Found: C, 72.19; H, 5.54; N, 4.09.

***trans*-3,4-Diacetoxy-3,4-dihydrobenz[*c*]acridine (11c).** The reaction of **9c** (175 mg, 0.5 mmol) with NBS in CCl_4 was effected as described for **10a**. The isomeric bromides **10c** and **10c'** were obtained in the ratio 2:1: ^1H NMR (major isomer) 8.6 (s, 1 H, H-7), 8.3 (d, 1 H, H-11), 7.1–8.0 (m, 5 H), 6.85 (t, 1 H, H-1), 6.5 (d, 1 H, H-4), 5.95–6.3 (m, 1 H, H-3), 2.5–3.1 (m, 2 H, H-2), 2.25 (s, 3 H, Me), 2.1 (s, 3 H, Me); $J_{3,4}$ = 8.4; ^1H NMR (minor isomer) 8.6 (s, 1 H, H-7), 8.3 (d, 1 H, H-11), 7.1–8.0 (m, 5 H), 6.85 (t, 1 H, H-1), 6.35 (d, 1 H, H-4), 5.4 (m, 1 H, H-3), 2.5–3.1 (m, 2 H, H-2), 2.25 (s, 3 H, Me), 2.1 (s, 3 H, Me); $J_{3,4}$ = 3.

Dehydrobromination of **10c** was performed as described for **11a** except that a reaction time of 1 h was suitable. The dihydrodiacetate **11c** (60 mg, 35% from **9c**) forms yellow fluorescent needles: mp 167 °C (after recrystallization from ethyl acetate/hexane); ^1H NMR 8.67 (s, 1 H, H-7), 8.35 (d, 1 H, H-1), 8.25 (d, 1 H, H-11), 7.4–8.0 (m, 5 H), 6.4 (d, 1 H, H-4), 6.32 (dd, 1 H, H-2), 5.80 (t, 1 H, H-3); $J_{1,2}$ = 9.9, $J_{2,3}$ = 4.2, $J_{3,4}$ = 6.3; IR (KBr) 1734 (C=O), 1222 (CO); UV (dioxane) 260 (130 000), 333 (5800, sh), 347 (6300), 366 (10 600), 385 (6800), 403 (5100, sh). Anal. Calcd for $C_{21}H_{17}NO_4$: C, 72.61; H, 4.93; N, 4.03. Found: C, 72.37; H, 5.03; N, 3.98.

***trans*-3,4-Dihydroxy-3,4-dihydrobenz[*c*]acridine (12c).** The hydrolysis of dihydro diol diacetate **11c** (250 mg, 0.7 mmol) was effected as described for the preparation of **12a**. Purification of **12c** by column chromatography with ethyl acetate (silica gel) gave **12c** as a yellow solid: mp 201 °C; 155 mg (85%); ^1H NMR (see Results and Discussion); IR (KBr) 3000–3500 (OH), 1090 (CO); UV (dioxane) 261 (94 000), 333 (2600, sh), 348 (5550), 365 (9400), 393 (5300), 415 (3700, sh); mass spectrum, *m/e* 263 (M^+). Compound **12c** could be retransformed to **11c** via acetylation.

Acknowledgment. We thank Dr. D. M. Jerina and Dr. E. Vogel for encouragement throughout this work.

Registry No. 3a, 225-11-6; **3c**, 225-51-4; **4a**, 77305-60-3; **4c**, 77305-61-4; **5a**, 77305-62-5; **5c**, 77305-63-6; **6a**, 77305-64-7; **7a**, 77305-65-8; 7c, 77305-66-9; **8a**, 77305-67-0; **8a** tetrahydrodiol, 77305-77-2; **8c**, 77305-68-1; **9a**, 77305-69-2; **9c**, 77305-70-5; **10a**, 77305-71-6; **10a'**, 77397-57-0; **10c**, 77305-72-7; **10c'**, 77397-58-1; **11a**, 77305-73-8; **11c**, 77305-74-9; **12a**, 77305-75-0; **12c**, 77305-76-1.

Synthesis of Enamides and Amides by Hydrozirconation–Acylation of Schiff Bases

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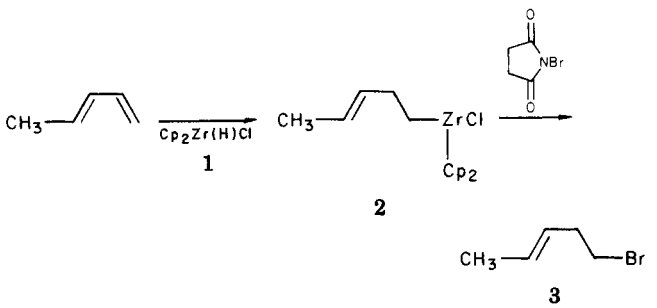
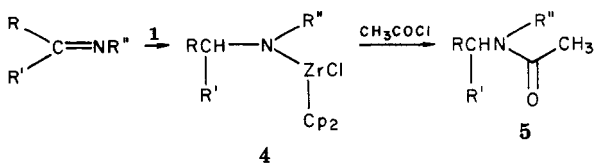
Schiff bases containing α-hydrogens react with hydridochlorodicyclopentadienylzirconium and then with acetyl or methyl oxalyl chloride to give enamides and imides or amides as products. Schiff bases derived from 2-methylcyclohexanone react with high regioselectivity, the thermodynamically more stable enamide being formed as the major or only unsaturated amide.

The hydrozirconation of olefins and dienes by hydridochlorodicyclopentadienylzirconium (1) is a useful reaction in organic chemistry.[2,3] Cleavage of the organozirconium intermediate, such as **2**, by electrophilic (e.g., *N*-bromosuccinimide) and other reagents can afford organic products not readily available by other methods (e.g., **3**).

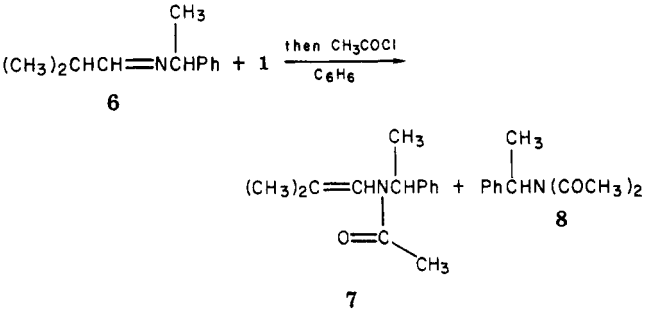


It seemed conceivable to us that Schiff bases would undergo hydrozirconation to give zirconium complexes of structural type **4** and that treatment of the latter with acid halides would afford amides such as **5**. We how report the results of this investigation.



Results and Discussion

We were surprised to observe that no reaction occurred between *N*-benzylidenemethylamine ($PhCH{=}NCH_3$) and the zirconium reagent **1** in benzene at room temperature, either in the presence or absence of an acid chloride. Reaction did take place, however, if the Schiff base function contained α-hydrogens. For example, treatment of imine **6** (derived from 2-methylpropanal and α-phenethylamine) first with **1** in benzene and then with acetyl chloride afforded the enamide **7** in 30% yield and the imide **8** in 20% yield. If one effected the reaction by first



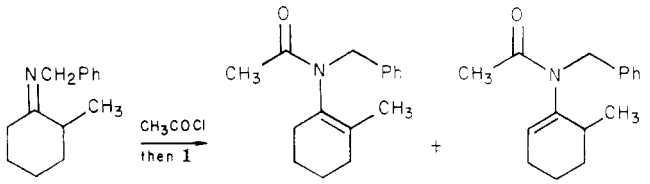
treating **6** with acetyl chloride and then with **1**, **7** was obtained in 25% yield and α-phenethylacetamide (**9**) in 10% yield, but **8** was not detected. Enamides have been synthesized by exposure of imines to an acid chloride and triethylamine,[4] raising the possibility that the zirconium reagent is functioning in the same manner as triethylamine. However, the enamide **7** was obtained as the sole product

(1) E. W. R. Steacie Fellow, 1980–82.
(2) Schwartz, J. *Pure Appl. Chem.* **1980**, *52*, 733.
(3) Schwartz, J. *J. Organomet. Chem. Libr.* **1976**, *1*, 461.
(4) Chupp, J. P., Weiss, E. R. *J. Org. Chem.* **1968**, *33*, 2357.

0022-3263/81/1946-2899$01.25/0

(82% yield) by reaction of **6** with acetyl chloride and then triethylamine.

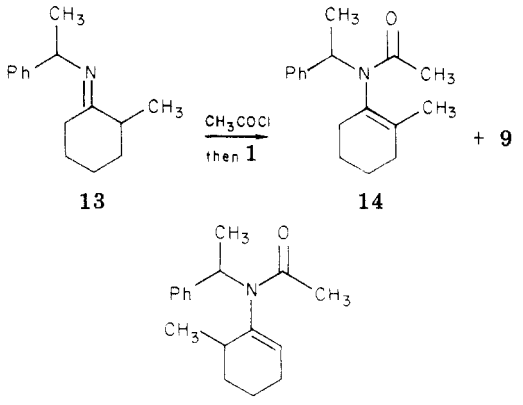
The regiochemistry of the hydrozirconation–acylation reaction is also different than the triethylamine process. Treatment of **10** (from 2-methylcyclohexanone and benzylamine) with acetyl chloride and then **1** afforded an isomeric mixture of **11** and **12** in a 6:1 ratio. The reaction



10 **11** **12**

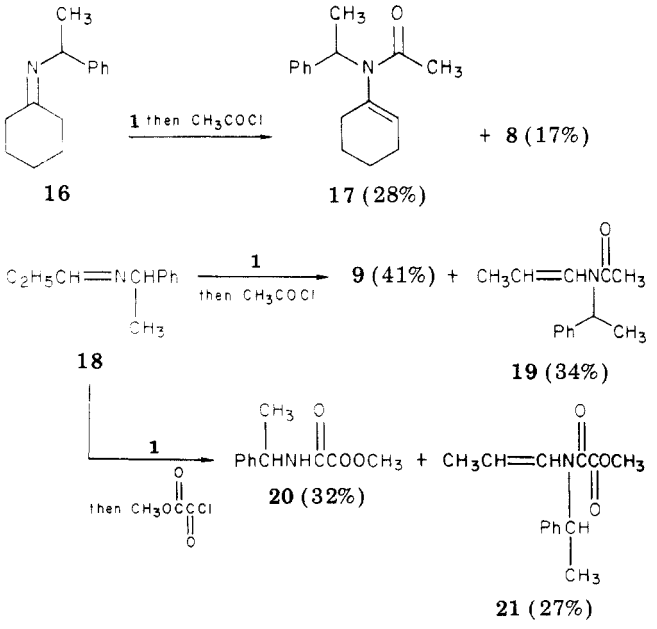
of **10** with acetyl chloride and triethylamine is less regioselective, with **11** and **12** being formed in a 3:1 ratio.

Enamide **14** was found in 44% yield by reaction of **13** with acetyl chloride and **1** (**9** was a byproduct). The enamide resulting from kinetic control, i.e., **15** (analogous to **11**), was not detected.



13 **14** **15**

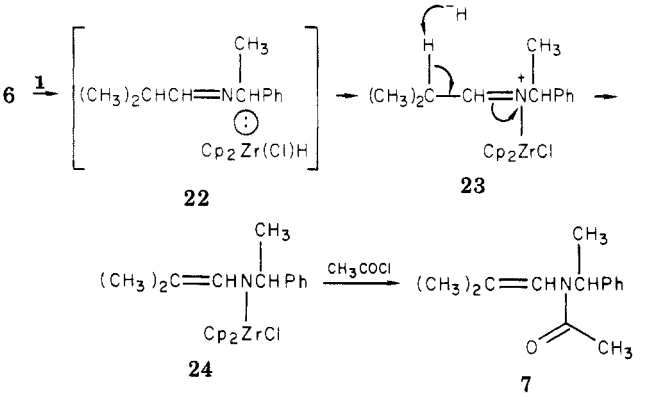
Both the enamide **17** and the imide **8** were obtained from imine **16**, which lacks a methyl group at the 2-position of the cyclohexanone ring. Another example of imine–zirconium reactions is the α-phenylethyl imine of propanal **18** (to give **19** → **21**).



16 **17** (28%) **18** **19** (34%) **20** (32%) **21** (27%)

The results described above suggest that the zirconium hydride (**1**) does not add to the carbon–nitrogen douuble bond of an imine. What may occur instead is interaction of the low-lying valence orbital of zirconium[5] with the nitrogen lone pair (Scheme I, illustrated for **6**) to give **22** and then **23** (the latter may be formed directly from **6**). Complex **23** may then be converted to the zirconium enamine **24**, the acylation of which would afford **7**. The amides may be formed from acylation of **23** followed by hydrolytic cleavage on workup. It is probable that N-acylation is the initial step when an imine is first treated with acetyl chloride and then with the zirconium reagent.

Scheme I



22 **23** **24** **7**

In conclusion, enamides and imides or amides are formed in fair to good yields by an interesting and unusual reaction of a zirconium hydride complex. Furthermore, as the results for Schiff bases derived from 2-methylcyclohexanone show, high or complete regioselectivity can be realized when compared with previous methods.

Experimental Section

Elemental analyses were carried out by Canadian Microanalytical Service Limited, Vancouver, British Columbia, and by Guelph Chemical Laboratories, Guelph, Ontario. The following instrumentation was used for spectral analyses: Varian T60 or HA-100 (^{1}H NMR), FT-80 (^{13}C NMR), MS 902 (mass), and a Unicam SP1100 (IR). Tetramethylsilane was the internal standard for NMR measurements, and carbon magnetic resonance spectra were recorded in the fully and partially decoupled modes.

The Schiff bases **6**, **10**, **13**, **16**, and **18** were prepared by refluxing, overnight, an equimolar mixture of an aldehyde or ketone with an appropriate amine in benzene. A Dean–Stark trap was used for the removal of water produced in the reaction. The carbonyl compounds and amines were commercial products, as was *N*-benzylidenemethylaminme and hydridochlorodicyclopentadienylzirconium. The acid chlorides and benzene were dried and distilled prior to use. All reactions were effected using dry nitrogen.

Reaction of 6 with 1 and Acetyl Chloride. A. Addition of 1 Followed by Acetyl Chloride. To the imine **6** (0.38 g, 2.2 mmol) in dry benzene (40 mL) was added 0.67 g (2.6 mmol) of **1**. The reaction mixture was stirred for 20 h at room temperature, acetyl chloride (0.3 mL) was then added, and the reaction mixxture was stirred for an additional 3 h. The mixture was poured into water and the organic products were extracted with ether. The ether extract was dried (Na_2SO_4) and then concentrated. The resulting oil was chromatographed on silica gel (200–300 mesh). Elution with ether–hexane (1:1) gave 0.090 g (20%) of the imide **8** followed by 0.15 g (30%) of the enamide **7**.

B. Addition of Acetyl Chloride Followed by 1. Acetyl chloride (0.15 mL) was added, drop by drop, to **6** (0.36 g, 2.0 mmol) in benzene (50 mL). The solution was stirred at room temperature for 4 h. The zirconium reagent (0.54 g, 2.1 mmol) was added and the resultant mixture was stirred for 18 h. Workup as described for procedure A gave 0.11 g (25%) of **7** and 0.033 g (10%) of α-phenylethylacetamide (**9**).

(5) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

7: IR (neat) ν_{CO} 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35 (d, 3 H, CH_3C=, J = 1.5 Hz), 1.42 (d, 3 H, CH_3CH, J = 6 Hz), 1.67 (d, 3 H, CH_3C=, J = 1.5 Hz), 1.95 (s, 3 H, $COCH_3$), 5.51 (m, 1 H, CH=), 6.05 (q, 1 H, $CHCH_3$), 7.27 (s, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 16.14, 17.65, 21.94, 22.37 (methyl carbons), 51.40 ($CHCH_3$), 119.95 (CH=), 127.23, 127.77, 128.14 (aromatic CH), 138.39, 140, 56 (quarternary carbons), 170.35 (carbonyl carbon). Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.00; H, 8.57; N, 6.68.

8: IR (neat) ν_{CO} 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.73 (d, 3 H, CH_3CH), 2.23 (s, 6 H, $COCH_3$), 5.85 (q, 1 H, $CHCH_3$), 7.32 (s, 5 H, Ph); mass spectrum, (m/e) 205 (M^+), 162 [$(M-COCH_3)^+$]. Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C. 70.04; H, 7.34; N, 6.46.

9: IR (neat) ν_{NH} 3250, ν_{CO} 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.48 (d, 3 H, CH_3CH, J = 8 Hz), 1.92 (s, 3 H, $COCH_3$), 5.10 (m, 1 H, CH), 6.15 (br s, 1 H, NH, undergoes D_2O exchange), 7.22 (s, 5 H, Ph); mass spectrum, m/e 163 (M^+).

Reaction of 6 with Acetyl Chloride and Triethylamine. To 0.40 g (2.3 mmol) of **6** in dry benzene (50 mL) was added acetyl chloride (0.3 mL). The solution was stirred for 15 min, 0.30 g (3.0 mmol) of triethylamine was added, and the reaction mixture was stirred at room temperature for 1.5 h and then refluxed for 2 h. Workup as in procedure A above gave **7** in 82% yield.

Reaction of 10 with Acetyl Chloride and 1. Acetyl chloride (0.2 mL) was added to 0.4 g (2.0 mmol) of **10** in benzene (50 mL), and the solution was stirred for 30 min at room temperature. Addition of the zirconium hydride (0.53 g, 2.0 mmol), followed by stirring for 17 h, and the usual workup conditons gave 0.27 g (56%) of **11**/**12** in a 6:1 ratio. Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70; N, 5.75. Found: C, 78.62; H, 9.15; N, 5.90.

11: IR (neat) ν_{CO} 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 3 H, CH_3C=), 1.3-1.7 (m, 4 H, CH_2CH_2), 1.75-2.30 (m, 4 H, allylic hydrogens), 1.96 (s, 3 H, $COCH_3$), 4.62 (s, 2 H, CH_2Ph), 7.32 (s, 5 H, Ph); mass spectrum, m/e 243 (M^+).

12: IR (neat) ν_{CO} 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.03 (d, 3 H, $CHCH_3$), 1.30-1.7 (m, 4 H, CH_2CH_2), 1.75-2.20 (m, 4 H, allylic hydrogens), 2.06 (s, 3 H, $COCH_3$), 4.63 (q, 2 H, CH_2Ph), 5.33 (m, 1 H, CH=), 7.32 (s, 5 H, Ph); mass spectrum, m/e 243 (M^+).

Reaction of 10 with Acetyl Chloride and Triethylamine. Reaction was effected in the manner described for **6** to give **11** and **12** in a 3:1 ratio (58% yield).

Reaction of 13 with Acetyl Chloride and 1. Reaction was effected as described for **10** to give the enamide **14** in 44% yield and **9** in 12% yield.

14: IR (neat) ν_{CO} 1645 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 3 H, CH_3C=), 1.47 (m, 3 H, CH_3CH), 1.93 (s, 3 H, $COCH_3$), 0.9-2.4 (m, 8 H, saturated protons of cyclohexene ring), 5.80 (m, 1 H, $CH(CH_3)$Ph), 7.23 (s, 5 H, Ph); mass spectrum, m/e 257 (M^+), 242 [$(M - CH_3)^+$], 214 [$(M - COCH_3)^+$]. Anal. Calcd for $C_{17}H_{23}NO$: C, 79.33; H, 9.00; N, 5.44. Found: C, 79.35; H, 9.32; N, 5.38.

Reaction of 16 with 1 and Acetyl Chloride. Reaction was effected as described in procedure A of **6** to give **17** in 28% yield and **8** in 17% yield.

17: IR (neat) ν_{CO} 1642 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.52 (d, 3 H, CH_3CHPh, J = 7 Hz), 2.03 (s, 3 H, $COCH_3$), 1.20-2.33 (m, 8 H, saturated protons of cyclohexene ring), 5.48 (m, 1 H, CH=), 6.00 (q, 1 H, $CH(Ph)CH_3$), 7.35 (s, 5 H, Ph); mass spectrum, m/e 243 (M^+), 200[$(M - COCH_3)^+$]. Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70; N, 5.75. Found: C, 78.96; H, 9.00; N, 5.64.

Reaction of 18 with 1 and Acetyl Chloride. Reaction was effected as described in procedure A of **6** to give **19** in 34% yield and **9** in 41% yield.

19: IR (neat) ν_{CO} 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.47 (d, 3 H, CH_3CHPh, J = 8 Hz), 1.58 (m, 3 H, CH_3CH=), 2.07 s, 3 H, $COCH_3$), 5.2-5.8 (m, 2 H, olefinic protons), 6.10 (q, 1 H, $CH(Ph)CH_3$), 7.23 (s, 5 H, Ph); mass spectrum, m/e 203 (M^+). Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 77.02; H, 8.43; N, 6.54.

Reaction of 18 with 1 and Methyl Oxalyl Chloride. Reaction was effected in the same manner as described in the previous procedure (except that methyl oxalyl chloride was used instead of acetyl chloride), affording **20** in 32% yield and **21** in 27% yield.

20: IR (neat) ν_{CO} 1740, 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.52 (d, 3 H, CH_3CH, J = 7 Hz), 3.78 (s, 3 H, OCH_3), 5.98 (q, 1 H, $CHCH_3$), 6.20 (br m, 1 H, NH), 7.30 (s, 5 H, Ph); mass spectrum, m/e 207 (M^+). Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.31; N, 6.76. Found: C, 64.11; H, 6.38; N, 6.58.

21: IR (neat) ν_{CO} 1730, 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.58 (d, 3 H, CH_3CH, J = 7 Hz), 1.82 (dd, 3 H, CH_3CH=, J_{CH_3CCH} = 2.5 J_{gem} = 7 Hz), 3.95 (s, 3 H, OCH_3), 5.1-5.7 (m, 2 H, olefinic protons), 6.30 (q, 1 H, $CHCH_3$), 7.38 (s, 5 H, Ph); mass spectrum, m/e 247 (M^+). Anal. Calcd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.66. Found: C, 67.91; H, 7.16; N, 6.02.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council for support of this work.

Registry No. **1**, 37342-97-5; **6**, 18805-19-1; **7**, 76947-29-0; **8**, 76947-30-3; **9**, 6284-14-6; **10**, 31887-88-4; **11**, 76947-31-4; **12**, 76947-32-5; **13**, 76947-33-6; **14**, 76947-34-7; **16**, 6115-06-6; **17**, 76947-35-8; **18**, 56063-09-3; **19**, 76947-36-9; **20**, 76947-37-0; **21**, 76947-38-1; acetyl chloride, 75-36-5; methyl oxalyl chloride, 5781-53-3.

Silanes in Organic Synthesis. 10. Cleavage Reactions of Silylcyclopropanes with Titanium Tetrachloride and Hydrogen Chloride[1]

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Received January 13, 1981

Seven trimethylsilyl-substituted cyclopropanes, both mono- and bicyclic, were treated with titanium tetrachloride and anhydrous hydrogen chloride to determine the regioselectivity and stereoselectivity of electrophilic attack on their strained three-membered ring. Whereas cleavage of *exo*-6-(trimethylsilyl)bicyclo[3.1.0]hexane with $TiCl_4$ occurs predominantly at the zero bridge, the principal product obtained from treatment with HCl is the result of peripheral bond scission. In the case of *exo*-7-(trimethylsilyl)bicyclo[4.1.0]heptane, addition to an edge bond occurs regiospecifically with both reagents. Substrates **11** and **12** were examined to assess the importance of carbonium ion intervention. Structural isomerizations mediated by such intermediates were observed with both silylcyclopropanes. For 1-(trimethylsilyl)bicyclo[4.1.0]heptane and 1-(trimethylsilyl)-1-pentylcyclopropane, the altered position of the silicon substituent was seen to have a major effect on the course of ring opening. Although the present data allow some analogies to be drawn with vinylsilanes, it is clear that silylcyclopropanes have a broader range of reaction pathways available to them than do their olefinic counterparts.

Spectroscopic[2] and chemical studies[3] of vinylsilanes have played an important role in the development of our understanding of the manner in which the olefinic π cloud interacts with neighboring silicon's vacant d orbitals.[4] The

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