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Stereochemistry of the Lead(IV) Acetate Fragmentation of 1-(Trimethylsiloxy)bicyclo[n.1.0]alkanes

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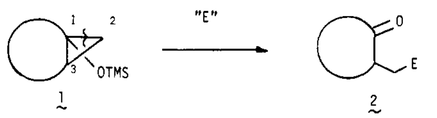
Abstract: The preparation of a series of *exo*- and *endo*-methyl-substituted 1-(trimethylsiloxy)bicyclo[*n*.1.0]alkanes **6** and **7** has been carried out and the compounds have been treated with lead(IV) acetate (LTA) then diazomethane to give the methyl (*E*)- and (*Z*)-alkenoates **10** and **11**. The fact that **6** gives only **10** and that **7** gives only **11** proves that the fragmentation is stereospecific. The reaction is best interpreted by assuming electrophilic ring opening, with inversion, followed by a Grob-type fragmentation with lead(II) acetate as the leaving group. The reaction is solvent dependent in a way that points to the intervention of cyclopropanols in the fragmentation of **6** and **7**.

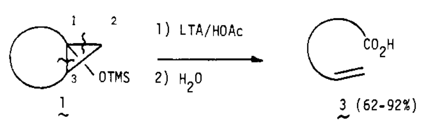
Studies of the reaction chemistry of bicyclic siloxy cyclopropanes **1** have, for the most part, focussed on the attack on **1** by electrophiles.[1] In general, such attack leads to one bond cleavage resulting in the production of **2** (eq 1).[2] Treatment of **1** with



(1)

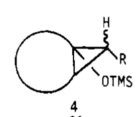
$Hg(OAc)_2$,[3] $AgBF_4$ or $Cu(BF_4)_2$,[4] and ZnI_2[5] is typical of the use of metal-containing electrophiles, and in each case, products can be rationalized by invoking C_1–C_2 scission as the initial reaction step. With $FeCl_3$[6] and electrolysis[7] C_1–C_3 cleavage occurs in processes that have been assumed to involve radical intermediates.

With the well-established pattern of behavior noted above, it was somewhat surprising to discover that the reaction between **1** and $Pb(OAc)_4$ (LTA) gave high yields of the corresponding alkenoic acids **3**, the products of two-bond cleavage (eq 2).[8] Here,



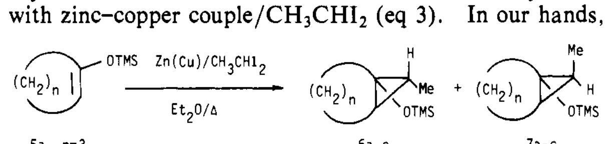
(2)

both C_1–C_2 and C_1–C_3 scission had occurred. This unique reaction seems to be general[9] and holds great potential as a synthetic method for the controlled introduction of "remote" functionality.[10] An important aspect of the reaction that has not heretofore been explored is the stereochemistry resulting from LTA-promoted cleavage of substituted siloxy cyclopropanes of type **4**. Reported here are the results of our studies in this area.



Results and Discussion

In order to test the stereochemical point in question, the enol silyl ethers **5** were converted to mixtures of **6** and **7** by treatment with zinc–copper couple/CH_3CHI_2 (eq 3). In our hands, the

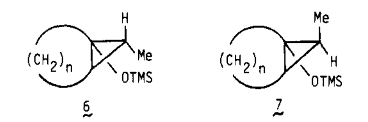


(3)

n	% yield	6/7
3	70	2.9/1
4	65	3.1/1
5	88	3.1/1

use of copper couple prepared from zinc dust/cuprous chloride was most advantageous.[11] During the course of our studies it was reported that this same reagent system affords excellent yields of cyclopropylcarbinols when applied to the appropriate allylic alcohols.[12] As noted in eq 3, **6** and **7** were formed in a ratio of approximately 3 to 1 with **6** predominating. Isomer ratios of **6a**/**7a** and **6b**/**7b** were determined by GLC analysis, and separation of the isomers was carried out with preparative GLC. With **6c**/**7c**, separation by GLC could not be realized so isomer ratios were determined by ^1H NMR with the signals for the trimethylsilyl (TMS) groups. Experiments involving the *tert*-butyldimethylsilyl

Table I. Summary of the Pertinent ^1H NMR and ^{13}C NMR Data for the Silyl Cyclopropyl Ethers **6** and **7**[a]



n	6 or 7	δ ^1H Me[b]	δ ^1H Me*CH*[b]	δ ^{13}C Me[b]
3	**6a**	1.01[c]	0.47–0.82[c]	11.77
3	**7a**	0.96[c]		6.87
4	**6b**	1.07	0.33–0.80	12.42
4	**7b**	1.00		7.42
5	**6c**[d]	1.07	0.42–0.74	13.09
5	**7c**[d]	0.97		8.49

[a] Spectra obtained on a Jeol FX-90Q spectrometer. [b] $CDCl_3$ as solvent. [c] CCl_4 as solvent. [d] Determined on a 3.1/1 mixture of **6c**/**7c**.

(1) For a number of reviews regarding the synthesis and chemistry of silyl cyclopropyl ethers, see: (a) Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: Berlin, 1983; pp 235–242. (b) Brownbridge, P. *Synthesis* **1983**, 1–28. (c) Rubottom, G. M. *J. Organomet. Chem. Libr.* **1982**, *13*, 127–269; **1981**, *11*, 267–414; **1980**, *10*, 277–424; **1979**, *8*, 263–377. (d) Rasmussen, J. K. *Synthesis* **1977**, 91–110.

(2) The reactions of **1** with "E" = X_2 and H^+ are cases in point. For examples, see: (a) "E" = Br_2: Murai, S.; Seki, Y.; Sonoda, N. *J. Chem. Soc., Chem. Commun.* **1974**, 1032–1033. LeGoaller, R.; Pierre, J.-L. *Can. J. Chem.* **1978**, *56*, 481–486. (b) "E" = H^+: Wenkert, E.; Buckwalter, B. L.; Craviero, A. A.; Sanchez, E. L.; Sathe, S. S. *J. Am. Chem. Soc.* **1978**, *100*, 1267–1273.

(3) Ryu, I.; Matsumoto, K.; Ando, M.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1980**, *21*, 4283–4286.

(4) Ryu, I.; Ando, M.; Ogawa, A.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1983**, *105*, 7192–7194.

(5) Ryu, I.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1977**, 4611–4614.

(6) Ito, Y.; Fujii, S.; Nakatsuka, M.; Kawamota, F.; Saegusa, T. *Org. Synth.* **1979**, *59*, 113–122.

(7) Torii, S.; Okamoto, T.; Ueno, N. *J. Chem. Soc., Chem. Commun.* **1978**, 293–294.

(8) Rubottom, G. M.; Marrero, R.; Krueger, D. S.; Schreiner, J. L. *Tetrahedron Lett.* **1977**, 4013–4016.

(9) Rubottom, G. M.; Marrero, R.; Beedle, E. C.; Krueger, D. S.; Kim, C. W., unpublished results.

(10) Macdonald, T. L. *Tetrahedron Lett.* **1978**, 4201–4204.

(11) Rawson, R. J.; Harrison, I. T. *J. Org. Chem.* **1970**, *35*, 2057–2058.

(12) Friedrich, E. C.; Biresaw, G. *J. Org. Chem.* **1982**, *47*, 2426–2429; **1982**, *47*, 1615–1618.

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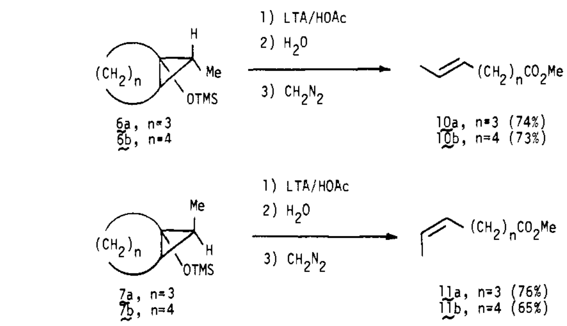
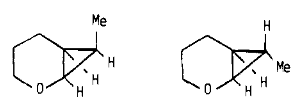
Scheme I



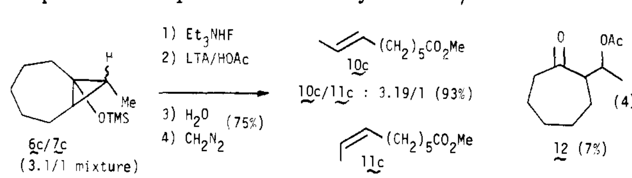
(TBS) enol ethers corresponding to **5** gave mixtures of **6**-TBS and **7**-TBS similar to those obtained from **5** except in the case of **5c**-TBS where the **6c**-TBS/**7c**-TBS ratio (GLC) was found to be 1/2.5. These substrates were not studied further.

Identification of **6** and **7** was readily accomplished based on the ^{1}H NMR and ^{13}C NMR spectra of the isomers. In each pair of isomeric silyl cyclopropyl ethers both the methyl ^{1}H and the methyl ^{13}C NMR signals for **6** appeared at lower field than the corresponding signals for **7**. Although the endo and exo methyl ^{1}H resonances of the 7-methylnorcarane isomers are found at δ 0.95 and 0.98, respectively,[13] introduction of oxygen into the system exerts a profound influence on the chemical shift of the methyl groups. Thus in **8** the methyl ^{1}H signal is found at δ 1.04 while that of **9** is located at δ 0.92.[13] A similar effect should be observed



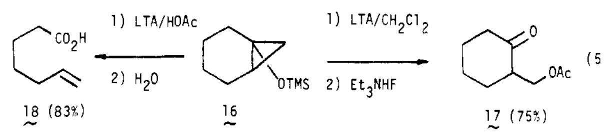
for the proton on carbon bearing methyl. This proton was observed upfield for **6** but was "buried" in the methylene region in **7**. In an analogous manner, the methyl ^{13}C signals for **6** were found at appreciably lower field than those for **7**. This is also consistent with the proposed structures.[14] The pertinent NMR data for **6** and **7** are summarized in Table I.

Pure compounds **6a**, **6b**, **7a**, and **7b** were treated with LTA/HOAc and, after an aqueous workup, the reaction mixtures were treated with excess diazomethane to afford **10** and **11** (Scheme I). GLC analysis of reaction mixtures prior to any purification step revealed that the **6** series gave greater than 99% of the (*E*)-alkenoic esters **10** while the **7** series gave greater than 99% of **11**, the (*Z*)-alkenoic esters. Oxidation of a 3.1/1 mixture of **6c**/**7c** was also carried out. In this experiment it was found necessary to treat **6c**/**7c** with Et_3NHF prior to treatment with LTA. This procedure prevented the occurrence of one bond cleavage and gave **10c**/**11c** in a ratio of 3.19/1 (GLC) accompanied by a small amount (7%) of **12** (eq 4). The yields cited for the production of **10** and **11** represent values for purified compounds subsequent to GLC analysis for **10**/**11** isomer ratios.



Identification of **10** and **11** rested upon the fact that (*E*)-alkenoic esters show a characteristic band at 980–970 cm^{-1} in the infrared.[15] Further, the ^{13}C NMR spectra of **10** show vinyl methyl resonances in the region of δ 17.7 while the corresponding signals for **11** occur in the region of δ 12.5.[16] Pertinent IR and ^{13}C NMR data for **10** and **11** are summarized in Table II. With **10c**/**11c**, ^{13}C NMR revealed that **10c** was the major isomer formed from the mixtures of **6c**/**7c**.

The results described above in which **6** gives only **10** while **7** gives only **11** confirm that the LTA-mediated two-bond cleavage of silyl cyclopropyl ethers is a stereospecific reaction. A mechanistic rationale for the observed data is presented in Scheme II with **7b** as an example of the general reaction. The assumption that alcohol **13** is precursor to **14** and **15** is based upon several experimental observations. First, the solvolysis of silyl cyclopropyl ethers in HOAc has been shown to be rapid in the presence of $Pb(OAc)_2$.[8] Further, the fact that **16** gives 75% of **17** with LTA/CH_2Cl_2 but 83% of **18** with LTA/HOAc[8] points to an alcohol precursor in the latter case (eq 5). The need to pretreat **6c**/**7c** with fluoride ion prior to LTA oxidation to subvert one-bond cleavage (see above) is most likely a reflection of slow solvolysis in these compounds although this point was not tested experimentally.



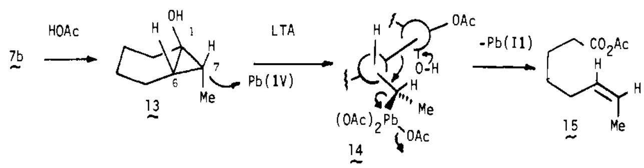
Attack of **13** by LTA occurs at C_7 on the rear of the C_1–C_7 bond, resulting in the formation of **14** in which the C_7 center has been inverted. This type of attack has been used to rationalize the inversion noted when cyclopropanols are reacted with Hg(OAc)$_2$.[17] The placement of the acetate group in **14** is arbitrary but is consistent with attack on the incipient carbocation center at C_1 from the least hindered side. The anti-periplanar relationship of the C_1–C_6 bond and the C_7–Pb bond of **14** is ideal for a Grob-type fragmentation.[18] The presence of an excellent leaving group in $Pb(OAc)_2$ coupled with the possibility for charge neutralization by loss of a proton make the transformation of **14** into **15** feasible. Apparently when OH is replaced by OTMS the displacement of lead by acetate is competitive with fragmentation and one-bond cleavage is observed. When the cyclopropyl ring is attacked by $Hg(OAc)_2$, the resulting C–Hg bond is too stable

Table II. Summary of the Pertinent ^{13}C NMR^a (Vinyl Methyl) and IR^b Data for **10** and **11**

n	**10**	δ ^{13}C Me	IR (cm^{-1})	*n*	**11**	δ ^{13}C Me	IR (cm^{-1})
3	**10a**	17.88	982	3	**11a**	12.93	
4	**10b**	17.49	970	4	**11b**	12.42	
5	**10c**	17.71	974	5	**11c**	12.57	

^{a}Spectra obtained on a Jeol FX-90Q spectrometer with $CDCl_3$ as solvent. ^{b}Spectra obtained on neat esters with KBr plates.

Scheme II



(13) Nishimura, J.; Kawabata, N.; Furukawa, J. *Tetrahedron* **1969**, *25*, 2647–2659.

(14) The cyclopropyl methyl group in **7** is cis to the two ring methylene groups and to the OTMS group. Due to the γ effect, the ^{13}C NMR signal for this methyl carbon would be expected to be shielded relative to the signal for the methyl group in **6** which is cis only to the OTMS group. For a discussion of this effect in the ^{13}C NMR spectra of *exo*- and *endo*-7-methylnorcaranes, see: Ishihara, T.; Ando, T.; Muranaka, T.; Saito, K. *J. Org. Chem.* **1977**, *42*, 666–670.

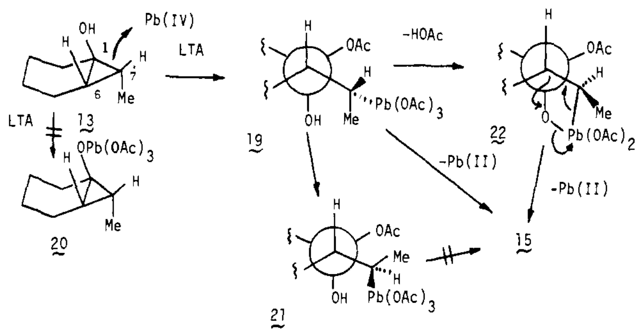
(15) Bellamy, L. J. "The Infra-red Spectra of Complex Molecules"; John Wiley & Sons: New York, 1975; pp 50–54.

(16) The shielding of the vinyl methyl group in **11** relative to the methyl group in **10** can be attributed to a through-space interaction in the *cisoid* isomer. For a discussion of this γ-like effect in alkenes, see: Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; pp 80–85.

(17) DeBoer, A.; DePuy, C. H. *J. Am. Chem. Soc.* **1970**, *92*, 4008–4013.

(18) For a review, see: Grob, C. A. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 535–546. For an account of the fragmentation of cyclic 1,3-diol monotosylates, see: Wharton, P. S.; Hiegel, G. A. *J. Org. Chem.* **1965**, *30*, 3254–3257.

Scheme III



to permit fragmentation and the mercurial is isolated in high yield.[3,17,19] Also, the presence of anhydride has been noted in reaction mixtures with LTA/HOAc when the reactions were monitored by ^{13}C NMR and IR prior to aqueous workup.[20]

The observed stereochemistry can also be rationalized by front side attack on the C_1–C_7 bond of **13** to give **19** in which retention has occurred at C_7 (Scheme III). This type of addition has been proposed for the reactions of the bicyclo[2.1.0]pentane system by mercury(II), thallium(III), and lead(IV) acetates.[21] The trans disposition of acetate group and the C_6–C_7 bond in **19** is also to be predicted from literature reports on the LTA oxidation of bicyclic cyclopropanes.[22] The use of HOAc as solvent in the reaction would seem to preclude any ligand exchange process leading to **20** prior to ring attack by Pb(IV).[23]

Bond rotation in **19** to give **21** containing an anti-periplanar disposition of the C_1–C_6 bond and the C_7–Pb bond would lead to the incorrect stereochemistry for the fragmentation and can thus be excluded. Syn-periplanar fragmentation or cyclization of **19** to afford **22** followed by "glycol-type" cleavage would lead to **15**.[24] Although either pathway noted above in Scheme II or Scheme III is feasible, the analogy cited for the cleavage of cyclopropanols with $Hg(OAc)_2$ giving inversion[17] seems to us to be compelling and we therefore favor the inversion route noted in Scheme II. It would be of great interest to explore the stereochemistry of the LTA-mediated one-bond-cleavage reaction, and we are currently engaged in studies along those lines. Information concerning this reaction can then hopefully be applied to the two-bond-cleavage question.

Conclusions

Substituted silyl cyclopropyl ethers **6** and **7** are fragmented stereospecifically by LTA to afford **10** and **11**, respectively. The most reasonable explanation for the process involves initial solvolysis in HOAc to give the corresponding cyclopropanols. The cyclopropanols then react with Pb(IV) to give alkenoic acid anhydrides by a series of reactions involving ring cleavage with inversion at the carbon bonded to lead followed by a Grob fragmentation. When CH_2Cl_2 is used in place of HOAc, solvolysis is subverted and the silyl cyclopropyl ethers give β-keto acetates by a reaction involving one-bond cleavage.

Experimental Section

Both ^1H NMR and ^{13}C NMR spectra were recorded on a Jeol FX-90Q spectrometer with tetramethylsilane as standard. IR spectra were obtained on Perkin-Elmer 599 and 621 infrared spectrometers. MS measurements were made with Hitachi Perkin-Elmer RMU 6E and VG 7070HS mass spectrometers. GLC measurements were carried out on Hewlett-Packard Model 700 and Model 5880A gas chromatographs. Elemental microanalyses were determined on a Perkin-Elmer Model 240 elemental analyzer. Commercial LTA (Alfa Ventron) was crystallized from glacial acetic acid prior to use, and triethylammonium fluoride was obtained as a hygroscopic white solid by the method of Hünig.[25] All reactions were run under a static atmosphere of dry nitrogen, and anhydrous magnesium sulfate was used as drying agent unless otherwise specified.

Preparation of Enol Silyl Ethers 5. Enol silyl ethers **5a–c** were prepared by the standard methods cited by House and co-workers.[26] Purification of **5a–5c** was effected by distillation at reduced pressure.

1-(Trimethylsiloxy)cyclopentene (5a). Compound **5a** was obtained in 76% yield; bp 150–153 °C (700 mm) [lit.[26] bp 158–159 (760 mm)]; n^{23}_D 1.4362 [lit.[26] n^{25}_D 1.4377].

1-(Trimethylsiloxy)cyclohexene (5b). Compound **5b** was obtained in 74% yield; bp 70–71 °C (20 mm) [lit.[26] bp 74–75 °C (20 mm)]; n^{23}_D 1.4458 [lit.[26] n^{24}_D 1.4451].

1-(Trimethylsiloxy)cycloheptene (5c). Compound **5c** was obtained in 75% yield; bp 78–81 °C (11 mm) [lit.[27] bp 76.5 °C (11 mm)]; n^{24}_D 1.4504 [lit.[27] n^{20}_D 1.4523].

General Method for the Preparation of *exo*- and *endo*-Methyl-Substituted 1-(Trimethylsiloxy)bicyclo[*n*.1.0]alkanes 6 and 7. A mixture of purified zinc dust[28] and cuprous chloride[11] was placed in a 100-mL 3-necked flask fitted with a stir bar, reflux condenser, and gas inlet tube. Dry ether (20 mL) was then added, and the mixture was refluxed with stirring for 20 min at which time 1 drop of 1,1-diiodoethane[29] was added and refluxing continued for 15 min. A solution of **5** in 5–10 mL of ether was then added in one portion, and the remainder of the 1,1-diiodoethane was added with continuous refluxing over the next 2.5 h. With the addition complete, refluxing was continued for 24 h at which time the mixture was cooled to room temperature[30] and diluted with 20 mL of pentane. The mixture was filtered through Celite and the filter pad washed with 80 mL of 1:1 pentane:ether. The combined filtrates were washed sequentially with 3 × 15 mL of saturated aqueous ammonium chloride solution and 2 × 10 mL of saturated aqueous sodium bicarbonate solution and were dried. Filtration and solvent removal in vacuo followed by vacuum distillation of the residues gave pure mixtures of *exo*- and *endo*-methyl-substituted 1-(trimethylsiloxy)bicyclo[*n*.1.0]-alkanes **6** and **7**. Pure samples of **6a**, **6b**, **7a**, and **7b** were obtained with preparative GLC while **6c** and **7c** could not be separated by GLC.

***exo*- and *endo*-6-Methyl-1-(trimethylsiloxy)bicyclo[3.1.0]hexane (6a and 7a).** From 13.29 g (203 mmol) of zinc dust, 1.98 g (20.0 mmol) of cuprous chloride, 6.34 g (40.6 mmol) of **5a**, and 45.83 g (163 mmol) of 1,1-diiodoethane there was obtained 5.21 g (70%) of a 2.9/1.0 mixture of **6a**/**7a** as determined by GLC (6 ft × 0.25 in. 12.5% SE-52), bp 93–98 °C (55 mm). Pure samples of **6a** and **7a** were obtained by preparative GLC (3 m × 0.25 in. 5% SE-30).

***exo*-6-Methyl-1-(trimethylsiloxy)bicyclo[3.1.0]hexane (6a):** IR (neat) 3028, 1256, 845 cm^{-1}; n^{21}_D 1.4426; ^1H NMR (CCl_4) δ 0.10 (s, 9 H), 0.47–0.82 (m, 1 H), 1.01 (d, 3 H, J = 5.5 Hz), 1.20–2.13 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 0.74, 11.77, 17.73, 21.36, 26.49, 30.06, 34.11, 68.80; MS m/z 184 (M^+, 100), 169 (93), 156 (40), 141 (20), 75 (27), 73 (30). Anal. Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.94. Found: C, 65.07; H, 11.14.

***endo*-6-Methyl-1-(trimethylsiloxy)bicyclo[3.1.0]hexane (7a):** IR (neat) 3018, 1256, 848 cm^{-1}; n^{21}_D 1.4443; ^1H NMR (CCl_4) δ 0.08 (s, 9 H), 0.95–2.13 (m, 8 H), 0.96 (d, 3 H, J = 3 Hz); ^{13}C NMR ($CDCl_3$) δ 0.61, 6.87, 22.78, 23.44, 24.39, 27.97, 31.72, 69.38; MS, m/z 184 (M^+, 100), 169 (92), 155 (21), 75 (31). Anal. Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.94. Found: C, 64.91; H, 10.90.

***exo*- and *endo*-7-Methyl-1-(trimethylsiloxy)bicyclo[4.1.0]heptane (6b and 7b).** From 4.43 g (67.7 mmol) of zinc dust, 0.67 g (6.8 mmol) of cuprous chloride, 2.32 g (13.6 mmol) of **5b**, and 13.41 g (47.6 mmol) of diiodoethane there was obtained 1.75 g (65%) of a 3.1/1.0 mixture of **6b**/**7b** as determined by GLC (6 ft × 0.25 in. 12.5% SE-52), bp 68–75 °C (23 mm). Pure samples of **6b** and **7b** were obtained by preparative GLC (6 ft × 0.25 in. 5% FFAP).

***exo*-7-Methyl-1-(trimethylsiloxy)bicyclo[4.1.0]heptane (6b):** IR (neat) 2970, 1250, 840 cm^{-1}; n^{22}_D 1.4509; ^1H NMR ($CDCl_3$) δ 0.20 (s, 9 H),

(19) The fact that solvolytic lability of carbon metal bonds decreases in the order C–Pb > C–Tl > C–Hg is well documented. Ouellette, R. J. In "Oxidation in Organic Chemistry", Part B; Trahanovsky, W. S., Ed.; Academic Press: New York, 1973; p 135.

(20) Spectral analysis of the oxidation product of **16** prior to treatment with water showed IR bands at 1820 and 1750 cm^{-1} and ^{13}C NMR resonance at δ 169.36, both consistent for a postulated anhydride.

(21) Katsushima, T.; Yamaguchi, R.; Iemura, S.; Kawanisi, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3318–3323.

(22) For a review, see: ref 19, pp 158–166.

(23) Criegee, R. In "Oxidation in Organic Chemistry", Part A; Wiberg, K. B., Ed.; Academic Press: New York, 1965; p 284.

(24) Rubottom, G. M. In "Oxidation in Organic Chemistry", Part D; Trahanovsky, W., Ed.; Academic Press: New York, 1982; p 27.

(25) Hünig, S.; Wehner, G. *Synthesis* **1975**, 180–182.

(26) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324–2336.

(27) Birkofer, L.; Dickopp, H. *Chem. Ber.* **1969**, *102*, 14–22.

(28) Schriner, R. L.; Neumann, F. W. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, pp 73–75.

(29) Letsinger, R. L.; Kammeyer, C. W. *J. Am. Chem. Soc.* **1951**, *73*, 4476.

(30) On several occasions, the conversion of **5** to **6** and **7** was not complete at this point. In these cases, additional couple and CH_3CHI_2 were added and refluxing continued until **5** was consumed (GLC).

0.33–0.80 (m, 1 H), 1.07 (d, 3 H, J = 6 Hz), 1.17–2.17 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 1.16, 12.42, 21.54, 21.90, 24.16, 26.01, 32.86, 59.38; MS, m/z 198 (M^+, 93), 183 (100), 169 (77), 75 (16), 73 (28). Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.59; H, 11.18. Found: C, 66.40; H, 10.96.

***endo*-7-Methyl-1-(trimethylsiloxy)bicyclo[4.1.0]heptane (7b)**: IR (neat) 2965, 1250, 840 cm^{-1}; n$^{22}_D$ 1.4517; ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9 H), 0.90–2.20 (m, 10 H), 1.00 (br s, 3 H); ^{13}C NMR ($CDCl_3$) δ 1.10, 7.42, 18.44, 20.23, 21.48, 21.96, 22.14, 28.57, 56.70; MS, m/z 198 (M^+, 90), 183 (100), 169 (84), 75 (20), 73 (35). Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.59; H, 11.18. Found: C, 66.83; H, 11.10.

***exo*- and *endo*-8-Methyl-1-(trimethylsiloxy)bicyclo[5.1.0]octane (6c and 7c)**. From 8.83 g (135 mmol) of zinc dust, 1.34 g (13.5 mmol) of cuprous chloride, 5.00 g (27.1 mmol) of **5c** and 26.82 g (95.2 mmol) of diiodoethane was obtained 5.08 g (88%) of a 3.1/1.0 mixture of **6c**/**7c** as determined by ^{1}H NMR (integration of the trimethylsilyl peaks), bp 95–100 °C (7.3 mm). Capillary GLC failed to resolve the mixture of **6c** and **7c**: IR (neat) 3015, 1257, 850 cm^{-1}; n$^{22}_D$ 1.4560; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, OTMS, **7c**), 0.15 (s, OTMS, **6c**), 0.42–0.74 (m, C_8-H, **6c**), 0.9–2.42 (m, **6c** and **7c**), 0.97 (d, 3 H, J = 4.4 Hz, **7c**), 1.07 (d, 3 H, J = 5.6 Hz, **6c**); ^{13}C NMR ($CDCl_3$) δ 1.22 (OTMS, **6c** and **7c**), 8.49 (C_8-Me, **7c**), 13.08 (C_8-Me, **6c**), 63.37 (C_1, **7c**), 64.98 (C_1, **6c**); MS, m/z 212 (M^+, 79), 197 (62), 183 (35), 169 (100), 75 (12), 73 (23). Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.85; H, 11.39. Found: C, 68.00; H, 11.62.

General Procedure for the LTA/HOAc Oxidation of the Silyl Cyclopropyl Ethers 6a, 6b, 7a, and 7b. A mixture of **6** or **7** and LTA in 5 mL of glacial acetic acid was stirred for 8 h at room temperature. Then 5 mL of water was added and stirring was continued for an additional 20 min. The mixture was then diluted with 20 mL of CH_2Cl_2 and filtered through Celite. The layers were separated and the organic layer was washed sequentially with 3 × 10 mL of water and 10 mL of brine solution and dried with anhydrous Na_2SO_4. The solution was filtered and solvent removed in vacuo to afford a residue that was treated with excess diazomethane.[31] Removal of solvent in vacuo gave an oil that was examined by GLC (30 m × 0.25 mm 1.0 μM DB-1 capillary column or 5 m × 0.25 in. 5% DC-550 column) prior to purification (see below).

The LTA Oxidation of 6a. From 0.215 g (1.17 mmol) of **6a** (99.7/0.3 **6a**/**7a** by capillary GLC) and 0.530 g (1.20 mmol) of LTA was obtained 0.123 g (74%) of methyl (E)-5-heptenoate (**10a**). GLC (capillary column) indicated a 99.4/0.6 E/Z ratio. Molecular distillation gave bp 60–63 °C (17 mm) [lit.[32] bp 69 °C (17 mm)]; n$^{25}_D$ 1.4307 [lit.[32] n$^{18}_D$ 1.4306]; IR (neat) 1740, 982 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.08–2.49 (m, 9 H), 3.66 (s, 3 H), 5.29–5.56 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.88, 24.87, 32.02, 33.48, 51.38, 125.96, 130.34, 174.12; MS, m/z 142 (M^+, 6), 111 (14), 110 (29), 74 (100), 69 (27), 68 (47), 55 (47), 43 (73), 41 (39).

The LTA Oxidation of 7a. From 0.077 g (0.42 mmol) of **7a** (97.9/2.1 **7a**/**6a** by capillary GLC) and 0.185 g (0.42 mmol) of LTA was obtained 0.044 g (73%) of methyl (Z)-5-heptenoate (**11a**). GLC (capillary column) indicated a 96.9/3.1 Z/E ratio. IR (neat) 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.8–2.50 (m, 9 H), 3.65 (s, 3 H), 5.15–5.70 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 12.93, 25.09, 26.52, 33.61, 51.49, 125.14, 129.79, 174.13; MS, m/z 142 (M^+, 6), 111 (10), 110 (29), 74 (100), 69 (28), 68 (46), 55 (46), 43 (77), 41 (43). Preparative GLC (3 m × 0.25 in. 5% SE-30) afforded an analytical sample. Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.55; H, 9.93.

The LTA Oxidation of 6b. From 0.071 g (0.36 mmol) of **6b** (>99% pure by GLC with 6 ft × 0.25 in. 5% FFAP) and 0.185 g (0.42 mmol) of LTA was obtained, after preparative TLC ($SiO_2/CHCl_3$), 0.046 g (76%) of pure methyl (E)-6-octenoate (**10b**). GLC analysis (5 m × 0.25 in. 5% DC-550) prior to TLC showed an E/Z ratio of >99/1. IR (neat) 1740, 970 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.05–2.37 (m, 11 H), 3.60 (s, 3 H), 5.20–5.55 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.49, 24.10, 28.69, 31.79, 33.58, 51.04, 124.75, 130.53, 173.80; MS, m/z 156 (M^+, 95), 121 (41), 120 (100), 91 (61), 87 (25), 83 (25), 82 (68), 74 (75).

The LTA Oxidation of 7b. From 0.023 g (0.12 mmol) of **7b** (>99% pure, 5% FFAP) and 0.052 g (0.12 mmol) of LTA was obtained, after preparative TLC ($SiO_2/CHCl_3$), 0.013 g (65%) of pure methyl (Z)-6-octenoate (**11b**). GLC analysis (5% DC-550) prior to TLC showed a Z/E ratio of >99/1. IR (neat) 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00–2.45 (m, 11 H), 3.66 (s, 3 H), 5.25–5.64 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 12.42, 24.28, 26.19, 28.75, 33.70, 51.10, 123.86, 129.76, 173.86; MS, m/z 156 (M^+, 67), 121 (40), 120 (100), 96 (62), 87 (26), 83 (30), 82 (76), 74 (80).

Oxidation of a mixture of **6b**/**7b** gave a mixture of **10b**/**11b**, bp 30 °C (1.0 mm, molecular distillation). Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.33. Found: C, 68.96; H, 10.57.

The LTA Oxidation of 6c/7c. To a solution of 1.20 g (5.7 mmol) of a 3.1/1.0 mixture of **6c**/**7c** (^{1}H NMR integration of OTMS signals) in 10 mL of CH_2Cl_2 was added 0.70 g (5.8 mmol) of triethylammonium fluoride.[25] The resulting solution was stirred at room temperature for 30 min at which time the solvent was removed in vacuo with a rotary evaporator. The resulting residue was dissolved in 10 mL of glacial acetic acid and the solution treated with 2.60 g (5.9 mmol) of LTA. The resulting slurry was stirred at room temperature for 8 h. The mixture was diluted with 10 mL of water and stirring continued for 20 min. Then, 30 mL of ether was added and the mixture was filtered through Celite. The filter cake was washed with an additional 50 mL of ether, and the combined filtrates were washed with 3 × 10 mL of water and 10 mL of brine solution and dried (Na_2SO_4). Filtration and removal of solvent in vacuo afforded an oil that was treated with excess diazomethane.[31] The solvent was removed in vacuo, and GLC analysis (capillary column) indicated a mixture of methyl (E)-7-nonenoate (**10c**) (70.6%), methyl (Z)-7-nonenoate (**11c**) (22.1%), and 2-(1-acetoxyethyl)cycloheptanone (**12**) (7.3%). These data represent a **10c**/**11c** ratio of 3.19/1.0. Vacuum distillation gave 0.727 g (75%) of pure **10c**/**11c**, bp 92–93 °C (3.5 mm). IR (neat) 1740, 974 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.1–2.57 (m), 3.66 (s), 5.20–5.60 (m); ^{13}C NMR of **10c** and **11c** ($CDCl_3$) δ 12.57, *17.71*, 123.68, *124.66*, 130.34, *131.16*; GC/MS, m/z of **10c**, 170 (M^+, 2), 139 (12), 138 (28), 96 (28), 87 (31), 74 (77), 69 (25), 59 (24), 55 (100), 43 (27), 41 (60); GC/MS, m/z of **11c**, 170 (M^+, 2), 139 (14), 138 (32), 96 (34), 87 (33), 74 (86), 69 (23), 59 (26), 55 (100), 43 (33), 41 (68). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.65. Found: C, 70.49; H, 10.35.

Preparative GLC (12.5% SE-52) from an independent oxidation experiment gave pure 2-(1-acetoxyethyl)cycloheptanone (**12**) as a mixture of diastereomers. IR (neat) 1732, 1706 cm^{-1}; partial ^{1}H NMR ($CDCl_3$) δ 1.21 (d, CHCH_3), J = 6.3 Hz), 1.23 (d, CHCH_3, J = 6.3 Hz), 2.00 (s, COCH_3), 2.02 (s, COCH_3), 5.16 (m, CHOAc), 5.42 (m, CHOAc); partial ^{13}C NMR ($CDCl_3$) δ 70.97, 169.78, 212.62; MS, m/z 198 (M^+, 0.5), 155 (4), 138 (17), 94 (21), 55 (20), 43 (100), 41 (27). Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.82; H, 9.53.

The LTA Oxidation of 16. A solution of 0.184 g (1.0 mmol) of **16**[8] in 2 mL of CH_2Cl_2 was added to a mixture of 0.443 g (1.0 mmol) of acetic acid free LTA[33] in 5 mL of CH_2Cl_2. After 8 h of stirring at room temperature, the reaction mixture was washed with 2 × 25 mL of water, dried, and filtered, and the resulting solution was treated with 0.240 g (2.0 mmol) of triethylammonium fluoride.[25] After 2 h of stirring, the solution was washed with 2 × 25 mL of water, dried, and filtered, and solvent was removed in vacuo to afford an oil that was purified by preparative TLC ($SiO_2/CHCl_3$). By this method was obtained 0.128 g (75%) of pure 2-(acetoxymethyl)cyclohexanone (**17**), bp 65 °C (2.5 mm, molecular distillation). IR (neat) 1740, 1705 cm^{-1} [lit.[34] IR 1740, 1710 cm^{-1}]; n$^{30}_D$ 1.4616 [lit.[34] n$^{25}_D$ 1.4628]; ^{1}H NMR (CCl_4) δ 1.00–2.90 (m, 9 H), 2.00 (s, 3 H), 3.73–4.50 (m, 2 H); MS, m/z 170 (M^+, 4), 111 (10), 110 (100), 82 (46), 81 (14), 73 (14), 72 (43), 43 (21).

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