1 H, C(2)H), 1.43 (s, 3 H, C(3)–CH_3), 1.67 (d, $J \simeq 1$ Hz, 3 H, C(4)–CH_3), 5.77 (m, 1 H, C(5)H), 8.17 (s, 1 H, NH), 6.93–7.77 (m, 5 H, C_6H_5), **21** δ 0.37 (s, 3 H, $GeCH_3$), 0.42 (s, 3 H, $GeCH_3$), 0.97–1.97 (m, 4 H, C(2)H and C(5)H), 1.77 (s, 3 H, C(3)–CH_3), 4.80 and 5.00 (2m, 2 H, CH_2=C), 8.50 (s, 1 H, NH), 6.98–7.80 (m, 5 H, C_6H_5). Anal. Calcd for $C_{15}H_{21}O_2N$ Ge: C, 56.31; H, 6.62. Found: C, 56.36 (**19**), 56.29 (**21**); H, 6.60 (**19**), 6.64 (**21**).

1,1,3-Trimethylgermole (6) and the Corresponding Tricarbonyliron Complex (12). The pyrolysis was conducted in a 25 × 1.4 cm vertical Pyrex tube enclosed in a thermoregulated electric tube furnace. Half of the column was filled with Pyrex chips heated to 310 °C. The carbamate **17** (1.10 g, 3.6 mmol) in 6 mL of pentane was mechanically added at a rate of 60 mL/h simultaneous with an argon flow of 10 mL/min. The pyrolyzate was collected in a liquid-nitrogen trap. Aniline and germole **6** were identified by ^{1}H NMR. Germole **6** was stable as the monomer at low temperature, and no transoid isomer **22**[16] was detected in the NMR spectrum (Table I). Like 1,1-dimethylgermole,[34] pure 1,1,3-trimethylgermole polymerized within 2–3 h at 20 °C.

The pyrolyzate resulting from carbamate **17** (1.10 g) was warmed from −78 up to 20 °C and immediately poured into a flask containing $Fe_2(CO)_9$ (1.30 g, 3.6 mmol) in benzene (30 mL) preheated to 60 °C. The mixture was magnetically stirred at 60 °C for 6 h. After filtration, the solvent was removed under vacuum (40 mmHg). Purification was accomplished by column chromatography (SiO_2, Merck 60) using hexane–benzene (80/20 ratio) as eluting solvent. A yellow liquid was isolated and identified as complex **12** (0.30 g, 27% yield). IR (liquid film, cm^{-1}) ν(CO) 1975, 2050; mass spectrum (70 eV), M^+ 210 (20), $[M - CO]^+$ 282 (54), $[M - 2CO]^+$ 254 (79), $[M - 3CO]^+$ 226 (100%), 210 (82), 208 (46), 196 (127), 168 (17), 170 (13), 153 (89). Anal. Calcd for $C_{10}H_{12}O_3FeGe$: C, 38.91; H, 3.92. Found: C, 38.96; H, 4.06.

1,1,3,4-Tetramethylgermole (7) and the Corresponding Tricarbonyliron Complex 13. Carbamate **19** (1.8 g, 6 mmol) was refluxed for 10 h in 40 mL of CCl_4. The solvent was removed under vacuum (50 mmHg), and distillation of the residue gave 0.9 g of germole **7** (85% yield): bp 75 °C (30 mm); ^{1}H NMR, see Table I. Anal. Calcd. for $C_6H_{14}Ge$: C, 45.40; H, 8.89. Found: C, 45.42, H, 8.87.

Germole **7** (1.03 g, 6.5 mmol) and $Fe_2(CO)_9$ (2.40 g, 6.5 mmol) in benzene were stirred at 60 °C for 3 h. A yellow liquid, identified as complex **13** (1.44 g, 65% yield), was isolated by column chromatography using hexane–benzene (80/20 ratio) as eluting solvent: ^{1}H NMR, see Table I; IR (cm^{-1}, liquid film) ν(CO) 1970, 2040; mass spectrum (70 eV), M^+ 324 (11), $[M - CO]^+$ 296 (43), $[M - 2CO]^+$ 268 (60), $[M - 3CO]^+$ 240 (100%), 224 (60), 222 (83), 210 (37), 167 (74). Anal. Calcd for $C_{11}H_{14}O_3FeGe$: C, 40.94; H, 4.37. Found: C, 40.91; H, 4.40.

Registry No. **2**, 4125-18-2; **3**, 18135-88-1; **4**, 82763-95-9; **5**, 78750-31-9; **6**, 82763-92-6; **7**, 82763-96-0; **8**, 42535-31-9; **9**, 85944-69-0; **10**, 87965-49-9; **11**, 85944-70-3; **12**, 94890-84-3; **13**, 94890-85-4; **14**, 82763-86-8; **16**, 82764-03-2; **17**, 94890-81-0; **18**, 82763-89-1; **19**, 94890-82-1; **20**, 82763-91-5; **21**, 94890-83-2; $Fe_2(CO)_9$, 15321-51-4; phenyl isocyanate, 103-71-9.

(34) Laporterie, A.; Manuel, G.; Dubac, J.; Mazerolles, P.; Iloughmane, H. *J. Organomet. Chem.* **1981**, *210*, C33.
(35) Maddox, M. L.; Stafford, S. L.; Kaesz, H. D. *Adv. Organomet. Chem.* **1965**, *3*, 1.

A Ring-Opening Reaction of 1-Siloxy-1-alkoxycyclopropanes. Preparation of Main-Group Metal Homoenolates of Alkyl Propionate

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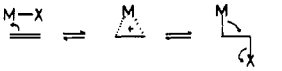
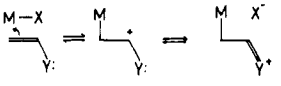
1-(Trimethylsiloxy)-1-alkoxycyclopropanes (1) react with a variety of main-group metal halides (Table III) to give the corresponding 3-metalated alkyl propionates (the metal homoenolates of propionates). Spectral properties (Tables I and II) indicate that these homoenolates generally possess a chelate structure (e.g., **3** and **4**), which endows a particular stability to the complex. The reaction mechanism is also discussed.

Heterometalation of olefins is an established method for the synthesis of organometallics yet is very limited in its scope.[1] The reaction as schematized in eq 1 involves development of electron deficiency on the carbon adjacent to the one forming the carbon–metal bond. In this case, it is well-known that the reverse reaction is overwhelmingly favored unless the carbon–metal bond is strong enough or the incipient cation is stable enough to favor the forward reaction. The picture shown in eq 2 illustrates the latter possibility[2] and, in fact, has been exploited in halostannylation of enol silyl ethers by $SnCl_4$.[3]

An exact parallel of eq 1 is seen with the heterometalation of cyclopropanes, for which the reverse reaction



(1)



(2)

has ample precedent (eq 3).[4] A protocol (eq 4) to facilitate this reaction by a scheme similar to eq 2, however, does not work so well. Hydroxylated and siloxylated cyclopropane derivatives react with Hg(II) much faster than the unsubstituted ones,[5] but they still do not react well with other metals.[6]

(1) Negishi, E. "Organometallic in Organic Synthesis"; Wiley: New York, 1980; Vol. 1, p 48. Matteson, D. S. "Organometallic Reaction Mechanisms"; Academic Press: New York, 1974; Chapter 4.
(2) House, H. O.; Auerbach, R. A.; Gall, M.; Peet, N. P. *J. Org. Chem.* **1973**, *38*, 514.
(3) Nakamura, E.; Kuwajima, I. *Chem. Lett.* **1983**, 59.
(4) Cf. Sommer, L. H.; Van Strien, R. E.; Whitmore, F. C. *J. Am. Chem. Soc.* **1949**, *71*, 3056. Hawthorne, M. F.; Dupont, J. A. *J. Am. Chem. Soc.* **1958**, *80*, 5830. Kuivila, H. G.; Scarpa, N. M. *J. Am. Chem. Soc.* **1970**, *92*, 6990.
(5) Gibson, D. H.; DePuy, C. H. *Chem. Rev.* **1974**, *74*, 605.

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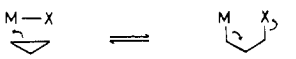
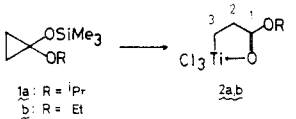


(3)

(4)

We were therefore struck by a reaction in which $TiCl_4$ reacts with 1-siloxy-1-alkoxycyclopropane **1**[7] with ease to form a titanium alkyl species **2** (eq 5).[8] Two cation-stabilizing groups on a cyclopropane ring instead of one (cf. eq 4) does bring about a facile ring cleavage/metalation reaction. In addition, the resulting chelated complex **2** turned out to have extraordinary thermal stability. This reaction was of particular interest because it provided the first breakthrough into the chemistry of the homoenolates[9] involving purified stable species.

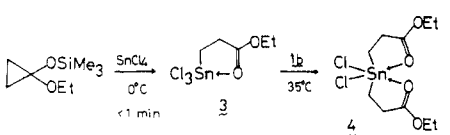


(5)

We thus set out to study the reaction of **1** with a variety of metal halides to establish the scope of this novel ring-opening reaction as a new methodology for carbon–metal bond formation and also as an entry to synthetically useful metal homoenolates.

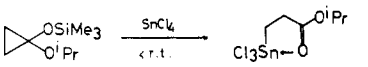
Results

Group 14 Metal Halides.[17] With the assumption that the Lewis acidity of $TiCl_4$ is crucial for the reaction, we started with $SnCl_4$, a typical Lewis acid. The ethoxycyclopropane **1b** was added to a $CDCl_3$ solution of $SnCl_4$ (1 equiv) at 0 °C, and the ^1H NMR spectrum was recorded immediately afterward. The characteristic signals of the cyclopropane (at 0.4 ppm) had already disappeared and a pair of A_2B_2 signals had appeared around 2–3 ppm, in addition to the chlorotrimethylsilane (Me_3SiCl) signal. The expected tin homoenolate **3** had formed (67% NMR yield). Addition of another equivalent of the cyclopropane converted the initially formed compound into a new one (50% conversion after ca. 70 min at 35 °C). The ^1H NMR spectrum of this compound was similar to that of the starting one, but the signals appeared consistently at higher fields. The reaction was complete after 18 h, and the product was isolated after concentration of the reaction mixture and distillation of the residue (eq 6). Elemental analysis of the crystalline product established the structure of the product as a dialkylated tin compound **4**.



(6)

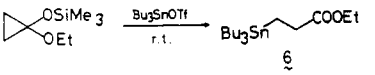
The reaction of the isopropoxycyclopropane **1a** with 1 equiv of $SnCl_4$ proceeded in higher yield (87%) to give the monoalkyltin **5**, whose spectral properties are essentially identical with that of **3** (eq 7). Since the isopropoxycyclopropane **1a** gives a consistently higher yield of the homoenolate than the ethoxy compound **1b** both with $TiCl_4$[8] and with $SnCl_4$, **1a** was used for most of the subsequent studies.



(7)

The ^1H and ^{13}C NMR spectra (Tables I and II) of **3–5** established the attachment of the tin atom at the 3-position of the propionate moiety. The IR spectra of the mono- and dialkylated tin compounds in dilute CCl_4 solution showed a single weakened carbonyl band (Table I, entries 3 and 9). This has been fully corroborated by the X-ray crystal structure performed on the methyl esters corresponding to **4** and **5**, in which the carbonyl groups coordinate to the metal by its nonbonding electrons to form virtually planar five-membered chelate structures.[10]

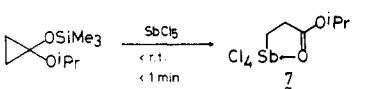
The cyclopropane was inert to tributyltin chloride, and a more acidic analogue, tributyltin trifluoromethanesulfonate (triflate), therefore was examined. The reaction in methylene chloride proceeded smoothly at room temperature, to afford the 3-(tributylstannyl)propionate **6**[11] in good yield (eq 8). The IR spectrum showed no sign of chelation (Table I, entry 1), in line with the known lack of Lewis acidity of the tetraalkyltin moiety.



(8)

The cyclopropane **1a** was inert to $GeCl_4$, $SiCl_4$, Me_3SiCl, and trimethylsilyl triflate. $PbCl_2$ was unreactive, and Pb(IV) is known to oxidatively cleave cyclopropanes.[1]

Group 15 Metal Halides. The strongly Lewis acidic $SbCl_5$ was examined. One equivalent of cyclopropane **1a** was added to $SbCl_5$ in $CDCl_3$ at −60 °C. The ^1H NMR spectrum taken after 15 min at 35 °C indicated the formation of the homoenolate **7** in 87% yield (eq 9). Addition of another equivalent of the cyclopropane gave a complex mixture. Although the product could only be isolated as a relatively unstable colored oil, ^1H and ^{13}C NMR and IR spectra fully supported the hexacoordinated structure **7** (Table I, entry 4); particularly, the intramolecular chelation was evident from the carbonyl stretching band on the IR spectrum (1600 cm^{-1}). Attempts to purify the homoenolate through complex formation failed. In contrast to the usual $RSbCl_4$,[12] **7** was stable at room temperature for many hours but rapidly decomposed on attempted distillation.



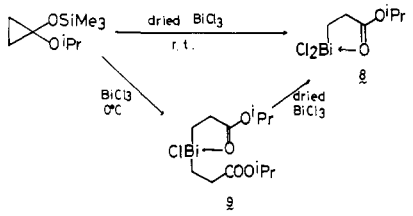
(9)

Bismuth trichloride, which had previously been activated by heating in vacuo, reacted with the cyclopropane **1a** in $CDCl_3$ under ultrasonic irradiation to give the monoalkylbismuth compound **8** in 89% yield (eq 10). The homoenolate was isolated as white crystals and shown by IR analysis (1650 cm^{-1}) to possess a chelate structure similar to that of **5**.

Interestingly, when $BiCl_3$ directly from the bottle was allowed to react with 1 equiv of the cyclopropane under ultrasonic irradiation for 2 h, the dialkylated compound **9** formed first in 57% yield with consumption of the cyclopropane **1a**, and then gradually it was transformed into **8**, now with consumption of the metal halide. When the oily product that was isolated was allowed to react with

(6) Cf. Ryu, I.; Ando, M.; Ogawa, A.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1983**, *105*, 7192.
(7) Salaun, J.; Marguerite, J. *Org. Synth.* to be submitted for publication Rühlmann, K. *Synthesis* **1971**, 236.
(8) Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1983**, *105*, 651.
(9) Review: Werstiuk, N. H. *Tetrahedron* **1983**, *39*, 205.
(10) Harrison, P. G.; King, T. J.; Healy, M. A. *J. Organomet. Chem.* **1979**, *182*, 17.
(11) Kuivila, H. G. *Adv. Organomet. Chem.* **1964**, *1*, 47.
(12) Okawara, R.; Matsumura, Y. *Adv. Organomet. Chem.* **1976**, *14*, 187.

1 equiv of $BiCl_3$, the monoalkyl species **8** was formed in high yield (eq 10). This confirmed the structure of the oily product as the dialkylbismuth **9**. The oily dialkylbismuth compound exists also as a tetracoordinated complex, as indicated by two carbonyl stretching bands, one coordinated and another free, of equal intensities (Table I, entry 10).

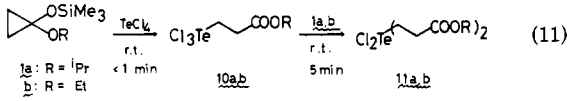


(10)

The faster formation of the dialkylated product may be due to the insolubility of $BiCl_3$ in $CDCl_3$; thus, **8** in an organic phase reacts faster than the solid $BiCl_3$.

The cyclopropane **1a** was inert to PCl_3. Arsenic halides were not examined.

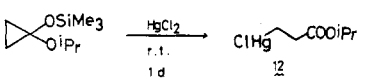
Group 16 Metal Halides. Tellurium tetrachloride is the only compound examined in this group. It readily reacted with cyclopropane **1b** in a stepwise manner, giving the monoalkyltellurium compound **10b** and the dialkyl compound **11b** in accordance with the stoichiometry of the reagents. The reaction did not proceed beyond the second alkylation, and 3.3 equiv of cyclopropane **1a** reacted with $TeCl_4$ to give the dialkylated compound **11a** in 64% yield (eq 11). The carbonyl stretching band of **11a** was quite normal, appearing at 1708 and 1730 cm^{-1} (0.02 M, CCl_4).



(11)

Group 13 Metal Halides. This group of metal halides includes typical Lewis acids, yet only $GaCl_3$ reacted with **1a** (very slowly) to afforded the homoenolate (76%), whose structure was tentatively assigned by ^1H NMR (Table I, entry 7). $AlCl_3$ caused only slow decomposition of the cyclopropane (1 h at 35 °C in $CDCl_3$). Since an aluminum homoenolate, if formed at all, must be reasonably stable (cf. generally stable Al–C bonds and the effect of the internal ester ligand to stabilize the metal–carbon bond[8]), the failure to detect any ^1H NMR signals due to homoenolate structure must be taken as a sign of failure to form the homoenolate.

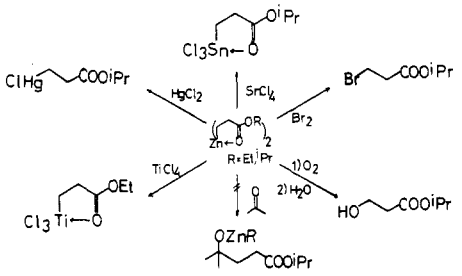
Group 12 Metal Halides. Hg(II) is very well-known to react with cyclopropanes,[1,5] and indeed $Hg(OAc)_2$, $Hg(OCOCF_3)_2$, and $HgCl_2$ reacted equally well with cyclopropanes **1a** or **1b** in high yield. For example, $HgCl_2$ reacted in a period of a day to give the ester **12** in 63% yield (eq 12). $CdCl_2$ also reacted slowly (room temperature, 15 h, under ultrasonic irradiation, 96%) to give the cadmium homoenolate, whose structure as assigned by ^1H NMR (Table I, entry 7).



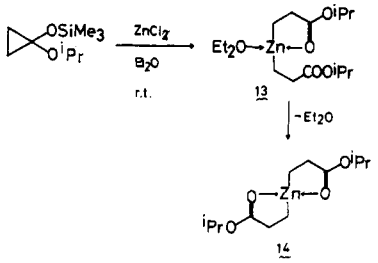
(12)

$ZnCl_2$ reacted with the cyclopropane more cleanly in ether than in $CDCl_3$. The zinc homoenolate was considerably different from the other metal homoenolates in its physical and chemical properties. The expected higher chemical reactivity, in particular, made us examine the formation and the properties of the zinc homoenolate more closely. Thus a mixture of freshly fused $ZnCl_2$ and 2 equiv of the cyclopropane **1a** in ether for 4 h at 20 °C gave an almost quantitative yield of the zinc homoenolate etherate

Scheme I



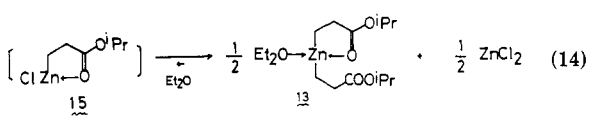
13 and Me_3SiCl as determined by ^1H NMR. Removal of the volatile material followed by hexane extraction afforded the ether-free **14** as an oil (ca. 70% yield), which is soluble in a variety of aprotic solvents (eq 13).



(13)

The structure of **14** followed from the absence of chlorine and its spectral properties (Table I, entry 8; Table II, entry 1). Both the ^{13}C and ^1H NMR signals of the methylene group attached to the metal appeared at a field much higher than found for any of the other homoenolates prepared thus far, almost next to the signal of tetramethylsilane (1.7 and 0.37 ppm, respectively, for ^{13}C and ^1H NMR). The ^1H NMR spectrum in $CDCl_3$ remained unchanged in the temperature range of 35 to −60 °C. The IR spectrum of **14** in a dilute CCl_4 solution showed a very strong carbonyl band at 1645 cm^{-1}, and this indicates the major contribution of a monomeric tetracoordinated structure **14**. The cryoscopic molecular weight determined in benzene was somewhat variable between 1 and 1.5 times the formula weight. The internal chelation is broken by addition of a strongly basic ligand; addition of 4 equiv of pyridine moved the carbonyl bands up to 1710 and 1725 cm^{-1}. A less basic ether, when used as a solvent for **14**, replaces only one of the ester groups to form the etherate **13**, as indicated by the IR spectrum in ether showing two strong band of equal intensity at 1662 and 1740 cm^{-1}. The internal ligand exchange is very fast at room temperature as indicated by the appearance of a single set of NMR peaks of **13**. Attempts to purify the homoenolate **14** through complex formation with ether, THF, or dioxane failed; the solvent molecule was readily lost in vacuo, giving back the starting **14**.

It is interesting to note that the same homoenolate **13** formed when $ZnCl_2$ reacted with 1 equiv of the cyclopropane in ether as indicated by ^1H NMR and IR spectra of the crude solution. This lack of the formation of the monoalkylzinc homoenolate **15** may stem from the Schlenk equilibrium favoring the dialkylated **13** (eq 14).



(14)

The chemical proof of the structure of the homoenolate **14** (Scheme I) was provided by the ready oxidation of the carbon–metal bond with oxygen and bromine. Transmetalation to $TiCl_4$ and $HgCl_2$ readily proceeded to give the respective metal homoenolates. The zinc alkyl al-

Table I. ^{1}H NMR and IR Spectra of Metal Homoenolates of Isopropyl Propionate (= R)

entry	Cl_nMR_m	^{1}H NMR,[b] ppm isopropyl	C-3[a]	C-2[a]	IR,[b] cm^{-1}
1	Bu_3SnR[c]	4.05	1.24	2.44	1740
2	ClHgR	4.92, 1.22	1.85	2.66	1715, 1721
3	Cl_3SnR	5.15, 1.30	2.13	2.83	1650
4	Cl_2BiR	5.09, 1.38	6.03	2.88	1650
5	Cl_3TiR	5.65, 1.51	2.40	3.38	1610
6	Cl_4SbR	5.39, 1.42	2.8-3.5		1600
7	ClCdR[d]	4.96, 1.35	1.04	2.27	
8	Cl_2GaR[d]	5.33, 1.49	1.18	2.91	
9	ZnR_2	5.01, 1.25	0.37	2.57	1645, 1720
10	Cl_2SnR_2	5.06, 1.29	1.85	2.83	1686
11	$ClBiR_2$	4.97, 1.27	4.05	2.88	1660, 1708
12	Cl_2TeR_2	5.02, 1.27	2.9-3.6		1708, 1730

[a] See structure 1 in eq 5 for numbering. [b] See Experimental Section for details of conditions of measurement. [c] This is for the homoenolate of ethyl ester 6. [d] The monoalkylated structure was assigned tentatively on the basis of the stoichiometry (1:1) of the reactants used.

kylates $SnCl_4$, giving either the mono- or dialkylated tin homoenolate according to the stoichiometry. Transmetalation to copper can be achieved in an HMPA/ether mixture and has been used for the conjugate addition of the homoenolate.[13] The homoenolate, however, does not react with aldehydes and ketones either in ether or in methylene chloride.[14]

Metal Halides in Other Groups. The cyclopropane reacts with none of the groups 1 and 2 metal chlorides in $CDCl_3$ under ultrasonic irradiation for an extended period. Among early transition-metal halides other than $TiCl_4$ which has already been examined,[8] $NbCl_5$ reacted in moderate yield[15] to give the same homoenolate as obtained by transmetalation from the titanium homoenolate onto the metal chloride under 1:1 stoichiometry. $ZrCl_4$, $TaCl_5$, $CrCl_3$, $MoCl_5$, and WCl_5 did not give any characterizable products.[15] The titanium homoenolate **2** gives access to the tin, antimony, and tellurium homoenolates through transmetalation reactions.

Discussion

We have surveyed the scope of the reaction of the electron-rich cyclopropane **1**. Several interesting trends are readily perceived by the analysis of the reactivities of various metal halides in terms of their positions in the periodic table. All the reacting metal halides are Lewis acids in a general sense, and they involve the heavier elements of a given family. The former point is strengthened by the obvious differences of reactivity between tributyltin chloride and tributyltin triflate and between $SnCl_4$ and $SnCl_2$. The contrasting behavior of such pairs as tributyltin triflate vs. trimethylsilyl triflate, $SnCl_4$ vs. $SiCl_4$ (and $GeCl_4$), and $GaCl_3$ vs. $AlCl_3$ illustrates the latter point.

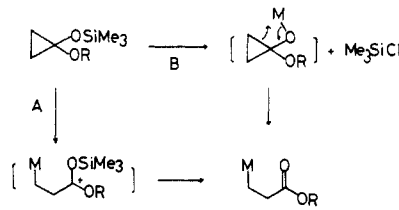
The isolated homoenolates represent a variety of possible structural types expected. It is clear from the inspection of the IR spectra in dilute solution (Table I) that most of the homoenolates possess a chelate structure. With the tin homoenolates, this structural assignment is fully supported by their crystal structures.[10] With monoalkylmetal homoenolates, comparison of the ^{1}H NMR chemical shift values of the C(2)-methylene and the carbonyl bond frequency (Table I, entries 1–6) reveals a good correlation between these parameters. The ^{13}C NMR signals (Table II) of the carbonyl carbons show a downfield shift as compared with those of the simple alkyl propionates: The extent of the shifts ranges from almost negligible (for tellurium where little chelation was observed) to as much as 20 ppm (for bismuth). NMR spectra excluded any possibility of the isomeric cyclopropanolate formulation of the homoenolate structure, which has a plane of symmetry (cf. **1**).

Table II. ^{13}C NMR Spectra (ppm) of the Homoenolates of Isopropyl Propionate (= R)

entry	Cl_nMR_m	isopropyl	C-3[a]	C-2[a]	C-1[a]
1	ZnR_2	70.7, 21.9	1.7	32.6	185.4
2	Cl_3SnR	75.0, 21.5	24.2[b]	28.2[c]	180.5
3	Cl_4SbR	79.9, 21.5	60.8	29.5	182.4
4	Cl_2BiR	80.0, 21.6	73.2	30.1	195.2
5	Cl_3TiR	77.7, 21.6	100.6	44.1	189.8
6	Cl_2TeR_2	69.7, 21.8	39.4	29.7	172.5

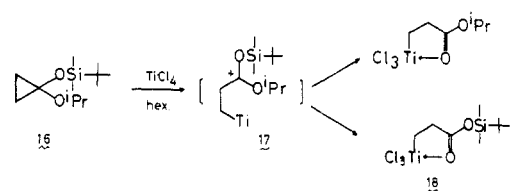
[a] See structure **2** in eq 5 for numbering. [b] $^1J_{Sn-Cl}$ = 553.9 Hz. [c] $^2J_{Sn-Cl}$ = 67.4 Hz.

Scheme II



The major chemical manifestation of the internal chelation is the enhanced thermal stability of the metal homoenolates. This has already been demonstrated for the titanium homoenolate **2**[8] and seen again for the antimony compound **7**. It is known that ligand-free $RSbCl_4$ and R_2SbCl_3 are unstable even at room temperature,[12] and the high thermal stability of **7** is, therefore, consistent with the hexacoordinated chelate structure assigned on the basis of spectral studies.

Two types of mechanistic possibiities may be considered for the present ring cleavage reaction (Scheme II). The point of departure resides in the timing of the formation of the carbon–metal bond in relation to the rupture of the silicon–oxygen bond. Path A has been substantiated already by the finding that the (*tert*-butyldimethylsiloxy)-cyclopropane **16** reacts with $TiCl_4$ to give an abnormal product **18** in addition to the normal **2a**, indicating the involvement of a species like **17**.[16]



16 17 18 (15)

A set of experiments to determine the generality of path A was carried out by examining the rate of silicon–oxygen bond cleavage with various metal halides. The trimethylsilyl ether of menthol **19** was taken as a reference, and the rate of its trimethylsilyl group exchange with trimethylsilyl triflate (eq 16) was compared with that of

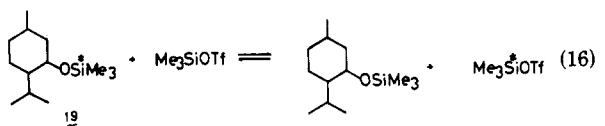
(13) Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1984**, *106*, 3368. Submitted to *Org. Synth.* The procedure is currently being checked.
(14) The homoenolate reacts with a carbonyl compound if the latter is appropriately activated: Unpublished results by H. Oshino.
(15) Experiments by Y. Horiguchi.
(16) Unpublished observation by H. Oshino.
(17) The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

Table III. Interaction of Metal Chlorides with Menthol Silyl Ether 19 and the Siloxycyclopropane 1a[a]

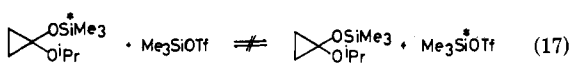
entry	metal chloride	19	1a
1	$TiCl_4$	+	+
2	$GaCl_3$	+	+
3	$SbCl_5$	+	+
4	$TeCl_4$	*b*	+
5	$SnCl_4$	−	+
6	$ZnCl_2$	−	+
7	$CdCl_2$	−	+
8	$HgCl_2$	−	+
9	$BiCl_3$	−	+
10	$GeCl_4$	*b*	−

[a] Key: (+) indicates the formation of the expected product; (−) indicates no reaction over a period of 15 h at room temperature. The silicon–oxygen bond cleavage reaction with 19 was very fast (<5 min at room temperature). [b] About 50% conversion after 15 h at room temperature.

the siloxycyclopropane 1a (eq 17). Measurement of the line broadening in CCl_4 (ca. 0.3 M) at 35 °C indicated rapid exchange for 19 ($t_{1/2} = 3.6 \times 10^{-3}$ s) and no exchange for 1a. Most probably, the electron-withdrawing isopropoxy group of 1a reduces the reactivity of the siloxy oxygen and thus also the rate of the exchange. Consequently, any metal which does not undergo silicon–metal exchanges with menthol silyl ether would not do so with the cyclopropane either. It is clear from the results in Table III that many of the metals which form homoenolates do not undergo the exchange reaction. Operation of path B is, therefore, excluded for these metals except $GaCl_3$ and $SbCl_5$ (entries 2 and 3). Even these exceptions, however, may well react also via path A (cf. the case of $TiCl_4$, entry 1). A similar argument has been made for the interaction of $SnCl_4$ with enol silyl ethers.[3]



(16)



(17)

In summary, a wide variety of metal halides take part in the heterometalation-type ring cleavage of the electron-rich cyclopropane 1. The reaction represents the first demonstration of the general utility of such a reaction for organometallic synthesis and also provides a rare example of a cyclopropane which strongly interacts with the main-group metals. The notably mild conditions make the reaction particularly attractive for synthetic applications. The chemistry of the resulting metalated propionates has already proven as interesting as the route forming them[13] and will be the subject of further studies.

Experimental Section

General Data. All the reactions dealing with air- and moisture-sensitive compounds were carried out in a dry reaction vessel under nitrogen or argon. Liquid samples were introduced either neat via a microsyringe or in an organic solvent via a hypodermic syringe. Solid samples were weighed into a vessel in a nitrogen-filled bag.

^1H NMR spectra were taken at 60 MHz on a Hitachi R24B spectrometer. NMR yields were determined with 1,1,2,2-tetrachloroethane as an internal standard. ^{13}C NMR spectra were taken at 22.25 MHz on a JEOL FX90Q instrument. Spectra are reported in parts per million from internal tetramethylsilane. IR spectra were recorded on a Hitachi 260-10 instrument; absorptions are reported in inverse centimeters. Ultrasonic irradiation was performed with a Branson, Smithkline Co. Model 11Ht 310-W instrument.

Ethereal solvents were distilled from benzophenone ketyl immediately before use. CH_2Cl_2 was distilled successively from P_2O_5 and K_2CO_3 and stored over molecular sieves. The solvent used for the homoenolate reaction was distilled under nitrogen. $CDCl_3$ was distilled from P_2O_5 under nitrogen. Hexane was distilled from $LiAlH_4$ under nitrogen and stored over potassium mirror.

Metal halides were purchased from Yoneyama Chemical (purest grade) except for zinc chloride, which was obtained from Alfa (ultra pure grade). Liquid metal halides were distilled under reduced pressure, and solid ones were used as such. Distillation of small amounts of oily samples were carried out on a Büchi Kügelrohr apparatus.

Dichlorobis[2-(ethoxycarbonyl)ethyl]stannane (4). To a solution of 58 μl (0.50 mmol) of $SnCl_4$ in 0.60 mL of $CDCl_3$ in an NMR tube cooled at −20 °C was injected 100 μL (0.50 mmol) of the ethoxycyclopropane 1b. The mixture was swirled and immediately put into an NMR probe (35 °C) for ^1H NMR measurement. The reaction was complete after about 30 s, affording the monoalkyltin 3 in 59% NMR yield. The sample tube was cooled again at −20 °C, and an additional 100 μL of the cyclopropane was injected. NMR monitoring indicated 50% conversion after 65 min at 35 °C, at which point the title compound was formed in 38% yield. After it has been left to stand for 1.5 days at about 30 °C, the reaction mixture was submitted for bulb-to-bulb distillation to give the title compound (95 mg, 48% yield. the distillate solidified at room temperature and was recrystallized from hexane/ethyl acetate to give an analytical sample: bp 140 °C (0.07 mm); mp 84.5–85 °C; IR (0.014 M in CCl_4) 1686 (vs), 1372 (m), 1343 (m), 1250 (w), 1205 (s), 1132 (w), 1033 (w); ^1H NMR (CCl_4) 1.31 (t, 3 H, J = 7 Hz, CH_3CH_2), 1.90 (t, 2 H, J = 7 Hz, CH_2Sn), 2.91 (t, 2 H, J = 7 Hz, CH_2CO), 4.25 ppm (q, 2 H, J = 7 Hz, CH_2O); MS (70 eV), m/e (relative intensity) 357 (M^+ − 35), 291 (3), 263 (2), 256 (2), 221 (2), 199 (2), 155 (5), 137 (3), 120 (2), 101 (2), 73 (7), 59 (19), 56 (12), 55 (69), 29 (100).

Anal. Calcd for $C_{10}H_{18}O_4SnCl_2$: C, 30.65; H, 4.63: Found: C, 30.82; H, 4.52.

Trichloro[2-(isopropoxycarbonyl)ethyl]tin (5). To a solution of $SnCl_4$ (117 μl, 1.0 mmol) in 1 mL of benzene was added the isopropoxycyclopropane 1a (188 mg, 1.0 mmol) at room temperature. After 1 min, the solvent was removed and the residue was distilled to give the title compound as analytically pure crystals: bp 100–105 °C (bath temperature, 0.01 mm); mp 77.0–77.5 °C; IR (0.3 M CCl_4) 2910, 1650 (vs), 1398, 1388, 1323, 1255, 1220, 1098, 890 cm^{-1}; ^1H NMR ($CDCl_3$) 1.50 (d, 6 H, J = 6 Hz), 2.13 and 2.83 ppm (A_2B_2 t, 4 H, J = ca. 7 Hz); ^{13}C NMR ($CDCl_3$) 21.5 (q), 24.2 (t, $^1J_{^{119}Sn-C}$ = 553.9 Hz), 28.2 (t, $^2J_{^{119}Sn-C}$ = 67.4 Hz), 75.0 (d), 180.5 ppm (s). An NMR yield determined in a separate run was 87%.

Anal. Calcd for $C_6H_{11}O_2Cl_3Sn$: C, 21.18; H, 3.26. Found: C, 21.32; H, 3.24.

Ethyl 3-(Tributylstannyl)propionate (6). Trifluoromethanesulfonic acid (25 μL, 0.32 mmol) was added dropwise to tri-*n*-butylstannane (96 mg, 0.33 mmol), and the mixture was stirred for 1 h. The tin triflate thus prepared was diluted with 0.5 mL of methylene chloride, and the ethoxycyclopropane 1b (71 mg, 0.425 mmol) was added. After 3 h at room temperature, the solvent was removed and the residue was chromatographed on silica gel (with 2% ethyl acetate in hexane as eluant) to give the title compound as a colorless oil (79 mg, 60%): IR (neat) 1740 (s), 1470 (m), 1200 (m); ^1H NMR (CCl_4) 0.6–1.7 (m, involving t, J = 8 Hz, at 1.24, which is coupled with t at 2.44), 2.44 (t, J = 8 Hz, 2 H), 4.05 ppm (q, J = 7 Hz, 2 H); MS, m/e (relative intensity) 335 (M^+ − Bu, 100), 307 (5), 291 (20), 235 (22), 179 (20).

Anal. Calcd for $C_{17}H_{36}O_2Sn$: C, 52.20; H, 9.28. Found: C, 52.71; H, 9.60.

Tetrachloro[2-(isopropoxycarbonyl)ethyl]antimony (7). To a solution of $SbCl_5$ (127 μL, 1.00 mmol) in hexane (2 mL) was added the isopropoxycyclopropane 1a (207 μL, 1.00 mmol) at −70 °C. The black oily product formed on warming to room temperature was separated from the supernatant and washed once with hexane to give the unstable title compound after concentration: IR (0.3 M $CDCl_3$) 2965, 1703 (w), 1600 (vs), 1492, 1419 (s), 1383, 1332, 1280, 1213, 1090 (s); ^{13}C NMR ($CDCl_3$) 21.5 (q), 29.5 (t), 60.8 (t, CH_2Sb), 79.9 (d), 182.4 (s). The NMR yield as

determined in a separate run in $CDCl_3$ was 87%.

The Preparation of Bismuth Homoenolates. (a) Dichloro[2-(isopropoxycarbonyl)ethyl]bismuth (8). To a suspension of $BiCl_3$ dried at ca. 300 °C for 10 min (276 mg, 0.874 mmol) in $CDCl_3$ (1 mL) was added the isopropoxycyclopropane **1a** (180 μL, 1.874 mmol) at −60 °C with stirring. After the mixture was stirred for 1.5 h at room temperature under ultrasonic irradiation, the monoalkylbismuth complex (89% yield) formed. The solvent was removed, and the residual white solid was recrystallized from benzene to give a pure sample: mp 144.0–145.0 °C (dec); IR (KBr) 2975, 2925, 1700 (sh), 1650 (s), 1458, 1407 (sh), 1380 (s), 1328, 1267 (s), 1217 (s), 1100 (s), 1018, 923, 905, 887, 810 cm^{-1} ^1H NMR ($CDCl_3$) 1.38 (d, 6 H, J = 6 Hz), 2.88 (t, 2 H, J = 7 Hz), 5.09 (qq, 1 H, J = 6 Hz), 6.03 ppm (t, 2 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) 21.6 (q), 30.1 (t, $CH_2C{=}O$), 73.2 (t, CH_2Bi), 80.0 (d), 195.2 ppm (s).

Anal. Calcd for $C_6H_{11}O_2Cl_3Bi$: C, 18.24; H, 2.80. Found: C, 18.35; H, 2.78.

(b) Chlorobis[2-(isopropoxycarbonyl)ethyl]bismuth (9). To $BiCl_3$ (as received; 175 mg, 0.555 mmol) in 0.5 mL of $CDCl_3$ was added the isopropoxycyclopropane **1a** (115 μL, 0.555 mmol) without stirring at −60 °C. The mixture was left standing for 2 h at 0 °C. The supernatant liquid was removed and the residue extracted once with $CDCl_3$. NMR analysis of the combined $CDCl_3$ solutions indicated the formation of the dialkylbismuth complex (44% based on **1a**) and the recovery of **1a** (33%). Removal of the solvent in vacuo gave the dialkylbismuth compound as an oil, for which reasonable elemental analysis could not been obtained due to partial decomposition during distillation under reduced pressure: IR (0.3 M $CDCl_3$) 3015, 2960, 2145, 1708 (vs), 1660 (vs), 1453, 1367, 1323, 1247, 1201 (s), 1445, 1098 cm^{-1} (s); ^1H NMR ($CDCl_3$) 1.27 (d, 6 H, J = 6 Hz), 2.28 (t, 2 H, J = 7 Hz), 4.05 (t, 2 H, J = 7 Hz), 4.97 ppm (qq, 1 H, J = 6 Hz).

When the reaction mixture was stirred further at room temperature, the monoalkylbismuth complex **8** formed in over 80% yield.

The isolated monoalkylbismuth reacted rapidly (2 min at room temperature) with the cyclopropane **1a** to give the dialkylbismuth **9**, which constitutes a chemical proof of the structure of **9**.

Dichlorobis[2-(isopropoxycarbonyl)ethyl]tellurium (11a). To a suspension of $TeCl_4$ (141 mg, 0.522 mmol) in 2 mL of methylene chloride was added the isopropoxycyclopropane **1a** (328 mg, 1.74 mmol) at room temperature, and the mixture was stirred for 1 h. The solvent was removed in vacuo, and the residue was extracted three times with 2-mL portions of hexane. NMR analysis of the liquid product obtained after concentration of the extracts indicated a 63% yield (1,1,2,2-tetrachloroethane). Distillation gave an analytical sample: bp 160–170 °C (bath temperature, 0.003 mm); IR (0.019 M CCl_4) 2920, 2820, 1730 (m, sh), 1708 (vs), 1460, 1400, 1370 (m), 1330 (m), 1200 (vs), 1098 (m), 920, 900 cm^{-1}; ^1H NMR ($CDCl_3$) 1.27 (d, 6 H, J = 6 Hz), 2.9–3.6 (A_2B_2 m, 4 H), 5.02 ppm (qq, 1 H, J = 6 Hz); ^{13}C NMR ($CDCl_3$) 21.8 (q), 29.7 (t), 39.4 (t, CH_2Te), 69.7 (d), 172.5 ppm (s).

Anal. Calcd for $C_{12}H_{22}O_4Cl_2Te$: C, 33.61; H, 5.17. Found; C, 33.87; H, 5.14.

Chloro[2-(isopropoxycarbonyl)ethyl]mercury (12). To a suspension of $HgCl_2$ (146 mg, 0.54 mmol) in 0.5 mL of $CDCl_3$ was added the isopropoxycyclopropane **1a** (112 μL, 0.539 mmol), and the mixture was stirred overnight at room temperature to form the title mercurial in 63% NMR yield. The supernatant liquid was removed, and the residue was washed twice with chloroform to obtain the product as an oil, which was pure by spectroscopy. Distillation under reduced pressure afforded an analytically pure sample: bp 100–105 °C (bath temperature, 0.06 mm); ^1H NMR (CCl_4) 1.22 (d, 6 H, J = 7 Hz), 1.85, 2.66 (A_2B_2, 4 H, J = 7 Hz), 4.92 ppm (qq, 1 H, J = 7 Hz); IR (0.3 M $CDCl_3$) 3010 (w), 2440 (vw), 1720 (sh), 1715 (vs), 1450 (vw), 1410 (vw), 1368 (m), 1807 (vw), 1250 (w), 1 206 (vs), 1233 (w), 1199 cm^{-1} (s).

Anal. Calcd for $C_6H_{11}O_2HgCl$: C, 21.12; H, 3.25. Found: C, 20.77; H, 3.30.

The structure of the mercurial was further confirmed by conversion to isopropyl 3-bromopropionate by bromine/pyridine treatment.

Bis[2-(isopropoxycarbonyl)ethyl]zinc (14). About 550 mg of anhydrous zinc chloride was placed in a reaction vessel and heated to the melting point under vacuum (ca. 1 mm). The salt was weighed (506 mg, 3.71 mmol). Ether (16 mL) was added, and the mixture was sonificated until dissolution of the salt. The isopropoxycyclopropane **1a** (1.75 g, 9.28 mmol) was added and the mixture stirred for 4 h. About 13 mL of ether was removed, and the residue was diluted with 15 mL of hexane. The supernatant liquid was taken up, and the solvent was removed to give 750 mg (2.54 mmol, 68% yield by weight) of the title homoenolate as an oil. ^1H NMR analysis of a 108.9-mg portion with 20.0 μL (0.189 mmol) of 1,1,2,2-tetrachloroethane as an internal standard indicated a 71% yield based on the alkyl portion of the zinc alkyl, which is in good agreement with the yield based on the weight. Analysis of the chlorine content (a 22.6-mg portion was dissolved in 6 N HNO_3 and titrated with $AgNO_3$) indicated that less than 3 mol % of chlorine atom was contained in the zinc alkyl. The isolated product in $CDCl_3$ was stable at least for 3 days and was distillable (with some decomposition) at 105–120 °C (0.005 mm). This homoenolate could not be made pure enough for elemental analysis. Chemical proofs, other than the spectral ones, involve the conversion to other homoenolates **2a**, **5**, and **12** upon treatment with respective metal halides in methylene chloride. No change in the ^1H NMR chemical shifts ($CDCl_3$) was observed on addition of either ether, dioxane, or acetophenone. In a separate run, the NMR yield determined on the material obtained after simple removal of ether was 92%. The homoenolate showed the following spectral properties: IR (0.3 M $CDCl_3$) 3003, 2985, 2245, 1721 (s), 1625 (vs), 1455, 1425, 1362, 1320, 1278, 1240 (vs), 1205 (s), 1095 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) 0.37 (t, J = 7 Hz, 2 H), 1.25 (t, J = 6 Hz, 2 H), 2.57 (t, J = 8 Hz, 2 H), 5.01 ppm (qq, J = 6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 1.7 (C–Zn), 21.9, 32.6, 70.7, 185.4 ppm.

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Registry No. **1a**, 84098-44-2; **1b**, 27374-25-0; **3**, 59586-03-7; **3** coordination entry, 94645-24-6; **4**, 10175-02-7; **4** coordination entry, 12084-81-0; **5**, 70508-46-2; **5** coordination entry, 94645-25-7; **6**, 21247-29-0; **7**, 94645-26-8; **8**, 94645-21-3; **8** coordination entry, 94645-27-9; **9**, 94645-22-4; **9** coordination entry, 94645-28-0; **11a**, 94645-23-5; **12**, 94645-29-1; **14**, 90147-74-3; **19**, 18419-38-0; $SnCl_4$, 7646-78-8; $SbCl_5$, 7647-18-9; $BiCl_3$, 7787-60-2; $TeCl_4$, 10026-07-0; $HgCl_2$, 7487-94-7; $ZnCl_2$, 7646-85-7; $TiCl_4$, 7550-45-0; $GaCl_3$, 13450-90-3; $CdCl_2$, 10108-64-2; $GeCl_4$, 10038-98-9; $Cl_3TiCH_2CH_2COOPr$-*i*, 84098-53-3; $ClCdCH_2CH_2COOPr$-*i*, 94645-30-4; $Cl_2GaCH_2CH_2COOPr$-*i*, 94645-31-5; $Cl_2TeCH_2CH_2COPr$-*i*, 94645-23-5; trifluoromethanesulfonic acid, 1493-13-6; tri-*n*-butylstannane, 688-73-3; tri-*n*-butyltin triflate, 68725-14-4.