMR ($CDCl_3$) 150.6, 141.5, 133.4, 130.3, 129.3, 128.5, 127.9, 120.5, 110.3, 107.2, 31.8. mass spectrum, *m/e* 298, calcd 297.966 35, found 297.966 ± 0.006.

3b: ^{1}H NMR (CCl_4) 7.4–7.2 (m, 6 H), 6.45 (br s, 1 H), 6.16 (m, 1 H), 5.96 (m, 1 H), 3.74 (br s, 2 H); ^{13}C NMR ($CDCl_3$) 150.3, 141.6, 133.9, 132.0, 129.4, 128.4, 128.1, 110.3, 107.9, 107.3, 34.1; mass spectrum *m/e* 342, calcd 341.915 89, found 341.916 ± 0.007.

4a: IR ($\bar{\nu}$, liquid film) 3105, 3050, 1610, 1580, 1502, 1475, 1440, 735, 690 cm^{-1}; ^{1}H NMR (CCl_4) 7.44–7.2 (m, 6 H), 6.18 (m, 1 H), 5.96 (m, 1 H), 5.40 (br s, 1 H), 5.16 (br s, 1 H), 3.48 (br s, 2 H); ^{13}C NMR ($CDCl_3$) 150.4, 141.6, 134.7, 129.2, 127.9, 118.6, 110.3, 107.3, 37.2; mass spectrum, *m/e* 264, calcd 264.005 32, found 264.005 ± 0.004. Anal. Calcd: C, 59.33; H, 49.60. Found: C, 59.44; H, 4.72.

4b: isolated as a mixture of *E* and *Z* isomers; IR ($\bar{\nu}$, liquid film) 3050, 2985, 1580, 1505, 1478, 735 cm^{-1}; ^{1}H NMR (CCl_4) 7.4–7.0 (m, 6 H), 6.14–5.74 (m, 3 H), 4.08 and 3.61 (quadruplets, J = 7 Hz, 1 H), 1.78 (d, J = 7 Hz, 3 H), 1.40 (d, J = 7 Hz, 3 H); mass spectrum, *m/e* 292, calcd 292.036 62, found 292.036 ± 0.006. Anal. Calcd: C, 61.86; H, 5.54. Found: C, 61.52; H, 5.34.

4c: isolated as a mixture of *E* and *Z* isomers; ^{1}H NMR (CCl_4) 7.4–7.0 (m, 6 H), 6.16–5.70 (m, 3 H), 3.5 and 3.44 (2 br s, 2 H), 2.4–1.9 (2 quintet, J = 7.5 Hz, 2 H), 1.1–0.88 (2 t, J = 7.5 Hz, 3 H); mass spectrum *m/e* 292, calcd 292.036 62, found 292.036 ± 0.006. Anal. Calcd: C, 61.86; H, 5.54. Found: C, 61.54; H, 5.44.

4d: IR ($\bar{\nu}$, liquid film) 3050, 2905, 1578, 1500, 1475, 1438, 732, 690; ^{1}H NMR (CCl_4) 7.3–7.0 (m, 6 H), 6.1 (m, 1 H), 5.80 (m, 1 H), 3.60 (br s, 2 H), 2.0 (s, 3 H), 1.92 (s, 3 H); mass spectrum, *m/e* 292, calcd 292.036 62, found 292.036 ± 0.006. Anal. Calcd: C, 61.86; H, 5.54. Found: C, 61.62; H, 5.53.

5a was isolated together with the corresponding β isomer 5a′: IR ($\bar{\nu}$, liquid film) 3050, 2890, 1610, 1580, 1490, 1475, 1440, 1300, 740, 710, 690 cm^{-1}; ^{1}H NMR (CCl_4) 7.5–7.2 (m, 6 H), 6.32 (m, 1 H), 5.80 (m, 1 H), 5.4–5.0 (m, 2 H), 3.6–3.2 (m + s, 5 H); mass spectrum, *m/e* 277, calcd 277.036 95, found 277.037 ± 0.005. Anal. Calcd: C, 60.87; H, 5.47. Found: C, 61.08; H, 5.44.

5d + 5d′: ^{1}H NMR (CCl_4) 7.05 (m, 5 H), 6.2 and 5.7 (m, 3 H), 3.40 and 3.18 (br s, 5 H), 1.99 (s, 3 H), 1.91 (s, 3 H).

6a was isolated together with its β isomer **6a′**: ^{1}H NMR (CCl_4) 7.6–6.6 (m, 8 H), 5.42, 5.34, 5.14, 5.09 (br s, 2 H), 3.66 and 3.48 (br s, 2 H); mass spectrum, *m/e* 280, calcd 279.982 48, found 279.983 ± 0.005. Anal. Calcd: C, 55.91; H, 4.33. Found: C, 55.96; H, 4.49.

7: ^{1}H NMR (CCl_4) 7.2–6.84 (m, 5 H), 6.04 (m, 1 H), 5.72 (m, 2 H), 3.72–3.46 (m, 11 H); mass spectrum, *m/e* 398, calcd 398.018 47, found 398.018 ± 0.008.

8: **1H** NMR (CCl_4) 7.18 (br s, 1 H), 6.15 (m, 1 H), 5.98 (m, 1 H), 5.67 (g, J = 7 Hz, 1 H), 3.68 (g, J = 6 Hz, 1 H), 1.71 (d, J = 6 Hz, 3 H), 1.44 (d, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 156.0, 141.3, 131.3, 123.9, 110.1, 105.9, 43.7, 18.1, 16.8. Anal. Calcd: C, 50.25; H, 5.15. Found: C, 50.20; H, 5.12.

Tri-*n*-butyltin Hydride Reduction of 5d + 5d′ to 13 + 14. A 500-mg (1.6 × 10^{-3} mol) sample of a mixture of **5d** and **5d′** was refluxed for 4.5 h in 5 mL of benzene solution containing 1 g (3.4 × 10^{-3} mol) of tri-*n*-butyltin hydride and 100 mg of azobis(isobutyronitrile) (AIBN). The reaction mixture was then cooled to room temperature, and water was added. Extraction with ether, drying over magnesium sulfate and evaporation of the solvents gave 1.6 g of crude product. This was then bulb-to-bulb distilled [bp 120 °C (15 mmHg)] to give 200 mg of product mixture still containing some tin derivatives, which was purified by PLC (SiO_2, eluent pentane/ether, 95:5, v/v). A mixture of **13** and **14** (160 mg, 67%) was thus isolated as a colorless liquid: ^{1}H NMR (CCl_4) 6.4–6.2 (m, 1 H), 6.0–5.7 (m, 2 H), 5.4–5.1 (m, 1 H), 3.52 and 3.44 (s, 3 H), 3.15–3.04 (m, 2 H), 1.72 and 1.69 (s, 6 H); mass spectrum, *m/e* 149, calcd 149.120 44, found 149.120 ± 0.003.

In the same way **12** was obtained from **4d** (70% yield) after 2.5 h of reflux in benzene solution: ^{1}H NMR (CCl_4) 7.24 (br s, 1 H), 6.22 (m, 1 H), 5.92 (m, 1 H), 5.28 (t, J = 6 Hz, 1 H), 3.30 (d, J = 6 Hz, 2 H), 1.72 and 1.66 (2 s, 6 H).

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Registry No. (*E*)-**1a**, 87728-65-2; (*E*)-**1b**, 87728-66-3; **2a**, 8728-67-4; (*Z*)-**2b**, 87405-71-8; (*E*)-**2b**, 87405-70-7; (*Z*)-**2c**, 87728-68-5; (*E*)-**2c**, 87728-69-6; **2d**, 87405-68-3; **3a**, 87728-70-9; **3b**, 87728-71-0; **4a**, 87728-72-1; (*E*)-**4b**, 87728-73-2; (*Z*)-**4b**, 87728-74-3; (*E*)-**4c**, 87728-75-4; (*Z*)-**4c**, 87728-76-5; **4d**, 87728-77-6; **5a**, 87728-78-7; **5a′**, 87728-79-8; **5d**, 87728-80-1; **5d′**, 87728-81-2; **6a**, 87728-82-3; **6a′**, 87728-83-4; (*E*)-**7**, 87728-84-5; (*Z*)-**8**, 87728-85-6; (*E*)-**8**, 87728-86-7; **13**, 87728-87-8; **14**, 87728-88-9; (*Z*)-3,4-dibromo-2-pentene, 87760-77-8; (*E*)-3,4-dibromo-2-pentene, 87760-78-9; furan, 110-00-9; *N*-methylpyrrole, 96-54-8; thiophene, 110-02-1; 1,3,5-trimethoxybenzene, 621-23-8.

Reaction of Olefins with a Mixture of Phenylselenenyl Chloride and Mercury(II) Thiocyanate. Selective Syntheses of β-(Phenylseleno)alkyl Isothiocyanates as Precursors of Vinylic Isothiocyanates

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The reaction of olefins with a mixture of phenylselenenyl chloride and mercury(II) thiocyanate in benzene as the solvent affords β-(phenylseleno)alkyl isothiocyanates selectively in good to excellent yields. The mercury salt not only increases the N selectivity in a kinetically controlled reaction but also accelerates the isomerization of β-(phenylseleno)alkyl thiocyanates to the corresponding isothiocyanates. Oxidative elimination of the β-(phenylseleno)alkyl isothiocyanates gives predominantly vinylic isothiocyanates together with a small amount of allylic isothiocyanates. This sequence constitutes a convenient method for conversion of olefins to vinylic isothiocyanates.

It has been reported that the ambident nature of thiocyanate ion is affected by the presence of a mercury salt to increase the N selectivity in nucleophilic substitution reactions.[1] It was deemed valuable to introduce simul-

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Table I. Isomer Ratio of 1 to 2 under Various Conditions[a]

entry	selenium reagent (5 mmol)	$M(SCN)_n$ (mmol)	$CHCl_3$, mL	time, h	ratio[b] of 2/1
1	PhSeCl	$Hg(SCN)_2$ (2.5)	10	0.16	43:57
2	PhSeCl	$Hg(SCN)_2$ (2.5)	10	1	31:69
3	PhSeCl	$Hg(SCN)_2$ (2.5)	10	5	11:89
4	PhSeCl	$Hg(SCN)_2$ (2.5)	10	24	2:98
5	PhSeBr[c]	$Hg(SCN)_2$ (2.5)	10	0.16	50:50
6	PhSeI[d]	$Hg(SCN)_2$ (2.5)	10	0.16	69:31
7	PhSeCl	$Hg(SCN)_2$ (2.5)	50	0.16	53:47
8	PhSeCl	$Hg(SCN)_2$ (2.5)	50	5	44:56
9	PhSeCl	NaSCN (5)	10	0.16	98:2
10	PhSeCl	NaSCN (5)	10	120	93:7

[a] Carried out using cyclohexene (5 mmol) at 25 °C. [b] Yields and isomer ratios were determined by high-pressure liquid chromatography. Yields were almost quantitative in all cases. [c] Prepared in situ from diphenyl diselenide and bromine. [d] Prepared in situ from diphenyl diselenide and iodine.

taneously into olefins the isothiocyanato group[2] and the phenylseleno group which can be easily removed by oxidation. We have found that the reaction of mono- and 1,2-disubstituted olefins with a mixture of phenylselenenyl chloride and mercury(II) thiocyanate in benzene as the solvent affords β-(phenylseleno)alkyl isothiocyanates selectively in good to excellent yields. The direction of elimination of selenoxides bearing a nitrogen functional group on a vicinal position depends on the nature of the nitrogen functional group. Thus, allylic amides are formed selectively by oxidation of β-amidoalkyl phenyl selenides,[3] while nitroalkenes are produced selectively from β-nitroalkyl phenyl selenides.[4] The formation of allylic isomers is slightly favored over that of vinylic isomers in the cases of β-azidoalkyl[5] and β-(dialkylamino)alkyl[6] phenyl selenides. In the case of β-(phenylseleno)alkyl isothiocyanates, we have found that their ozonization produces predominantly the corresponding vinylic isothiocyanates accompanied by a small amount of the allylic isothiocyanates except where the vinylic isothiocyanate is unstable due to the strain of the carbon skeleton. Since vinylic isothiocyanate can be separated readily from other products (allylic isothiocyanate, diphenyl diselenide, etc.), these two procedures constitute a convenient method for the conversion of olefins to vinylic isothiocyanates. We describe here the details of these two procedures as one of our series of studies on organoselenium chemistry.[3,7]

Results and Discussion

Preparation of β-(Phenylseleno)alkyl Isothiocyanates. When phenylselenenyl chloride (2 equiv) was added to a suspension of mercury(II) thiocyanate (1 equiv) in benzene, the color changed gradually from dark red to orange probably due to the formation of phenylselenenyl thiocyanate[8a] and mercury(II) chloride (Scheme I). Reaction of cyclohexene (2 equiv) with this mixture at ambient temperature for 20 h gave *trans*-1-isothiocyanato-2-(phenylseleno)cyclohexane (1) as the sole product in 99% isolated yield. The formation of the isomer, 1-thiocyanato-2-(phenylseleno)cyclohexane (2), was detected by TLC analysis at the first stage of this reaction. To investigate the isomerization of 2 to 1, the ratio and yield of each was estimated by liquid chromatography at various reaction times by using chloroform as the solvent. Although the isomerization is slightly faster in benzene than in chloroform, benzene interferes with liquid chromatographic analysis of the products. The results are summarized in Table I. Yields are almost quantitative (>95%) in all cases. As the isomerization is slow in the cases of entries 7 and 8, entry 7 approximates the isomer ratio of a nearly kinetically controlled reaction. At higher reactant concentrations, the isomerization is faster and almost completed within 24 h (entries 1–4). In the absence of mercury salt, (entries 9 and 10), 2 is formed predominantly (98%) in a kinetically controlled reaction as reported by Garratt et al. (vide infra), and the isomerization of 2 to 1 was also extremely slow, affording 1 only in 7% yield after 5 days of reaction. Thus, it can be concluded that the mercury salt not only increases the N selectivity in a kinetically controlled reaction but also accelerates the isomerization of 2 to 1. The role of the mercury salt is postulated to interact with 2 to regenerate the episelenonium ion and form a complex anion, $(NCS-HgCl_2)^-$,

Scheme I

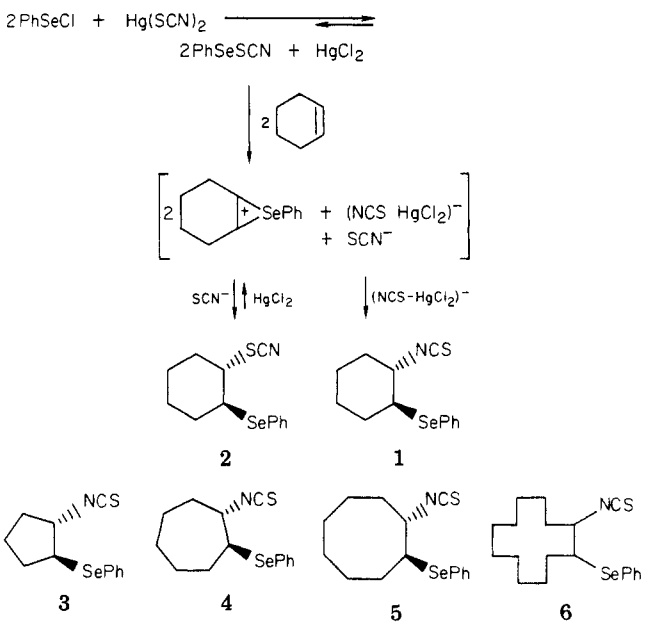

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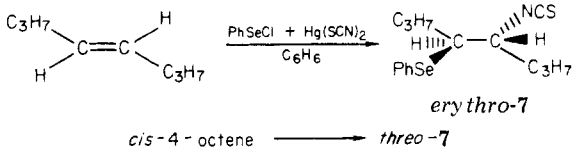
Table II. Preaparation of Various β-(Phenylseleno)alkyl Isothiocyanates[a]

olefin	time, h	product(s)	yield,[b] % (isomer ratio)
cyclopentene	14	3	99
cyclohexene	20	1	99
cycloheptene	0.5	4	97
cyclooctene	5	5	91
cyclooctene	20	5	92
cyclododecene	96	6	93
cis-4-octene	3	*threo*-7	84
cis-4-octene	20	*threo*-7	98
trans-4-octene	3	*erythro*-7	94
trans-4-octene	20	*erythro*-7	99
1-octene[c]	20	8a + 8d	84 (>95:<5)[d]
styrene	2	8b	72
styrene	20	8b	70
3,3-dimethyl-1-butene	15	8c	93

[a] Carried out by using olefin (5 mmol), phenylselenenyl chloride (5 mmol), and mercury(II) thiocyanate (2.5 mmol) in benzene (10 mL) at ambient temperature. [b] Isolated yield by column or preparative thin-layer chromatography. [c] Carried out at reflux temperature. [d] The isomer ratio was determined by comparison of peak intensities of the ^{13}C NMR signals.

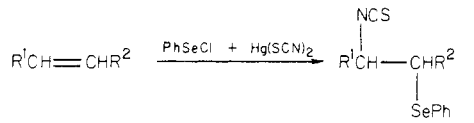
Scheme II



which then attacks the episelenonium ion to afford **1** (Scheme I). The use of phenylselenenyl bromide or iodide instead of the chloride showed that the N selectivity cannot be improved under kinetically controlled conditions (entries 5 and 6). The rate of isomerization was roughly measured by the addition of mercury(II) chloride to the reaction system of entry 9 (**2**/**1**, 98:2). After 1 h the ratio of **2** to **1** was found to be 70:30, this isomerization rate agreeing quite well with that observed in entries 1–4.

The reaction of olefins with phenylselenenyl thiocyanate in dichloromethane as the solvent has been reported by Garratt et al.[8] to afford β-(phenylseleno)alkyl isothiocyanates selectively in the cases of acyclic tetra-, tri-, and 1,2-disubstituted olefins either under conditions of kinetic control or by subsequent isomerization. However, there were no data on the isomerization in the cases of cyclic and monosubstituted olefins. The remarkable effect of the mercury salt in the cyclohexyl system, as described above, prompted us to apply the reaction to various cyclic as well as mono- and 1,2-disubstituted olefins that were expected to afford various products convenient for the study of selenoxide elimination reactions. As shown in Table II, β-(phenylseleno)alkyl isothiocyanates could be prepared in good to excellent yields in every case. The reactions were carried out until the β-(phenylseleno)alkyl thiocyanate could no longer be detected by TLC analyses. The times required are listed in Table II. The stereochemistry of **1** was confirmed to be trans by a large diaxial coupling constant (9 Hz) of protons attached respectively to carbons bearing the phenylseleno and isothiocyanato groups. This result indicates that the isomerization proceeds with retention of configuration, probably via an episelenonium ion intermediate. This stereospecificity was further confirmed by the reactions with *cis*- and *trans*-4-octenes. The trans isomer gave the erythro product and the cis the threo product (Scheme II). The products can be distinguished from each other by their ^{13}C NMR. In the case of cyclododecene a mixture of isomers (trans/cis, 63:37) was used as the starting substrate, and thus a mixture of isomers of **6** was formed in the same ratio, as expected. The isomerization of **2** to **1** was found to be slower than that of the corresponding thiocyanate to **4** or **5**, reflecting a higher energy barrier to a diaxial conformation of both substituents in the cyclohexane ring. That conformation is necessary for the formation of an episelenonium ion. The extremely slow isomerization in the case of cyclododecene may be due to the transannular interaction.

Scheme III



8a, $R^1 = n\text{-}C_6H_{13}$; $R^2 = H$
b, $R^1 = C_6H_5$; $R^2 = H$
c, $R^1 = H$; $R^2 = t\text{-}C_4H_9$
d, $R^1 = H$; $R^2 = n\text{-}C_6H_{13}$

Only in the case of 1-octene was the isomerization found to be extremely slow at ambient temperature. The thiocyanate adduct was detected by TLC analysis after reaction for 4 days. After 20 h at reflux temperature, the isomerization was complete, affording the isothiocyanate adduct, which consisted mainly of the Markovnikov adduct **8a** (>95% by ^{13}C NMR) accompanied by a small amount of the anti-Markovnikov adduct **8d** (Scheme III). In the case of styrene the reaction proceeded smoothly at ambient temperature, and the Markovnikov adduct **8b** was formed selectively. The anti-Markovnikov adduct **8c** was obtained as the sole product from 3,3-dimethyl-1-butene. The identification of the products is based on their ^1H NMR spectra in which absorption due to the protons geminal to isothiocyanato group (~4 ppm) can be distinguished from those geminal to phenylseleno group (~3 ppm). The structure of **8c** was unambiguously determined by triplet at 3.06 ppm and ABX octet at 3.77 and 3.86 ppm. The result indicates that even in a thermodynamically controlled reaction the isothiocyanato group or its complex ion with mercury salt suffers the steric hindrance of the *t*-Bu group and attacks the less positively charged primary carbon atom. This is in sharp contrast to the addition of phenylselenenyl bromide to 3,3-dimethyl-1-butene[9] where the Markovnikov adduct is obtained under thermodynamically controlled conditions.

Oxidation of β-(Phenylseleno)alkyl Isothiocyanates. Ozonization of **1** in dichloromethane at −78 °C followed by addition of the resulting solution to refluxing carbon tetrachloride affords 1-isothiocyanatocyclohexene (**9b**) as a major product accompanied by a small amount of 3-isothiocyanatocyclohexene (**10b**, Scheme IV). The formation of **9b** or **10b** could not be detected by TLC or GLC analysis when the dichloromethane solution of selenoxide was allowed to warm to ambient temperature. Oxidation by other reagents such as hydrogen peroxide and *m*-chloroperbenzoic acid resulted in the formation of an unworkable mixture of resinous products. The isomer ratio of **9a–f** to **10a–f** was estimated by GLC analysis, and **9a–f** were isolated by preparative TLC. As summarized in Table III, 1-isothiocyanatocycloalkenes are obtained as major products (**9a–d**/**10a–d**, ca. 4–6:1) in good to excellent yields by oxidative elimination of *trans*-1-isothiocyanato-2-(phenylseleno)cycloalkanes (**1**, **3–5**). Ozonization of *erythro*-**7** affords (*Z*)-**9f** in a good yield by retention of the carbon framework (trans → trans), reflecting the trans

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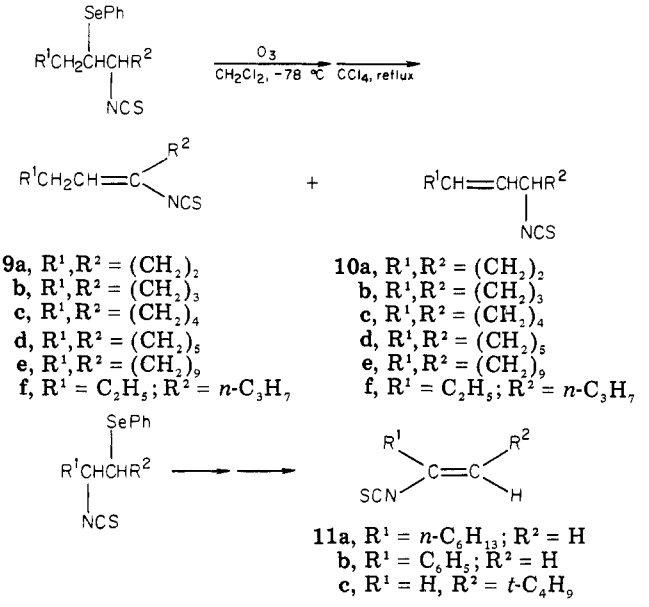
Table III. Oxidative Elimination of β-(Phenylseleno)alkyl Isothiocyanates[a]

selenide	time, h	product(s)	yield,[b] %	9/10[c] ratio	(Z)-/(E)-9 ratio
3	0.5	9a + 10a	53	82:18	
1	0.16	9b + 10b	64	83:17	
4	0.16	9c + 10c	59	80:20	
5	0.5	9d + 10d	83	86:14	
6 (erythro/threo, ca. 3:1)	0.5	9e + 10e	85	64:36	>99:<1
erythro-7	0.16	9f + 10f	76	94:6	>99:<1
threo-7	0.16	9f + 10f	77	46:54	11:89
8a	0.5	11a	50		
8b	0.16	11b	27[d]		
8c	0.16	11c	67		

[a] Ozonization was carried out using the selenide (3 mmol) in dichloromethane (20 mL) at −78 °C for 0.5 h, followed by addition to refluxing carbon tetrachloride and stirred under reflux for the time shown in the table. [b] Based on the isolated yield of vinyl isothiocyanate by preparative TLC. [c] Determined by GLC. [d] The product is unstable and decomposed during the purification by preparative TLC.

Scheme IV



addition of PhSe and NCS groups followed by cis elimination of the PhSe(O) group and hydrogen. The ratio of **9f** to **10f** is still higher (16:1) than those of cyclic olefins. Oxidative elimination of *threo*-**7**, however, affords a ca. 1:1 mixture of **9f** and **10f**, **9f** being a 9:1 mixture of *E* and *Z* isomers. It has been confirmed that (*E*)-**9f** (after purification by preparative TLC) isomerized to its *Z* isomer (10%/day) when it was allowed to stand in chloroform solution at ambient temperature. This observation indicates that only *E* isomer is produced initially from *threo*-**7** with retention of the carbon framework (cis → cis) which isomerizes to the mixture observed under present reaction conditions (reflux, 0.16 h). This instability of the *E* isomer forces the elimination away from the isothiocyanato group to give **10f** in a considerable amount. On ozonization of **6** (erythro/threo, ca. 3:2) the isomer ratio of the elimination products (vinylic vs. allylic) was found to be 64:36. GLC analysis revealed that the vinylic isomer is almost pure (>99%), and the absorption of the olefinic proton at 5.35 ppm[10] in the ^{1}H NMR spectrum suggests that it possesses the trans carbon framework. In the ^{1}H spectra of **10e** and **10f** the large coupling constants of olefinic protons show that they are trans isomers. In the cases of **8a**,[12] **8b**, and **8c** the selenoxides are so situated as to eliminate in one direction. The low yield of **11b** seemed to be due to decomposition during the isolation procedures. We could not obtain an analytically pure sample. The regiochemistry of **8c** was further confirmed by using off-resonance decoupling in the ^{13}C NMR spectrum of **11c** in which both olefinic carbons appeared as doublets. Although the coupling constant of the olefinic protons could not be observed in the ^{1}H NMR spectrum due to the overlapping of the two signals, their chemical shift (5.86 ppm) is consistent with a trans geometry (one proton is syn to the isothiocyanato group).

The regioselectivity of the selenoxide elimination described above suggests that the conjugation of the developing double bond[4] with the isothiocyanato group is larger than the repulsion of the dipole of the selenoxide and the carbon–nitrogen bond[3] (the conformer which is free from this repulsion may produce the allylic isothiocyanate). However, the former effect is not so dominating as to overcome the steric hindrance of (*E*)-**9e** or (*E*)-**9f** as shown by the formation of a considerable amount of **10e** or **10f**.

A general procedure for synthesis of vinylic isothiocyanates has not yet been established.[2,13] As vinylic isothiocyanates can be easily separated from other products such as allylic isothiocyanates and diphenyl diselenide, the formation of β-(phenylseleno)alkyl isothiocyanates followed by selenoxide elimination represents a convenient method for the conversion of olefins to vinylic isothiocyanates.

Experimental Section

IR spectra were recorded with Hitachi EPI-S2 and 260-50 spectrometers. ^{1}H and ^{13}C NMR spectra were obtained with JEOLCO JNM-PFT-100 instruments on solutions in $CDCl_3$ with Me_4Si as an internal standard. GLC analyses were carried out with a Shimadzu 4BMPF apparatus by using a EGSS-X (3%)–Chromosorb W column (3 m; N_2 as carrier gas). Liquid chromatographic analyses were carried out with a Waters HPLC system equipped with a 6000A solvent delivery system and a Model 440 absorbance detector (at 254 nm) with a μ-Porasil (3.9 mm × 0.3 m) column [hexane–chloroform (9:1) as the eluent] by using benzyl thiocyanate as an internal standard. All organic and inorganic materials were commercial products.

Preparation of *trans*-1-Isothiocyanato-2-(phenylseleno)cyclohexane (1). General Procedure. Phenylselenenyl chloride (0.96 g, 5.0 mmol) in benzene (5 mL) was added to a

(10) It is generally known that olefinic protons syn to a heteroatom absorb at a lower magnetic field than those anti to a heteroatom in ^{1}H NMR spectra of olefins bearing a heteroatom substituent.[11] In our study olefinic protons syn to the isothiocyanato group appeared at 5.52–5.89 ppm [(*E*)-**9f** and **9a–d**], and those anti to the isothiocyanato group appeared at 5.23 and 5.27 ppm [(*Z*)-**9f** and **11b**]. We believe that the absorption at 5.35 ppm in the text falls into the latter group.

(11) See, for example: Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectroscopic Identification of Organic Compounds"; Wiley: New York, 1974; p 216.

(12) Pure **8a** was isolated by column chromatography and used as a starting material in the selenoxide elimination reaction.

(13) See also: (a) Hussein, A. Q.; Jochims, J. C. *Chem. Ber.* **1979**, *112*, 1948–1955. (b) *Ibid.* **1979**, *112*, 1956–1972.

suspension of mercury(II) thiocyanate (0.79 g, 2.5 mmol) in benzene (5 mL), and the resulting suspension was stirred at ambient temperature for 1 h (the color turned gradually to orange). Cyclohexene (0.41 g, 5.0 mmol) in benzene (5 mL) was added (the color turned immediately to pale yellow), and the suspension was stirred at ambient temperature until 1-thiocyanato-2-(phenylseleno)cyclohexane (**2**) could no longer be detected by TLC analysis (20 h). The yellow precipitates were filtered off and washed with benzene. The combined washings and organic solution were washed successively with aqueous potassium iodide, aqueous sodium thiosulfate, and brine and then dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residual oil was subjected to column chromatography [silica gel, hexane to hexane–ethyl acetate (10:1) as the eluent] to give a trace amount of diphenyl diselenide and pure **1**: 1.47 g (4.96 mmol, 99%); pale yellow oil; IR (film) 2110 (br) cm^{-1}; ^1H NMR δ 1.2–1.8 (m, 6 H), 2.1–2.3 (m, 2 H), 3.16 (dt, 1 H, J = 4, 9 Hz), 3.57 (dt, 1 H, J = 4, 9 Hz), 7.2–7.4 (m, 3 H), 7.5–7.7 (m, 2 H). Anal. Calcd for $C_{13}H_{15}NSSe$: C, 52.70; H, 5.10; N, 4.73. Found: C, 52.88; H, 5.15; N, 4.97.

Spectral and combustion analytical data of other β-(phenylseleno)alkyl isothiocyanates are as follows. **8b** was isolated by preparative thin-layer chromatography. All other compounds were isolated by column chromatography and, if necessary, further purified by preparative TLC.

3: IR (film) 2100 (br) cm^{-1}; ^1H NMR δ 1.5–2.5 (m, 6 H), 3.45–3.68 (m, 1 H), 3.81–3.96 (m, 1 H), 7.2–7.3 (m, 3 H), 7.4–7.6 (m, 2 H). Anal. Calcd for $C_{12}H_{13}NSSe$: C, 51.06; H, 4.64; N, 4.96. Found: C, 51.22; H, 4.64; N, 5.32.

4: IR (film) 2050 (br) cm^{-1}; ^1H NMR δ 1.25–2.3 (m, 10 H), 3.45 (ddd, 1 H, J = 8, 6.5, 3 Hz), 3.94 (ddd, 1 H, J = 6.5, 5.5, 3 Hz), 7.1–7.35 (m, 3 H), 7.4–7.6 (m, 2 H). Anal. Calcd for $C_{14}H_{17}NSSe$: C, 54.19; H, 5.52; N, 4.51. Found: C, 54.55; H, 5.60; N, 4.71.

5: IR (film) 2050 (br) cm^{-1}; ^1H NMR δ 0.8–2.4 (m, 12 H), 3.45 (ddd, 1 H, J = 10, 7.5, 2.5 Hz), 3.92 (ddd, 1 H, J = 10, 5, 3.5 Hz), 7.2–7.4 (m, 3 H), 7.3–7.5 (m, 2 H). Anal. Calcd for $C_{15}H_{19}NSSe$: C, 55.55; H, 5.90; N, 4.32. Found: C, 56.05; H, 5.97; N, 4.60.

6: IR (film) 2070 (br) cm^{-1}; ^1H NMR δ 1.0–2.1 (m, 20 H), 3.2–3.4 (m, 1 H), 3.88 (ddd, 1 H, J = 8.5, 5.5, 2 Hz), 7.1–7.3 (m, 3 H), 7.4–7.6 (m, 2 H). Anal. Calcd for $C_{19}H_{27}NSSe$: C, 60.14; H, 7.17; N, 3.69. Found: C, 60.26; H, 7.26; N, 4.15.

***erythro*-7**: IR (film) 2090 (br) cm^{-1}; ^1H NMR δ 0.8–1.1 (m, 6 H), 1.1–1.9 (m, 8 H), 3.05–3.2 (m, 1 H), 3.81 (dt, 1 H, J = 8, 4.5 Hz), 7.2–7.3 (m, 3 H), 7.4–7.6 (m, 2 H); ^{13}C NMR δ 13.4 (q), 13.8 (q), 19.7 (t), 21.2 (t), 33.2 (t, $J_{C_\beta\text{-}Se}$ = 13 Hz), 35.9 (t), 50.5 (d, $J_{C_\alpha\text{-}Se}$ = 69 Hz), 62.8 (d), 131.8 (s), and phenyl signals. Anal. Calcd for $C_{15}H_{21}NSSe$: C, 55.20; H, 6.49; N, 4.29. Found: C, 54.97; H, 6.58; N, 4.75.

***threo*-7**: IR (film) 2080 (br) cm^{-1}; ^1H NMR δ 0.8–1.1 (m, 6 H), 1.1–2.0 (m, 8 H), 3.1–3.3 (m, 1 H), 3.82 (ddd, 1 H, J = 8.5, 5, 3 Hz), 7.2–7.4 (m, 3 H), 7.5–7.6 (m, 2 H); ^{13}C NMR δ 13.5 (q), 13.7 (q), 19.7 (t), 21.3 (t), 34.9 (t, $J_{C_\beta\text{-}Se}$ = 13 Hz), 35.3 (t), 50.8 (d, $J_{C_\alpha\text{-}Se}$ = 69 Hz), 62.5 (d), 132.1 (s), and phenyl signals. Anal. Found: C, 55.29; H, 6.60; N, 4.60.

8a: IR (film) 2070 (br) cm^{-1}; ^1H NMR δ 0.84 (t, 3 H), 1.0–1.4 (m, 8 H), 1.4–1.8 (m, 2 H), 3.03 (d, 2 H, J = 6 Hz), 3.75 (quintet, 1 H, J = 6.5 Hz), 7.1–7.3 (m, 3 H), 7.3–7.5 (m, 2 H); ^{13}C NMR δ 14.0 (q), 22.5 (t), 25.8 (t), 28.6 (t), 31.5 (t), 33.3 (t), 35.5 (t), 58.7 (d), 131.8 (s), and phenyl signals. Anal. Calcd for $C_{15}H_{21}NSSe$: C, 55.20, H, 6.49; N, 4.29. Found: C, 55.46; H, 6.61; N, 4.62.

8b: IR (film) 2050 (br) cm^{-1}; ^1H NMR δ 3.29 (d, 2 H, J = 7 Hz), 4.85 (t, 1 H, J = 7 Hz), 7.15–7.4 (m, 8 H), 7.4–7.5 (m, 2 H). Anal. Calcd for $C_{15}H_{13}NSSe$: C, 56.60; H, 4.18; N, 4.40. Found: C, 56.69; H, 4.10; N, 4.81.

8c: IR (film) 2100 (br) cm^{-1}; ^1H NMR δ 1.10 (s, 9 H), 3.06 (t, 1 H, J = 6 Hz), 3.77 (ABX q, 1 H, J = 15, 6 Hz), 3.86 (ABX q, 1 H, J = 15, 6 Hz), 7.1–7.3 (m, 3 H), 7.4–7.5 (m, 2 H). Anal. Calcd for $C_{13}H_{17}NSSe$: C, 52.34; H, 5.74; N, 4.70. Found: C, 52.73; H, 5.84; N, 5.11.

8d (detected as a mixture with **8a**): ^{13}C NMR δ 27.4 (t), 28.8 (t), 32.2 (t), 44.3 (d), 49.7 (t) (other signals overlapped with those of **8a**).

1-Thiocyanato-2-(phenylseleno)cyclohexane (2) (isolated by column chromatography with aluminium oxide packing): IR (film) 2050 cm^{-1}; ^1H NMR δ 1.1–2.0 (m, 6 H), 2.15–2.6 (m, 2 H), 3.1–3.45 (m, 2 H), 7.3–7.5 (m, 3 H), 7.6–7.8 (m, 2 H). Anal. Calcd for $C_{13}H_{15}NSSe$: C, 52.70; H, 5.10; N, 4.73. Found: C, 52.38; H, 4.96; N, 5.01.

Ozonization of *trans*-1-Isothiocyanato-2-(phenylseleno)cyclohexane (1) and Thermal Decomposition of the Selenoxide. General Procedure. A solution of **1** (0.89 g, 3.0 mmol) in dichloromethane (20 mL) was cooled to −78 °C under nitrogen, and ozone was introduced into the solution until the color of the solution became blue (~0.25 h). The solution was stirred at the same temperature for 0.5 h. Then nitrogen was bubbled through the solution to expel excess ozone. The colorless solution was rapidly introduced to refluxing carbon tetrachloride and heated under reflux for 10 min. The isomer ratio of **9b**/**10b** was revealed to be 83:17 by GLC analysis. After evaporation of the solvents the residual oil was subjected to preparative TLC to give pure **9b** (0.22 g, 1.6 mmol, 53%) and a mixture of **10b** and diphenyl diselenide. Pure **10b** was obtained by Kugelrohr distillation of this mixture (20 torr, bath temperature ~250 °C).

9b:[13b] IR (film) 2080 (br) cm^{-1}; ^1H NMR δ 1.4–1.8 (m, 4 H), 2.0–2.3 (m, 4 H), 5.73 (tt, 1 H, J = 4, 1.5 Hz). Anal. Calcd for C_7H_9NS: C, 60.39; H, 6.52; N, 10.06. Found: C, 60.16; H, 6.65; N, 10.09.

10b:[14] IR (film) 2060 (br) cm^{-1}; ^1H NMR δ 1.2–2.3 (m, 6 H), 4.1–4.3 (m, 1 H), 5.69 (ddt, 1 H, J = 10, 3.5, 2 Hz), 5.92 (dtd, 1 H, J = 10, 3.5, 1 Hz). Anal. Found: C, 60.23; H, 6.68; N, 10.27.

Spectral and combustion analytical data of several other vinylic[15] and allylic isothiocyanates are as follows.

9a: IR (film) 2050–2150 (br) cm^{-1}; ^1H NMR δ 1.8–2.2 (m, 2 H), 2.2–2.6 (m, 4 H), 5.64 (tt, 1 H, J = 2.5, 2 Hz). Anal. Calcd for C_6H_7NS: C, 57.56; H, 5.64; N, 11.19. Found: C, 57.16; H, 5.63; N, 11.14.

10a: IR (film) 2040–2150 (br) cm^{-1}; ^1H NMR δ 1.8–2.8 (m, 4 H), 4.6–4.8 (m, 1 H), 5.76 (dq, 1 H, J = 5.5, 2 Hz), 5.9–6.1 (m, 1 H). Anal. Found: C, 58.04, H, 5.75; N, 11.16.

9c: IR (film) 2050 (br) cm^{-1}; ^1H NMR δ 1.4–1.8 (m, 6 H), 2.05–2.2 (m, 2 H), 2.4–2.5 (m, 2 H), 5.89 (t, 1 H, J = 6.5 Hz). Anal. Calcd for $C_8H_{11}NS$: C, 62.70; H, 7.23; N, 9.14. Found: C, 62.92; H, 7.46; N, 9.31.

10c: IR (film) 2070 (br) cm^{-1}; ^1H NMR δ 1.4–2.4 (m, 8 H), 4.3–4.5 (m, 1 H), 5.6–6.0 (m, 2 H). Anal. Found: C, 62.69; H, 7.37; N, 9.24.

9d: IR (film) 2050–2100 (br) cm^{-1}; ^1H NMR δ 1.2–1.8 (m, 8 H), 1.9–2.2 (m, 2 H), 2.2–2.4 (m, 2 H), 5.69 (t, 1 H, J = 8.5 Hz). Anal. Calcd for $C_9H_{13}NS$: C, 64.62; H, 7.83; N, 8.37. Found: C, 64.58; H, 7.97; N, 8.58.

10d: IR (film) 2040–2100 (br) cm^{-1}; ^1H NMR δ 1.2–1.9 (m, 8 H), 2.0–2.3 (m, 2 H), 4.5–4.7 (m, 1 H), 5.56 (dd, 1 H, J = 10.5, 7 Hz), 5.77 (dtd, 1 H, J = 10.5, 8, 1 Hz). Anal. Found: C, 64.69; H, 7.96; N, 8.55.

9e: IR (film) 2050–2100 (br) cm^{-1}; ^1H NMR δ 1.0–1.7 (m, 16 H), 2.1–2.4 (m, 4 H), 5.35 (t, 1 H, J = 7.5 Hz). Anal. Calcd for $C_{13}H_{21}NS$: C, 69.90; H, 9.48; N, 6.27. Found: C, 70.23; H, 9.67; N, 6.56.

10e: IR (film) 2060–2150 (br) cm^{-1}; ^1H NMR δ 1.0–1.6 (m, 14 H), 1.6–1.9 (m, 2 H), 2.0–2.3 (m, 2 H), 4.17 (dt, 1 H, J = 4.5, 7 Hz), 5.38 (dd, 1 H, J = 15, 7 Hz), 5.66 (dt, 1 H, J = 15, 7 Hz). Anal. Found: C, 70.14; H, 9.66; N, 6.65.

(*Z*)-9f: IR (film) 2090 (br) cm^{-1}; ^1H NMR δ 0.91 (t, 6 H, J = 7.5 Hz), 1.2–1.5 (m, 4 H), 2.14 (q, 2 H, J = 7.5 Hz), 2.19 (t, 2 H, J = 7.5 Hz), 5.23 (t, 1 H, J = 7.5 Hz). Anal. Calcd for $C_9H_{15}NS$: C, 63.86; H, 8.93; N, 8.27. Found: C, 63.60; H, 9.07; N, 8.49.

(*E*)-9f:[16] IR (film) 2050–2100 (br) cm^{-1}; ^1H NMR δ 0.91 (t, 3 H, J = 7 Hz), 0.94 (t, 3 H, J = 7 Hz), 1.39 (sextet, 2 H, J = 7 Hz), 1.56 (sextet, 2 H, J = 7 Hz), 2.03 (q, 2 H, J = 7.5 Hz), 2.25 (t, 2 H, J = 7.5 Hz), 5.52 (t, 1 H, J = 7.5 Hz). Anal. Found: C, 64.14; H, 9.06; N, 8.63.

10f: IR (film) 2050 (br) cm^{-1}; ^1H NMR δ 0.8–1.2 (m, 6 H), 1.2–1.8 (m, 4 H), 2.07 (quintet, 2 H, J = 7 Hz), 4.15 (q, 1 H, J = 6.5 Hz), 5.38 (ddt, 1 H, J = 15, 6.5, 1.5 Hz), 5.76 (dtd, 1 H, J

(14) Greenwood, F. L.; James, W. J. *J. Am. Chem. Soc.* **1951**, *73*, 4495. Emerson, D. W.; Booth, J. K. *J. Org. Chem.* **1965**, *30*, 2480–2481.

(15) For preparations on larger scales, **9a–f** and **11a,c** can be isolated by column chromatography (silica gel). All of them, except for (*E*)-**9f**, can be stored as solutions in inert solvent at least for 1 month in a refrigerator.

(16) Cambie, R. C.; Mayer, G. D.; Rutledge, P. S.; Woodgate, P. D. *J. Chem. Soc., Perkin Trans. 1*, **1981**, 52–57.

= 15, 6, 1 Hz). Anal. Found: C, 63.59; H, 9.13; N, 8.59.

11a: IR (film) 2030, 2080 (br) cm^{-1}; ^1H NMR δ 0.88 (t, 3 H), 1.1–1.7 (m, 8 H), 2.27 (t, 2 H, J = 7 Hz), 4.79 (br s, 1 H), 4.92 (s, 1 H). Anal. Calcd for $C_9H_{15}NS$: C, 63.85; H, 8.93; N, 8.27. Found: C, 63.38; H, 8.97; N, 8.42.

11b: ^1H NMR δ 5.27 (d, 1 H, J = 1 Hz), 5.53 (d, 1 H, J = 1 Hz), 7.1–7.6 (m, 5 H).

11c: IR (film) 2070–2130 (br) cm^{-1}; ^1H NMR δ 1.04 (s, 9 H), 5.86 (s, 2 H); ^{13}C NMR δ 29.1 (q), 32.5 (s), 113.3 (d), 132.3 (s, N=C=S), 144.0 (d). Anal. Calcd for $C_7H_{11}NS$: C, 59.53; H, 7.85; N, 9.92. Found: C, 59.64; H, 8.07; N, 9.91.

Registry No. **1**, 87656-40-4; **2**, 87656-41-5; **3**, 87656-42-6; **4**, 87656-43-7; **5**, 87656-44-8; **6** (isomer 1), 87656-45-9; **6** (isomer 2), 87726-15-6; *threo*-**7**, 87656-46-0; *erythro*-**7**, 87656-47-1; **8a**, 87656-48-2; **8b**, 78386-96-6; **8c**, 87656-49-3; **8d**, 87656-50-6; **9a**, 87656-51-7; **9b**, 71055-61-3; **9c**, 87656-52-8; **9d**, 87656-53-9; (*Z*)-**9e**, 87656-54-0; (*Z*)-**9f**, 87656-55-1; (*E*)-**9f**, 77425-32-2; **10a**, 52566-12-8; **10b**, 2696-79-9; **10c**, 87656-56-2; **10d**, 87656-57-3; (*E*)-**10e**, 87656-58-4; (*E*)-**10f**, 87656-59-5; **11a**, 87656-60-8; **11b**, 87656-61-9; (*E*)-**11c**, 87656-62-0; cyclohexene, 110-83-8; cyclopentene, 142-29-0; cycloheptene, 628-92-2; cyclooctene, 931-88-4; (*Z*)-cyclododecene, 1129-89-1; (*E*)-cyclododecene, 1486-75-5; *cis*-4-octene, 7642-15-1; *trans*-4-octene, 14850-23-8; 1-octene, 111-66-0; styrene, 100-42-5; 3,3-dimethyl-1-butene, 558-37-2; phenylseleneyl chloride, 5707-04-0; mercuric thiocyanate, 592-85-8.

Intramolecular Carbon–Hydrogen Insertions of Alkylidenecarbenes. 1. Selectivity

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Base-promoted reaction between dialkyl ketones having γ-hydrogens and dialkyl (diazomethyl)phosphonates leads to formation of cyclopentenes in modest to high yields. The relative reactivity of various types of carbon–hydrogen bonds for the process, which involves insertion by an alkylidenecarbene, has been assessed, and the result has been compared to those reported when the carbene is generated by α elimination and by 1,2-shifts. The comparison suggests that a common species, viz., an alkylidenecarbene, may be responsible for formation of the cyclopentenes obtained from (a) flash vacuum pyrolysis of alkynes and (b) decomposition of diazoethenes, whereas that derived from α elimination of terminal vinyl halides is more selective, a result consonant with production of a carbenoid.

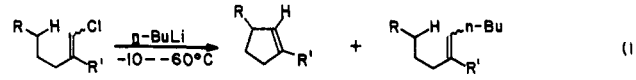
Recent years have witnessed a burgeoning interest in the generation and chemistry of unsaturated carbenes **1**.[2]

$$R_2C{=}(=C{=})_n{=}C$$

1

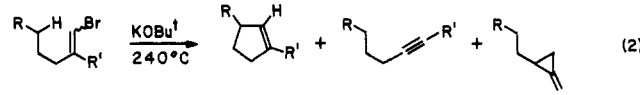
These species undergo many of the same types of reactions as do their saturated relatives[3] among which is insertion into various types of σ bonds.[4,5] The present paper is concerned with the intramolecular insertion of alkylidenecarbenes **1** (n = 0) into carbon–hydrogen bonds.

Several previous studies of such an intramolecular reaction have been reported. Koebrich et al. in a brief communication noted that α elimination of terminal vinyl chlorides with n-butyllithium at −10 to −60 °C afforded cyclopentenes, accompanied by coupling products, in "good" yields (eq 1) and cited unpublished work showing



(1)

that insertion occurs exclusively at C-5.[5c] Similarly, Wolinsky et al. found that base-promoted α elimination of vinyl bromides at 240 °C gave cyclopentenes (in yields ranging from 13% to 58%) along with alkynes and, in some cases, methylenecyclopropanes (eq 2).[5a,e] They were unable to detect products of insertion into the carbon–hydrogen bonds at C-4 or C-6, however.[6] This result reinforces the conclusion drawn from the earlier work[5d] that a considerable kinetic preference exists for reaction by way of a six-centered transition state. By assuming that the ratios of cyclopentenes to alkynes formed in their reactions were a reflection of the relative reactivities of the carbon–hydrogen bonds at C-5 toward insertion, Wolinsky et al. found the trend to be tertiary > secondary (benzylic) > secondary ≫ primary.[5e] Finally, Brown et al.[5d,f] and Dreiding et al.[5g,i,j] have made the remarkable observation



(2)

(1) This work taken in part from the dissertations of U.W. and D.H.G., submitted in partial fulfillment of requirements for the Ph.D. degree, University of Texas at Austin, 1980 and 1981.

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