reotopic methyl groups C2′ and C2″ were split by 1.5 ppm. Anal. Calcd for $C_7H_{16}O_2$: C, 63.60; H, 12.20. Found: C, 64.06; H, 12.38.

Acknowledgment. We thank Deutsche Forschungsgemeinschaft and Fonds der chemischen Industrie for support.

Registry No. 3, 37002-45-2; **4**, 57495-46-2; **5**, 19132-06-0; **6**, 69087-52-1; **7**, 72300-85-7; **8**, 63864-69-7; **9**, 68972-82-7; **9**, trimethylsilyl derivative, 72269-27-3.

Sila- and Germacyclopentan-2-ones from Metallated Enol Ethers[1a]

John A. Soderquist*

Department of Chemistry, University of San Francisco, San Francisco, California 94117

Alfred Hassner*

Department of Chemistry, State University of New York, Binghamton, New York 13901

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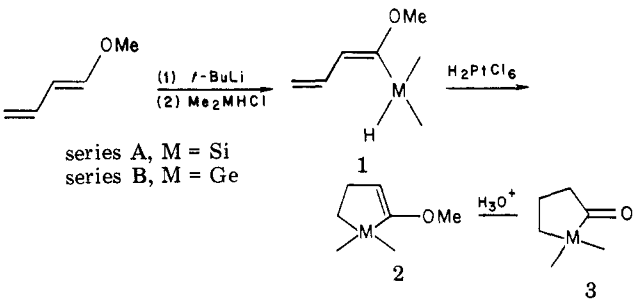
We wish to report the synthesis of the novel sila- and germacyclopentan-2-one systems (**3**) using the reaction sequence outlined in Scheme I. These compounds represent the smallest known cyclic acylsilane[2,3] and the first cyclic acylgermane. Larger silicon-containing ring systems have been prepared using the dithiane route.[4] However, this method fails in the hydrolysis step for the 1-silacyclopentan-2-one case.

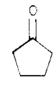
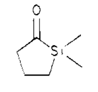
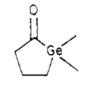
The reaction sequence shown in Scheme I illustrates several important new features which warrant mention. For one, the formation of **1** from *trans*-1-methoxybutadiene indicates for the first time that this compound can be metallated regio- and stereospecifically giving isolable butadienyl adducts.[5,8] The cyclization of **1** to give **2** is the first example of an intramolecular hydrosilylation or hydrogermylation in which a functionalized ring system is formed. Previous attempts to obtain silacycloalkanes with masked ketone functionality using this approach failed to give the cyclic product.[6] Other 2-functionalized silacyclopentanes are presently available only by very tedious and circuitous routes.[7] Finally, the formation of **3** from **2** in good yield illustrates the utility of enol ethers as metallated ketone precursors. In fact, we found this method to constitute a general synthesis of acyl silanes, germanes, and stannanes from lithiated vinyl ethers.[1a,8,11]

Scheme I



series A, M = Si
series B, M = Ge

Table I. Spectroscopic Properties of the Carbonyl Moiety in Metallacyclopentan-2-ones[a]

			
UV, nm[b]	299 (20)	398 (108)	387 (130)
^{13}C NMR, ppm[c]	217.2	258.3	250.5
IR, cm^{-1}	1745	1674	1672

[a] Values for cyclopentanone were taken from ref 20. Neat films were used for the IR analysis, whereas $CDCl_3$ and C_6H_{14} were used as solvents for the ^{13}C NMR and UV studies, respectively. The cited UV absorbance is the most intense band of five juxtaposed peaks. [b] The molar extinction coefficient follows λ_{max} in parentheses. [c] For the C=O carbon.[12]

Metallation of *trans*-1-methoxybutadiene was accomplished by treating a THF solution of this compound at −78 °C with an equimolar amount of *tert*-butyllithium in pentane followed by a slow warm-up to −20 °C. Treatment of the lithium compounds with an equimolar amount of the chlorodimethylsilane (or germane) in pentane at −78 °C gave the desired butadienyl adducts (**1**) as the *Z* isomers exclusively in 70–80% yield. Cyclization of **1** was accomplished in benzene solution at reflux temperature for **1A** or at 160 °C for the neat **1B** using 0.3 mol% chloroplatinic acid catalysis. Yields of 20–30% were routinely obtained. Attempts to improve on this value by varying the conditions and catalyst were unsuccessful. Acid-catalyzed hydrolysis of **2** proceeds cleanly at 25 °C in aqueous acetone to give the ketones **3** in 50–60% isolated yields.

The spectroscopic properties of the yellow-green metallacyclopentan-2-ones (**3**) are given in Table I. These data clearly show the important spectroscopic differences between these metalloidal carbonyl derivatives and cyclopentanone. The n → π* band[3,9] in **3A** (at 398 nm) is slightly shifted, as expected,[10] from the corresponding silacyclohexan-2-one system[3] (at 380 nm).

The ^{13}C NMR downfield carbonyl absorbance of **3A** relative to cyclopentanone agrees well with spectra of the acyclic ketone counterparts.[8,11,12] The ^{1}H NMR spectra of **3** were consistent with the assigned structures. Additional supportive information was obtained by using a

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(1) (a) This paper is part 3 of Vinylmetalloids. For part 2, see J. A. Soderquist and A. Hassner, *J. Organomet. Chem.*, **156**, C12 (1978); see also A. Hassner and J. A. Soderquist, *ibid.*, 131, C1 (1977).

(2) A 3,4-benzosilacyclopent-3-en-2-one system has been reported (S. J. Ferguson, M.Sc. Thesis, University of Toronto, 1966).

(3) A. G. Brook, *Adv. Organomet. Chem.*, **7**, 95 (1968).

(4) A. G. Brook and H. W. Kucera, *J. Organomet. Chem.*, **87**, 263 (1975).

(5) Metallated 1-methoxybuta-1,3-diene has been shown to add to benzaldehyde to give, after hydrolysis, the α-crotonylbenzyl alcohol [J. E. Baldwin, F. A. Hofle, and O. W. Lever, *J. Am. Chem. Soc.*, **96**, 7125 (1974)].

(6) A. G. Brook, J. M. Duff, and N. R. Davis, *J. Am. Chem. Soc.*, **89**, 431 (1967).

(7) G. Manuel, P. Mazerolles, and J. Gril, *J. Organomet. Chem.*, **122**, 335 (1976).

(8) J. A. Soderquist and A. Hassner, *J. Am. Chem. Soc.*, in press. See also ref 11 and A. G. Brook, J. W. Harris, J. Lennon, and M. E. Sheikh, *J. Am. Chem. Soc.*, **101**, 83 (1979).

(9) In 95% ethanol **3A** shows λ_{max} 396.5 nm (ε 100). This absorbance has also been interpreted in terms of a σ → π* transition [B. G. Ramsey, A. G. Brook, A. R. Bassindale, and H. Bock, *J. Organomet. Chem.*, **74**, C41 (1974)].

(10) Compare cyclopentanone and cyclohexanone absorptions [A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", 2nd ed., Edward Arnold, Inc., London, 1957, p 54].

(11) E. M. Dexheimer and L. Spialter, *J. Organomet. Chem.*, **107**, 229 (1976).

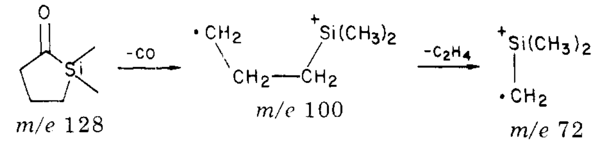
(12) For instance, absorbances at 48.8, 19.6 and 13.1 ppm were observed for the ring carbons at positions 3, 4, and 5, respectively. The methyl groups on silicon were found at −5.7 ppm. For **3B**, similar values were observed at 48.1, 21.3, 14.7 and −5.0 ppm, respectively.

europium shift reagent in conjunction with decoupling experiments.[13]

Of particular interest to our studies on the thermo- and photochemistry of these compounds[14] was the behavior of **3** upon electron impact in the mass spectrometer; for **3A** the major ions were found at *m/e* 128 (35), 100 (28), and 72 (100). Exact mass measurements gave good agreement with $C_6H_{12}OSi$, $C_5H_{12}Si$, and C_3H_8Si formulations for these ions, indicating initial loss of CO rather than of $CH_2{=}CH_2$. 4-Silacycloalkanones are known to lose ethylene rather than carbon monoxide from the molecular ion.[15]

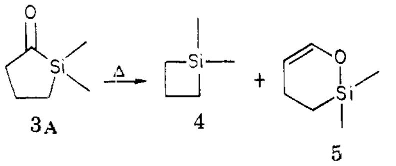
Metastable ions were observed at *m/e* 78.2 and 51.8, suggesting the 128 → 100 and 100 → 72 transitions were occurring.

On the basis of these data we view the fragmentation of **3A** as proceeding through initial loss of CO from the molecular ion with subsequent loss of ethylene.



The 100 → 72 transition is observed for the fragmentation of 1,1-dimethyl-1-silacyclobutane.[16] The decomposition of **3B** gives a very similar fragmentation pattern to that observed for **3A**, showing the corresponding peaks at *m/e* 174 (44), 146 (26), and 118 (100).

Vapor-phase pyrolysis of **3A** at 550 °C led to a 50:50 mixture of products **4** and **5** (60–80% yield). We envisage



the silacyclobutane **4** arising by decarbonylation of **3A**, and the silapyran **5** by migration of silicon from C to O (Brook rearrangement)[17] with a subsequent 1,2-hydride shift in the resulting siloxycarbene.

Further investigation of the chemistry of these compounds is currently under way.

Experimental Section

All reactions were carried out under a nitrogen atmosphere, and, prior to the hydrolysis step, oven-dried glassware was used. The chlorodimethylsilane (Aldrich) was used without further purification. Chlorodimethylgermane[19] was prepared from the reduction–selective oxidation of dichlorodimethylgermane (Laramie). Spectra were obtained using Varian (EM-360 and FT-80A), Perkin-Elmer (457), Du Pont (21-491B), and Cary (14) instruments. The cited mass spectral data for the germanium compounds are given for the ^{74}Ge isotope (36.54%) and are uncorrected. Elemental analyses were performed at Atlantic Microlabs, Inc.

(*Z*)-1-Methoxy-1-(dimethylsilyl)-1,3-butadiene (1A) was prepared by the dropwise addition of (*E*)-1-lithio-1-methoxy-1,3-butadiene (0.12 mol) in THF–pentane solution[8] to chlorodimethylsilane (12.0 g, 0.127 mol) in pentane (30 mL) at -78 °C. The mixture was allowed to warm to room temperature, filtered to remove lithium chloride, and distilled to give 13.1 g (77%) of **1A**: bp 151–153 °C (740 torr); NMR (CCl_4) δ 0.14 (d, 6 H, J = 3.8 Hz), 3.50 (s, 3 H), 4.34 (sept, 1 H, J = 3.8 Hz), 4.67–5.06 (m, 2 H), 5.74–6.70 (m, 2 H); mass spectrum *m/e* 142 (4), 127 (8), 97 (9), 95 (5), 89 (100), 75 (31), 59 (53), 44 (10), 42 (14); IR (thin film) 2150 (Si–H), 1567, 1623 (C═C) cm^{-1}. Anal. Calcd for $C_7H_{14}OSi$: C, 59.09; H, 9.92. Found: C, 58.81; H, 9.89.

(*Z*)-1-Methoxy-1-(dimethylgermyl)-1,3-butadiene (1B) was prepared in 66% yield from the lithiated derivative and chlorodimethylgermane: bp 67–69 °C (25 torr); NMR (CCl_4) δ 0.37 (d, 6 H, J = 3.5 Hz), 3.56 (s, 3 H), 4.43 (sept, 1 H; J = 3.5 Hz), 4.68–5.04 (m, 2 H), 5.67–6.66 (m, 2 H); mass spectrum *m/e* 188 (100), 173 (32), 141 (40), 135 (80), 105 (56), 89 (40); IR (thin film) 2060 (Ge–H), 1570, 1620 (C═C) cm^{-1}. Anal. Calcd for $C_7H_{14}OGe$: C, 45.01; H, 7.56. Found: C, 45.26; H, 7.64.

2-Methoxy-1,1-dimethyl-1-silacyclopent-2-ene (2A) was prepared by heating **1A** (9.4 g, 66 mmol) in benzene solution (50 mL) at reflux temperature for 2 h with chloroplatinic acid (0.11 g, 0.20 mmol). The mixture was filtered through neutral alumina (ca. 200 g) by using ether (300 mL) to elute any adsorbed product. Distillation gave 2.5 g (27%) of **2A**: bp 146–148 °C (740 torr); NMR (CCl_4) δ 0.18 (s, 6 H), 0.79 (m, 2 H), 2.36 (m, 2 H), 3.45 (s, 3 H), 5.31 (t, 1 H, J = 2.9 Hz); mass spectrum, *m/e* 142 (31), 127 (100), 101 (12), 99 (34), 97 (18), 89 (73), 85 (10), 83 (10), 75 (44), 71 (10), 69 (18), 61 (10), 59 (80); IR (thin film) 1588 (C═C) cm^{-1}. Anal. Calcd for $C_7H_{14}OSi$: C, 59.09; H, 9.92. Found: C, 59.17; H, 9.91.

2-Methoxy-1,1-dimethyl-1-germacyclopent-2-ene (2B) was prepared by heating a mixture of **1B** (13.6 g, 72.9 mmol) and chloroplatinic acid (0.11 g, 0.20 mmol) for 15 min at 160 °C. After the alumina workup as for **2A**, distillation gave 3.0 g (22%) of **2B** [bp 160–162 °C (740 torr)]. Using the reaction conditions described for **2A** did not alter the yield of **2B**. However, the reaction required 16 h at reflux temperature for complete disappearance of starting material. Minor amounts (ca. 5%) of *trans*-1-methoxy-5,5-dimethylhex-2-ene were always present in **2B**, precluding a satisfactory elemental analysis. This compound was separated subsequently from **3B** after the hydrolysis step. NMR (CCl_4) δ 0.39 (s, 6 H), 1.02 (m, 2 H), 2.50 (m, 2 H), 3.52 (s, 3 H), 5.16 (t, 1 H, J = 3.0 Hz); mass spectrum, *m/e* 188 (47), 173 (100), 143 (17), 105 (19), 89 (13); IR (thin film) 1598 (C═C) cm^{-1}.

1,1-Dimethyl-1-silacyclopentan-2-one (3A) was prepared from the hydrolysis of **2A** (2.0 g, 14 mmol) in acetone–2.0 M HCl (16 mL:4 mL) at 25 °C for 4 h. After ethereal workup, the organic layer was dried over magnesium sulfate and distilled to give 1.1 g (51%) of **3A**: bp 65–67 °C (12 torr); NMR (CCl_4) δ 0.18 (s, 6 H), 1.22 (m, 2 H), 1.92 (m, 4 H); mass spectrum, *m/e* 128 (35), 113 (2), 100 (28), 85 (7), 72 (100), 59 (13), 43 (12). Anal. Calcd for $C_6H_{12}OSi$: C, 59.19; H, 9.43. Found: C, 59.39; H, 9.50.

1,1-Dimethyl-1-germacyclopentan-2-one (3B) [bp 70–72 °C (14 torr)] was prepared in 54% yield from **2B** as described for **3A**: NMR (CCl_4) δ 0.24 (s, 6 H), 1.22 (m, 2 H), 192 (m, 4 H); mass spectrum, *m/e* 174 (44), 146 (26), 118 (100), 104 (37), 89 (50). Anal. Calcd for $C_6H_{12}OGe$: C, 41.72; H, 7.00. Found: C, 41.65; H, 7.02.

Pyrolysis of 3A. Samples of **3A** were allowed to vaporize against a pressure of ca. 1 torr into a pyrolysis tube at ca. 550 °C containing quartz chips. The yields of **4** and **5** were determined

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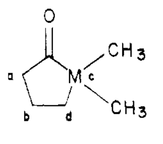
[13] For **3A** treatment with Eu(fod)$_3$ gives δ = 3.63 (t, 2 H) (a), 1.24 (q, 2 H) (b), 1.12 (s, 6 H) (c), and 1.00 (t, 2 H) (d). An apparent coupling



constant of 7.0 Hz was observed for the H_a–H_b and H_b–H_d protons. Decoupling a or d protons collapses b to a triplet, whereas irradiation of b gives singlets for a and d. For **3B**, treatment with Eu(fod)$_3$ gives δ = 3.78 (t, 2 H), 1.26 (q, 2 H), 1.13 (s, 6 H). Coupling constants and double resonance experiments gave data as for **3A**.

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by using gas chromatographic analysis of the collected pyrolysate containing *n*-decane as an internal standard. At higher temperatures, **4** was found to give a 1,3-disilacyclobutane product, as expected from earlier studies.[18]

Acknowledgment. This work was supported in part by Grant No. CA-19203 awarded by the National Cancer Institute, DHEW. The help of Professor P. J. Kocienski in obtaining the mass spectral data is gratefully acknowledged. The assistance of Mr. Ben Belinka in the preparation of analytical samples was much appreciated.

Registry No. 1A, 72301-23-6; 1B, 72301-24-7; 2A, 72301-25-8; 2B, 72301-26-9; 3A, 72301-27-0; 3B, 72301-28-1; 4, 2295-12-7; 5, 57787-03-8; (*E*)-1-lithio-1-methoxy-1,3-butadiene, 72301-29-2; chlorodimethylsilane, 1066-35-9; chlorodimethylgermane, 21961-73-9; *trans*-1-methoxy-5,5-dimethylhex-2-ene, 72301-30-5.

Nuclear Magnetic Resonance Configuration Correlation of Primary Amine Derivatives of α-Methyl-α-methoxy(pentafluorophenyl)acetic Acid

Edward J. Valente, Lance R. Pohl, and William F. Trager*[1]

Department of Pharmaceutical Sciences, School of Pharmacy, University of Washington, Seattle, Washington 98195

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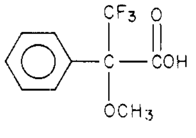
Resolved α-(trifluoromethyl)-α-methoxyphenylacetic acid (MTPA), **1**, and α-methyl-α-methoxy(pentafluorophenyl)acetic acid (MMPA), **2**, have been shown to be useful reagents for the determination of the enantiomeric composition of secondary alcohols and primary amines.[2-11] For example, the determination of the enantiomeric composition of α- and β-arylethylamine derivatives of **1** and **2** at the subnanogram level has been achieved by utilizing GLC.[9-11] Since many of these substances are biologically active, the technique has considerable utility. Moreover, the technique is not restricted to the determination of enantiomeric purity but can be extended to predict the absolute configuration of the starting alcohol or amine by utilizing ^{1}H NMR. The ^{1}H NMR spectra of the diastereomeric esters and amides derived from **1** and **2** display a pattern of nonequivalence which can be correlated to absolute configuration. An example of the technique used for this purpose can be found in the assignment of absolute configuration to a series of methyl- and methoxyamphetamines of unknown configuration.[9] Since there appears to be a fundamental correlation between configuration and the diastereomeric senses of nonequivalence[12] of the resonances found in the ^{1}H NMR spectra, determination of the factors responsible for the effect and their use in developing a conformational model could be both useful and instructive.



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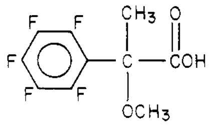

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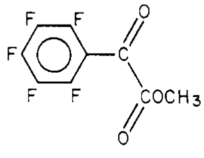

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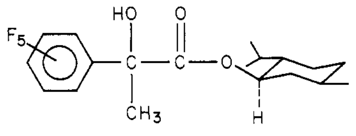
In order to develop such a model, we first found it necessary to assign the absolute configuration of the resolved acid **2**. In our initial approach we attempted to take advantage of Prelog's work[13] and derived relationships[14] in which absolute configuration can be assigned to asymmetric alcohols on the basis of the stereoselective reaction between prochiral precursor α-keto esters and Grignard reagents. Moreover, Hub and Mosher[15] have successfully established the absolute configuration of MTPA by using this same principle. They found that the reaction of phenylmagnesium bromide with (−)-menthyl trifluoropyruvate proceeded with 22% asymmetric induction to yield (−)-α-hydroxy-α-(trifluoromethyl)phenylacetic acid. Accordingly, methyl (pentafluorophenyl)glyoxylate, **3**, was hydrolyzed to the corresponding acid and esterified with (−)-menthol. Reaction of this material with methyl Grignard at 0 °C and lower temperatures gave diastereomeric methyl α-hydroxy-α-methyl(pentafluorophenyl)acetates, **4**, which were present in virtually identical amounts (GLC), indicating a lack of asymmetric induction. The lack of induction is surprising, particularly in view of Hub and Mosher's results.[15] One of a number of possible explanations is that the activation of the prochiral keto group by the pentafluorophenyl ring is so intense that product formation results from most collisions. Thus, energy differences in the transition states leading to the two diastereomeric products would be minimized. Other workers have found that asymmetric synthesis based on Prelog's generalization is dependent on subtle interactions between solvents, reagents, and conformational factors.[16]



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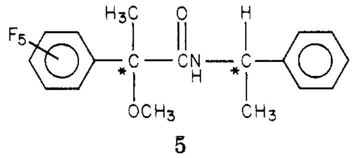

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An attempt to establish the absolute configuration of **2** by relating its circular dichroism (CD) spectrum to existing spectra of α-substituted phenylacetic acids was made.[17] There has been some debate recently concerning

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(1) This work was supported in part by NIH Research Career Development Award No. 1 KO4G MUO211 from the Institute of General Medical Science.

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