Notes

Competitive Intramolecular Reactions of *n*-Alkenyl- and *n*-Alkyl-Substituted Cyclopropylidenes: An Insertion Reaction into Nonactivated C−H Bonds†

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Introduction

The generation and reaction behavior of cyclopropylidenes and their corresponding carbenoids has been the subject of intensive study.[1] Because the reactions of carbenoids, in general, are similar to those of the corresponding free carbenes, the term cyclopropylidenes is applied to *both* intermediates here. Cyclopropylidenes can undergo a number of reactions leading to an assortment of products (Figure 1). Most notable of the intramolecular reaction pathways for *n*-alkenyl-substituted cyclopropylidenes are cyclopropylidene−allene rearrangements (**1** → **2**), additions to double bonds (**1** → **3**), and insertion reactions into C−H bonds (**1** → **4**). First of all, the prevalent rearrangement to allenes has been investigated extensively by experiment[1] as well as in theory.[2] Moreover, spiro-annulation of **1a**, discovered by Skattebøl,[3] has been used repeatedly for the construction of the tricyclo[4.1.0.0^{1,3}]heptane carbon skeleton.[4] Beyond that, few cases of intramolecular insertion reactions into C−H bonds have been reported.[1] It appears, however, that an activation of the target C−H bond by an adjacent heteroatom O, N, or S is a prerequisite.[1,5] Even fewer examples are known where the insertion takes place into an allylic C−H[6] or into a C−H bond, which is not activated at all.[1] It is known that only slight variations, such as the chain length of the substituents attached to the cyclopropylidene, can lead to dramatic changes in the product formation.[1] To gain more insight into the reaction behavior of alkenyl- and alkyl-substituted cyclopropylidenes, the reactions of 5-hexenylcyclopropylidene (**1c**)[3b] and *n*-hexylcyclopropylidene (**5**)[7] were reexamined. Cyclopropylidenes **1c** and **5** differ only by their termini. These two carbenes are, therefore, well-suited to reveal the effect of the double bond on the chemo-, regio-, and stereoselectivity of **1**.

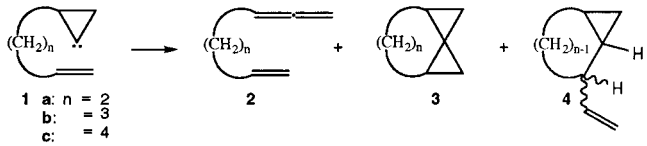

Figure 1. Reactions of alkenylcyclopropylidenes.

Results and Discussion

The precursors of cyclopropylidenes **1c** and **5** were synthesized by a single dibromocarbene addition to 1,7-octadiene and 1-octene, respectively. Application of ultrasound with finely powdered sodium hydroxide[8] and benzyltriethylammonium chloride (TEBA) as a phase-transfer catalyst gave 25 and 43% yields of the corresponding dibromocarbene adducts **6** and **7**, respectively.

The generation and reaction paths of cyclopropylidenes from geminal dihalocyclopropanes and alkyllithium have been shown to be temperature dependent.[3b,9] Therefore, all reactions were carried out at the same temperature and conditions. Methyllithium was added within 5 min to the ethereal solution of **6** or **7** at −78 °C, respectively. The reaction mixture was subsequently allowed to warm to a temperature above 0 °C within 30 min and then hydrolyzed.

The GC analysis from the reaction of 1,1-dibromo-2-(5-hexenyl)cyclopropane (**6**) (Figure 2) with methyllithium revealed that in addition to 1,2,8-nonatriene (**2c**),

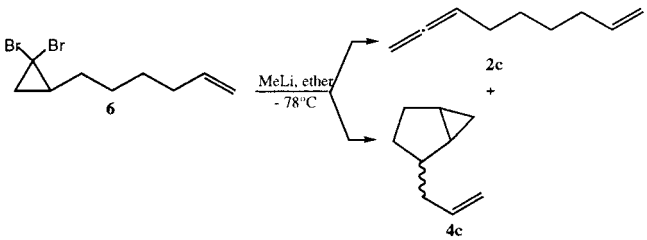

Figure 2. Reaction of 1,1-dibromo-2-(5-hexenyl)cyclopropane (**6**) with methyllithium.

a minor product **4c** (ratio **2c**:**4c** = 93:7) was formed. The allene **2c** could be separated by preparative GC (44% yield, 97% purity) from the minor product (2% yield, >99% purity). ^{1}H NMR spectroscopy confirmed that the lesser product was a mixture of yet unreported *syn*- and *anti*-2-(2-propenyl)bicyclo[3.1.0]hexane (**4c**) (syn:anti =

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† Carbene Rearrangements, Part 51. Part 50: Weber, J.; Haslinger, U.; Brinker, U. H. *J. Org. Chem.* **1999**, *64*, 6085.

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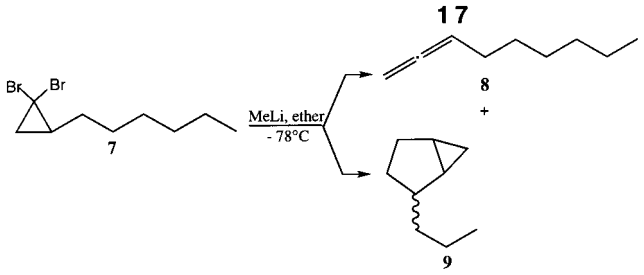


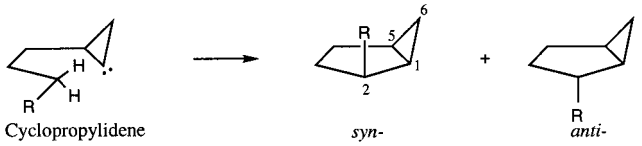
Figure 3. Reaction of 1,1-dibromo-2-hexylcyclopropane (**7**) with methyllithium.

70:30) formed by 1,5 C−H insertion reactions of cyclopropylidene **1c**. In addition, the GC chromatogram revealed about 3% of several products with higher retention times. However, a product resulting from a 1,6 C−H insertion was not observed.

The reaction of 1,1-dibromo-2-hexylcyclopropane (**7**) (Figure 3) with methyllithium has been often reported to yield allene **8**.[7] Though minor products were found, they were attributed to isomerizations of the allene group and not investigated further.[7] The reaction of **7** with methyllithium afforded three products. The major compound was the anticipated 1,2-nonadiene (**8**) in a 84:16 ratio (GC) with two lesser compounds. Because an attempt to separate the minor products from the allene **8** by preparative GC failed, **8** was first removed from the mixture by ozonolysis. After preparative GC, the two isomers of **9** were isolated in 5% yield. The ^{1}H NMR spectrum of these isomers (syn/anti = 60:40) revealed the characteristic signals for a 2-substituted bicyclo[3.1.0]-hexane system (vide infra). All observed data are consistent with an isomeric mixture of 2-propylbicyclo[3.1.0]-hexanes (**9**), which are 1,5 C−H insertion products of intermediate cyclopropylidene **5**.

Although the syntheses of allenes **2c** and **8** were already described over thirty years ago,[3b,7] two new aspects deserve special attention. They are the stereo- and regioselectivity of the C−H insertion reactions of carbenes **1c** and **5**. In both cases, substituted bicyclo-[3.1.0]hexanes are indeed formed in small amounts by 1,5 C−H insertions. The structures and stereochemistry of **4c** and **9** could be confirmed by examining the spectroscopic data for several syn- and anti-isomers of bicyclo[3.1.0]hexanes substituted at C-2. In addition, NOE studies performed on 2-dichloromethylbicyclo[3.1.0]-hexanes[10] were helpful.[11,12]

Table 1. Observed Ratios of Syn- to Anti-Isomers for Intramolecular 1,5 C−H Insertions (Error ca. ±3%)



1b, R = $-CH_dCH_2$	**4b,** 86:14[6a]
1c, R = $-CH_2-CH_dCH_2$	**4c**, 70:30
5, R = $-CH_2CH_2CH_3$	**9**, 60:40

While the chemoselectivities of **1c** and **5** are roughly comparable, the stereoselectivity shows a significant trend. This is especially true if the results from the reaction of 1,1-dibromo-2-(4-pentenyl)cyclopropane with methyllithium are included.[6a] The ratio of 1,2,7-nonatriene (**2b**) to 2-ethenylbicyclo[3.1.0]hexanes (**4b**) was 89:11 with a *syn*- to *anti*-**4b** ratio of 86:14 (see Table 1).

n-Hexylcyclopropylidene (**5**) forms the diastereomeric insertion product **9** with only slight stereoselectivity. In contrast, the presence of a double bond in **1c** leads to a preferred syn-insertion into the β-C−H bond. Furthermore, with the double bond in the α-position, as for 4-pentenylcyclopropylidene (**1b**), the stereoselectivity increases with a syn:anti ratio of 86:14. From these results, the following statements and conclusions can be made: (1) The introduction of a double bond favors *syn*-**4**. (2) The closer the double bond is to the C−H insertion center, the higher the syn:anti ratio. It is conceivable that if the reacting species are carbenoids, rather than free carbenes, an adjacent double bond could stabilize the activated complex through association with the lithium atom after halogen−metal exchange has taken place. Organolithium compounds show the tendency to engage in multicenter covalent bonding, and the complexation of lithium atoms with double bonds is well documented.[13] Since the activated complexes for the syn- and the anti-insertion are different, the extent of a possible interaction between the lithium atom and the double bond could be responsible for the observed stereoselectivity. This argument supports the notion that carbenoids rather than free carbenes are the reactive intermediates involved.

From this study and our earlier work[6a] it is obvious that the formation of a five-membered ring by a 1,5 C−H insertion is inherently favored. The preferred formation of a five-membered ring over a six-membered ring has been interpreted in terms of greater loss of rotational freedom for the activated complex of the six-membered ring formation.[14]The activation energies for the 1,5- and 1,6 insertion reaction calculated with the MINDO/3 method, are comparable at about 8−9 kcal/mol.[6b] With the activation energies being so close, an entropic control of these reactions is likely. During the insertion process, a partial positive charge build up is generated at the carbon atom from which the hydrogen moves away.[15] This view has been supported by theoretical calculations.[6a,b] For the insertion reactions of **1b**,**c**, an allylic double bond should also be capable of stabilizing a positive charge,

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(11) Additional support for the assigned stereochemistry could be found in the chemical shifts of the ^{13}C NMR signals for C-6. The syn-substituted diastereomers of **4c** and **9**, as for the bicyclo[3.1.0]hexanes with R = $-CHCl_2$, $-CHBr_2$[10] and R = $-CH_2CH{=}CH_2$ (**4b**),[6a,b] exhibit an upfield shift of 3−4 ppm relative to the anti-isomers. The magnitude of this shift is consistent with the expected γ gauche effect[12] of a substituent at C-2 in a syn-relationship with the three-membered ring.

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leading to an increased rate of the reaction. This, however, was not observed for **1c** experimentally. For the cyclopropylidenes **1b**,[6a] **1c**, and **5** the chemoselectivity of the allene formation versus C−H insertion is similar, within experimental accuracy (estimated to be ±3%). Furthermore, in the case of **1c**, insertion takes place in the 5-position rather than in the expected allylic 6-position. Therefore, it seems that the double bond in cyclopropylidene **1c** does not exhibit any particular activating effect, while it does appear to influence syn/anti selectivity.

Experimental Section

General Information. Melting points are uncorrected. Mass spectra (electron impact) were recorded at 70 eV as *m/e*. Proton and carbon-13 NMR spectra were recorded on 400 (100.6) and 360 (90.6) MHz spectrometers. IR spectra were obtained on a regular and an FT instrument. All reagents were obtained commercially and used without further purification. Where dry, water-free solvents were necessary, those were distilled from lithium aluminum hydride under N_2 or Ar atmosphere. Standard laboratory glassware was used under an inert atmosphere (N_2) and dried prior to use by heating and evacuating several times.

1,1-Dibromo-2-(5-hexenyl)cyclopropane (6).[3b] Finely powdered sodium hydroxide (20 g, 0.5 mol) and a small amount of triethylbutylammonium chloride (TEBA) were added to the solution of 1,7-octadiene (3.41 g, 31.0 mmol) and bromoform (7.83 g, 34.1 mmol ≡ 2.71 mL) in methylene chloride (50 mL). The mixture was ultrasonicated under reflux for 1 h. The solids were filtered off and washed with methylene chloride. Silica gel (ca. 20 g) was added to the combined filtrates and the solvent removed. The silica gel was washed with hexane, and after removal of the hexane the obtained yellow oil was fractionated in vacuo. **6** (2.38 g, 8.44 mmol ≡ 25%) was obtained in a purity of >99% (GC: glass capillary column, OV 101, 25 m × 0.272 mm i.d.; retention time, 9.7 min; injection temperature, 150 °C; detection temperature, 250 °C; initial oven temperature, 100 °C for 2 min; rate, 5 °C/min; final oven temperature, 200 °C). ^{1}H NMR (360 MHz, $CDCl_3$): δ 1.20 (t, 1H), 1.40−1.68 (m, 7H), 1.74 (dd, 1H), 2.07 (q, 2H), 4.96 ("dd", 1H), 5.02 ("dd", 1H), 5.82 (ddt, 1H). ^{13}C NMR (90.6 MHz, $CDCl_3$): δ 27.8, 28.0, 28.5, 29.5, 31.3, 32.4, 33.6, 114.5, 138.7.

Reaction of 1,1-Dibromo-2-(5-hexenyl)cyclopropane (6) with Methyllithium. The solution of **6** (2.38 g, 8.44 mmol) in ether (25 mL) was cooled to −78 °C, and methyllithium [7.3 mL of a 1.4 M solution (10.2 mmol) in ether] were added within 5 min. The cooling bath was removed, and the reaction mixture was allowed to warm above 0 °C and then carefully hydrolyzed with 10 mL of water under ice cooling. The aqueous layer was extracted three times with 10 mL of pentane each, and the combined organic layers were dried over K_2CO_3. Analytical GC showed two products with retention times in the range for C_9 hydrocarbons in a 97:3 ratio. ^{1}H NMR of the crude mixture indicated 1,2,8-nonatriene (**2c**) to be the main product. The ratio of the syn- and anti-isomer of the minor product, 2-(2-propenyl)-bicyclo[3.1.0]hexane (**4c**), was determined to be 70:30 (integration of characteristic signals for the methylene protons of the three-membered ring). In addition, less than 3% of several products with higher retention times were found. The solvent was distilled through a 20 cm Vigreux column, and the residue was short-path distilled under reduced pressure.

Preparative gas chromatography [column, 20% triscyanoethylpropane (TCEP) on Chromosorb HP, 80−100 mesh, 6 ft aluminum tubing, 0.190 in. i.d.; 175 mL He/min, 40 °C; retention time, 19.2 min] afforded nonatriene **2c** (455 mg, 3.72 mmol) in 96.8% purity (GC, same capillary column as before). Yield: 44%. The minor reaction product **4c** was reinjected on the preparative GC (retention time, 9.6 min; same column as before; 40 °C) for further purification. The isomeric mixture of **4c** (17 mg, 0.14 mmol) was obtained in a purity >99%. Yield: 2%. GC: retention time, 10.9 min; injection temperature, 150 °C; detection temperature, 250 °C; initial oven temperature, 100 °C for 2 min; rate, 5 °C/min; final oven temperature, 200 °C. **2c**: ^{1}H NMR (360 MHz, $CDCl_3$, 97:3 mixture with **4c**) δ 1.45 ("quint", 4H), 1.97−2.13 (m, 4H), 4.67 ("quint", 2H), 4.96 ("dd", 1H), 5.02 ("dd", 1H), 5.11 ("quint", 1H), 5.83 (ddt, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$, 97:3 mixture with **4c**) δ 28.1 (t, J_{C-H} = 128 Hz), 28.3 (t, J_{C-H} = 125 Hz), 28.6 (t, J_{C-H} = 126 Hz), 33.6 (t, J_{C-H} = 127 Hz), 74.6 (t, J_{C-H} = 167 Hz), 89.9 (d, J_{C-H} = 166 Hz), 114.3 (t, J_{C-H} = 155 Hz), 138.9 (d, J_{C-H} = 151 Hz), 200.1 (s); MS (70 eV), *m/e* (%) = 121 (1.2, $M^+ - 1$), 81 (27, $M^+ - C_3H_5$), 79 (100).

syn-**4c** (1α, 2α, 5α): ^{1}H NMR (360 MHz, 70:30 mixture of isomers in $CDCl_3$) δ 0.13−0.22 (m, 2H), 0.65−0.80 (m, 1H), 1.19−1.28 (m, 2H), 1.50−1.65 (m, 1H), 1.66−1.75 (m, 2H), 1.90−2.20 (m, 3H), 4.94 ("dd", 1H), 5.02 ("dd", 1H), 5.88 (ddt, 1H). *anti*-**4c** (1α, 2*β*, 5α): ^{1}H NMR (360 MHz, 70:30 mixture of isomers in $CDCl_3$) δ 0.11 ("dd", 1H), 0.32 (td, 1H), 1.06−1.13 (m, 1H), 1.26−1.36 (m, 1H). All other signals overlap or are hidden by the other signals.

syn-**4c**: ^{13}C NMR (90.6 MHz, 70:30 mixture of isomers in $CDCl_3$) δ 3.2 (t, J_{C-H} = 161 Hz), 16.4 (d, J_{C-H} = 165 Hz), 20.6 (d, J_{C-H} = 167 Hz), 26.4 (t, J_{C-H} = 130 Hz), 27.4 (t, J_{C-H} = 130 Hz), 38.1 (t, J_{C-H} = 121 Hz), 40.0 (d, J_{C-H} = 125 Hz), 114.4 (t, J_{C-H} = 157 Hz), 138.7 (d, J_{C-H} = 150 Hz). *anti*-**4c**: ^{13}C NMR (90.6 MHz, 70:30 mixture of isomers in $CDCl_3$) δ 6.7 (t, J_{C-H} = 160 Hz), 16.1 (d), 21.7 (d), 25.3 (t, J_{C-H} = 127 Hz), 39.6, 115.2 (t, J_{C-H} = 154 Hz), 138 (d, J_{C-H} = 145 Hz). All other signals overlap or are hidden by the other isomer. *syn*-**4c:** MS (70 eV), *m/e* (%) = M^+ not observed, 81 (100, $M^+ - C_3H_5$). *anti*-**4c**: MS (70 eV), *m/e* (%) = M^+ peak not observed, 81 (100, $M^+ - C_3H_5$).

1,1-Dibromo-2-hexylcyclopropane (7).[7] The mixture of 1-octene (5.61 g, 0.05 mol), bromoform (25.3 g, 0.10 mol), finely powdered NaOH (20 g, 0.5 mol), a small amount of TEBA, and methylene chloride (50 mL) was ultrasonicated for 1 h under reflux conditions. After the reaction had cooled to room temperature, the solids were filtered off and the solvents removed under reduced pressure. Fractionation in vacuo yielded as the main fraction **7** (6.09 g, 21.4 mmol) in a purity >92%. Yield: 43%. (GC: glass capillary column, OV 101, 25 m × 0.272 mm i.d.; retention time, 13.6 min; injection temperature, 150 °C; detection temperature, 250 °C; initial oven temperature, 100 °C for 2 min; rate, 5 °C/min; final oven temperature, 200 °C). ^{1}H NMR (360 MHz, $CDCl_3$): δ 0.9 (t, 3H), 1.19 (t, 1H), 1.24−1.41 (m, 6H), 1.41−1.67 (m, 5H), 1.74 (dd, 1H). ^{13}C NMR (90.6 MHz, $CDCl_3$): δ 14.0, 22.6, 28.3, 28.5, 28.9, 29.7, 31.5, 31.7, 32.6.

Reaction of 1,1-Dibromo-2-hexylcyclopropane (7) with Methyllithium. 7 (5.80 g, 0.0204 mol) was dissolved in dry ether (50 mL), and the solution was cooled to −78 °C. Within 5 min methyllithium [17.5 mL of a 1.4 M (24.5 mmol) solution in ether] was added. The cooling bath was removed, and the reaction mixture was warmed within ca. 30 min to a temperature >0 °C. Under ice cooling water (10 mL) was carefully added, and the aqueous layer was separated and washed with pentane. The combined organic phases were washed with water and brine and dried over K_2CO_3. Analytical GC (injection temperature, 150 °C; detection temperature, 250 °C; initial oven temperature, 100 °C for 2 min; rate, 5 °C/min; final oven temperature, 200 °C) showed three major products (94%) in a ratio of 79:9:6 (retention times: 11.4, 10.5, 10.8 min). The solvent was carefully removed under reduced pressure. The ^{1}H NMR spectrum showed, besides ether, all characteristic signals for the expected allene **8**. In addition, in the region 0.0−0.5 ppm, the characteristic signals of a bicyclo-[3.1.0]hexane system were observed. An attempt to separate the residue by preparative GC failed. The residue was, therefore, taken up in methanol (50 mL), cooled to −78 °C, and a stream of ozone was passed through the solution until the blue ozone color persisted. At 0 °C, formic acid (20 mL of a 88% solution) and hydrogen peroxide (10 mL of a 30% solution) were added. The mixture was warmed carefully and refluxed for 10 min. Pentane was added, and the aqueous layer was separated and washed three times with pentane. The combined organic phases were washed three times with sodium hydroxide (5% solution), once with brine, and then dried over K_2CO_3. After careful removal of the solvent under reduced pressure, the residue was condensed into a flask that had been cooled to −78 °C. Analytical GC showed the disappearance of the allene **8** with the two products **9** being unaffected. By preparative GC (column: 20% QF1 on Chromosorb W AW, 45−60 mesh, 15 ft, aluminum tubing, 0.190 in. i.d., 195 mL He/min; retention time, 4.8 min; oven temperature, 90 °C; injection temperature, 150 °C; detection temperature, 150 °C) 126 mg (1.02 mmol ≡ 5% yield) of a

60:40 mixture of the two isomeric compounds *syn*-**9** and *anti*-**9** were separated. **8**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.9 (t, 3 H), 1.21−1.48 (m, 8H), 2.0 (m, 2H), 4.65 ("quint", 2H), 5.08 ("quint", 1H). *syn*-**9**: ^{1}H NMR (360 MHz, 60:40 mixture of syn- and anti-isomers in $CDCl_3$) δ 0.11−0.18 (m, 2H), 0.62−0.75 (m, 1H), 2.01−2.14 (m, 1H). *anti*-**9**: δ 0.07 ("dd", 1H), 0.29 (td, 1H), 1.02−1.09 (m, 1H), 1.85−1.95 (m, 1H). All other signals overlap and cannot be assigned to one isomer: δ 0.87−0.95 (m), 1.09−1.46 (m), 1.47−1.64 (m), 1.64−1.77 (m). **9**: ^{13}C NMR (90.6 MHz, 60:40 mixture of syn- and anti-isomers in $CDCl_3$) *syn*-**9**: δ 3.0 (t, J_{C-H} = 158 Hz); *anti*-**9**: δ 6.7 (t, J_{C-H} = 158 Hz). All other signals overlap and cannot be assigned to one isomer: δ 14.3 (q), 14.4 (q, J_{C-H} = 124 Hz), 16.1 (d), 16.3 (d, J_{C-H} = 166 Hz), 20.7, 20.9, 22.0 (t), 22.1 (t), 25.4 (t, J_{C-H} = 128 Hz), 25.8 (t, J_{C-H} = 129 Hz), 26.8 (t, J_{C-H} = 129 Hz), 27.5 (t, J_{C-H} = 128 Hz), 36.1 (t, J_{C-H} = 125 Hz), 38.0 (t, J_{C-H} = 125 Hz), 39.7 (d, J_{C-H} = 125 Hz), 39.8 (d, J_{C-H} = 127 Hz). FT-IR ($CDCl_3$, 60:40 mixture of syn- and anti-isomers): 3065 and 3028 (cm^{-1}, $-CH_2-$ stretch, cyclopropane). GC-MS (70 eV), *m*/*e* (%): *syn*-**9**: 124 (2, M^+), 81 (100), 79 (25, $M^+ - C_3H_7$); *anti*-**9**: 124 (0.4, M^+), 81 (100), 79 (26, $M^+ - C_3H_7$).

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