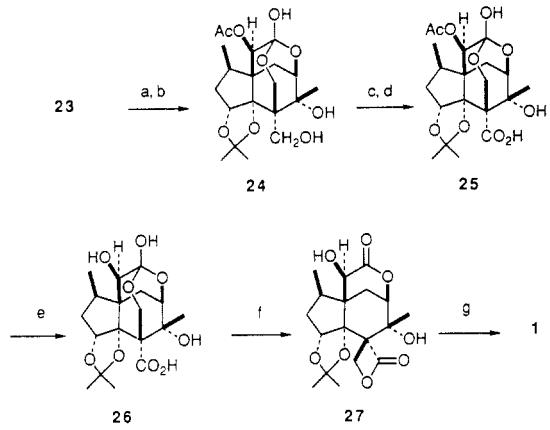
Scheme III[a]



[a] (a) Ac_2O, DMAP, CH_2Cl_2, 23 °C, 21 h; (b) AcOH–H_2O (4:1), 35 °C, 19 h; (c) PDC (1.6 equiv), CH_2Cl_2, 23 °C, 22 h; (d) $KMnO_4$ (12.5 equiv), NaH_2PO_4 (26 equiv), *t*-BuOH–H_2O, 23 °C, 20 min; (e) K_2CO_3, MeOH, 23 °C, 4 h; (f) $PhSO_2Cl$ (6 equiv), Py–toluene (1:1), 23 °C, 9 h; (g) 2 M HCl, DME, 80 °C, 2 h.

ymethyl groups in **18** as an acetonide, the oxymethylene group was oxidized with $RuCl_3$–$NaIO_4$[13] to give γ-lactone **19** (87% overall). Reaction of **19** with CH_3Li and subsequent acidic treatment of the resulting methyl ketone provided enol ether **20** (98% overall), which upon oxidation with OsO_4 afforded α-hydroxy ketone **21** (95%). Further oxidation of **21** with SO_3·Py–DMSO–Et_3N yielded keto hemiacetal **22** (96%) as a single diastereomer.[14] The latter can be regarded as a tautomer of the desired α-hydroxy δ-lactone **23**. Isomerization of **22** into **23** was achieved smoothly by adsorbing **22** on silica gel (Fuji-Davison silica gel BW-820 MH, 80–200 mesh; $CHCl_3$ was used for adsorption and was removed by a rotary evaporator) and leaving the dried silica gel at room temperature for 11 h. Elution with ethyl acetate gave **23** (mp 248–249 °C) quantitatively. The stereochemistry of the secondary OH group in **23** was confirmed by an NOE between the α-hydrogen of the δ-lactone moiety and the secondary methyl group.

At this point all that remained to complete a synthesis of anisatin was construction of the spiro β-lactone moiety and removal of the protecting groups. Acetylation of **23** followed by selective hydrolysis of the six-membered acetonide afforded ortho ester **24** (mp 120–122 °C, 56% overall) (Scheme III), which in turn was oxidized by a two-step sequence [(1) pyridinium dichromate (PDC); (2) $KMnO_4$–NaH_2PO_4][15] to give carboxylic acid **25** (37% overall). Basic methanolysis then furnished acid **26** (mp 197–199 °C, 93%). Construction of the spiro β-lactone was achieved by reaction of **26** with $PhSO_2Cl$–Py[4c,16] to yield anisatin acetonide **27** (mp 201–204 °C, 91%). Finally, deprotection with aqueous acid provided (−)-anisatin (**1**) [99%, mp 220–222 °C, $[\alpha]^{25}_D$ −22.5° (*c* 0.118, MeOH); natural **1**, mp 220–223 °C, $[\alpha]^{26}_D$ −21.9° (*c* 0.159, MeOH)]. Chiroptical properties including the sign of specific rotation and spectral properties (^{1}H NMR, IR, MS) of synthetic **1** were identical with those of natural anisatin. The absolute stereostructure of anisatin is therefore as depicted in formula **1**.

Acknowledgment. We thank the Ministry of Education, Science, and Culture, Japan, for financial support of this work (Grant-in-Aid for Scientific Research No. 01540453).

Supplementary Material Available: Spectral and physical data for compounds **6–15**, **17–21**, and **23–27** (6 pages). Ordering information is given on any current masthead page.

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Synthesis of the First Organodilithiosilane by Thermal Rearrangement

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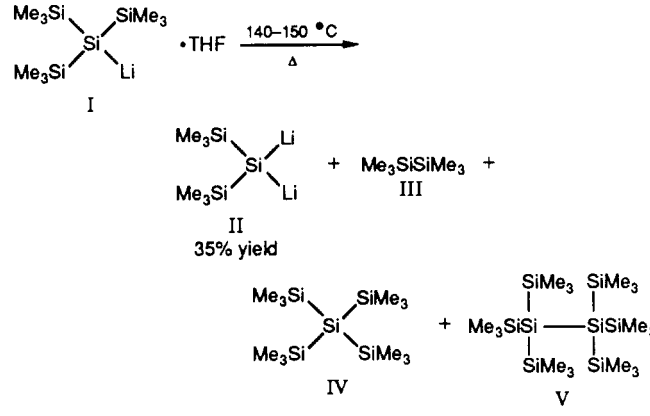
We report the synthesis of the first organodilithiosilane which we accomplished by the pyrolysis of [tris(trimethylsilyl)silyl]-lithium–THF in an inert atmosphere at 140–150 °C.



A new synthetic method has been developed in our laboratory involving pyrolysis of monolithio organic compounds which is broadly applicable in the synthesis of new substituted dilithiomethanes.[1,2] We have found that we can extend this Kawa–Lagow modified Ziegler synthetic technique[3] even beyond carbon centers to those of silicon and perhaps to other heteroatoms.

The synthesis of the first dilithiosilane, aside from having interesting possibilities for use as a chemical reagent, is of interest in view of the recent work of Streitwieser, Schleyer, and co-workers predicting the structures of both singlet and triplet dilithiosilanes.[4] Earlier, Schleyer and Reed studied the structure of tetralithiosilane and came to the conclusion that $SiLi_4$ may be the first fluxional eight-valence-electron tetracoordinate species.[5,6] Very flat potential energy surfaces and unusual geometries similar to that of the 10-electron species SF_4 are forecast for both species. It was also calculated that the potential energy surface is flat for $SiLi_4$. In 1977 our laboratory succeeded in preparing tetralithiosilane ($SiLi_4$) via lithium vapor reactions with silicon tetrachloride.[7]

The THF adduct of tris(trimethylsilyl)lithium was prepared by the reaction of tetrakis(trimethylsilyl)silane and methyllithium using a Et_2O/THF (1:4) solvent mixture.[8] The product was purified by recrystallization[9] at low temperatures. The THF adduct of compound I has excellent stability and can be stored for months at room temperature in an inert atmosphere.

$$\underset{\text{IV}}{(Me_3Si)_4Si} + MeLi \xrightarrow[4:1]{THF/Et_2O} \underset{\text{I}}{(Me_3Si)_3SiLi{\cdot}THF}$$

To prepare bis(trimethylsilyl)dilithiosilane, 0.6 g (184 mmol) of I was placed in a small flask coupled with a distillation apparatus. All manipulations were carried out in an oxygen-free

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and moisture-free argon atmosphere. The flask was placed in an oil bath and heated to 120 °C, where the solid liquefied, creating a yellow-green solution. The apparatus was then evacuated and back-filled with argon. The temperature was raised to 140–150 °C for 4 h with occasional evacuation and back-filling with argon. The vacuum is very important, for it removes trimethylsilanes III, IV, and V. During this time, the color of the solid changed from light yellow to pale yellow and finally to dark orange. A liquid byproduct was produced in the reaction and was determined to be a mixture of THF and hexamethyldisilane by ^{1}H NMR and mass spectroscopy. The orange solid was placed in a vacuum line trap under argon. The trap was then evacuated, and an excess of d_1-ethyl alcohol was transferred into the trap along with ethyl ether. The contents were stirred overnight to complete the hydrolysis reaction. Analysis of the mixture by GC/MS revealed four major components: $(Me_3Si)_2SiD_2$ (35%), $(Me_3Si)_3SiD$ (22%), $(Me_3Si)_4Si$ (10%), and $(Me_3Si)_3SiSi(SiMe_3)_3$ (27%). If the reaction is carried out for longer periods of time, more of the coupling product $Si_2(SiMe_3)_6$ (V) is produced at the expense of the dilithio compound. Mass spectral analysis of the deuterated product $(Me_3Si)_2SiD_2$ showed a molecular ion at 178 (10%) and a base peak at m/e 73 corresponding to Me_3Si^+; other peaks at 163 and 90 are indicative of $Me_5Si_3D_2$ and $Me_2Si_2D_2$.

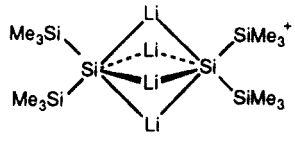
The product also derivatized with methyl iodide to give a 27% yield of bis(trimethylsilyl)dimethylsilane:[10]

$$\underset{\text{II}}{(Me_3Si)_2SiLi_2} \xrightarrow{CH_3I} \underset{27\%}{(Me_3Si)_2Si(CH_3)_2}$$

A solid sample of $(Me_3Si)_2SiLi_2$ was studied by flash vaporization mass spectroscopy using methods previously reported.[3,11] Direct observation of the parent ions for both the monomer and dimer of the new dilithiosilane revealed the parent ions

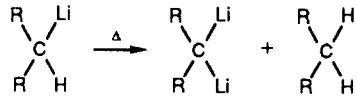
$$\underset{P_I}{[(Me_3Si)_2SiLi_2]_2^+} \qquad \underset{P_{II}}{[(Me_3Si)_2SiLi_2]^+}$$

plus $[P_I - (SiMe_3)]^+$, $(P_I - CH_3)^+$, $(P_I - H)^+$, $(P_{II} - CH_3)^+$, and $(P_{II} - H)^+$. The structure of the molecular ion of the dimer is most probably



The structures of the gas-phase monomers and dimers are under study.[12]

This reaction bears a similarity to our studies of the Kawa-Lagow modified Ziegler rearrangement[1,2] in which a disproportionation reaction takes place with proton transfer:



However, on the silicon center, the trimethylsilyl group is the moiety transferred. It is probable that species III and V are produced by thermal rearrangement of IV.

Acknowledgment. We are grateful to the National Science Foundation (CHE-9012405) and the Robert A. Welch Foundation (F-700) for support of this work.

(10) Mass spectral analysis of octamethyltrisilane m/e: M^+ 204 (23.5) $(M - Me)^+$ 189 (16), $(M - TMS)^+$ 131 (78.9), $(M - Me - TMS)^+$ 116 (44), $[(TMS)Si]^+$ 101 (8.5), and $(TMS)^+$ 73 (100). ^{1}H NMR (ppm): 0.062, 0.075.

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(12) Work in progress in collaboration with Josef Michl and co-workers.

Nucleophilic Attack at C2 of Neutral (η^5-Pentadienyl)manganese Complexes: Formation of σ,η^3-Manganese Complexes

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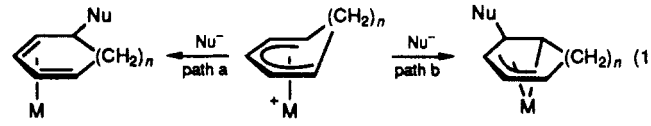
The reaction of nucleophiles with a wide variety of transition-metal π-complexes has been documented and utilized extensively in organic synthesis.[1] This literature includes many examples utilizing η^5-dienyl transition-metal complexes, mainly cationic (η^5-cyclohexadienyl)iron complexes.[2] In most cases, attack at the terminus of the π-system provides substituted η^4-diene metal complexes (eq 1, path a). The literature contains only



scattered reports of this reaction with η^5-pentadienyl complexes,[2c,3] however, and a growing body of evidence indicates that the use of certain η^5-pentadienyl[4] and also η^5-cycloheptadienyl[5] systems promotes nucleophilic attack at the internal C2 position, generating σ,η^3-transition-metal complexes (eq 1, path b).[6] It has also been determined that the use of relatively soft nucleophiles and electron rich metal centers promotes reaction at the C2 position of the η^5-dienyl π-system.[4a–c,e,5a,7] Although the chemistry of σ,η^3-complexes generated by this reaction has not been explored in detail, several noteworthy reactions of these pentenediyl complexes have been reported.[5a,d,8] Our interest in the chemistry of η^5-pentadienyl and σ,η^3-transition-metal complexes led us to investigate the reaction of nucleophiles with (η^5-pentadienyl)manganese complexes. In this paper we report that the reaction of certain

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