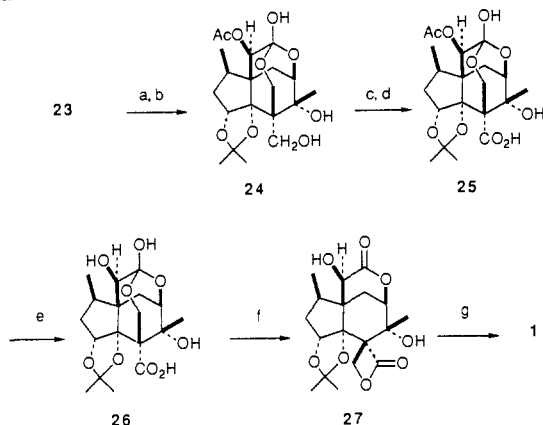


Scheme III^a

^a (a) Ac₂O, DMAP, CH₂Cl₂, 23 °C, 21 h; (b) AcOH-H₂O (4:1), 35 °C, 19 h; (c) PDC (1.6 equiv), CH₂Cl₂, 23 °C, 22 h; (d) KMnO₄ (12.5 equiv), NaH₂PO₄ (26 equiv), *t*-BuOH-H₂O, 23 °C, 20 min; (e) K₂C₂O₃, MeOH, 23 °C, 4 h; (f) PhSO₂Cl (6 equiv), Py-toluene (1:1), 23 °C, 9 h; (g) 2 M HCl, DME, 80 °C, 2 h.

methyl groups in **18** as an acetone, the oxymethylene group was oxidized with RuCl₃-NaIO₄¹³ to give γ -lactone **19** (87% overall). Reaction of **19** with CH₃Li and subsequent acidic treatment of the resulting methyl ketone provided enol ether **20** (98% overall), which upon oxidation with OsO₄ afforded α -hydroxy ketone **21** (95%). Further oxidation of **21** with SO₃·Py-DMSO-Et₃N 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; CHCl₃ 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) KMnO₄-NaH₂PO₄]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 PhSO₂Cl-Py¹⁶ to yield anisatin acetonide **27** (mp 201-204 °C, 91%). Finally, deprotection with aqueous acid provided (-)-anisatin (**1**) [99%, mp 220-222 °C, [α]_D²⁵ -22.5° (*c* 0.118, MeOH); natural **1**, mp 220-223 °C, [α]_D²⁶ -21.9° (*c* 0.159, MeOH)]. Chiroptical properties including the sign of specific rotation and spectral properties (¹H 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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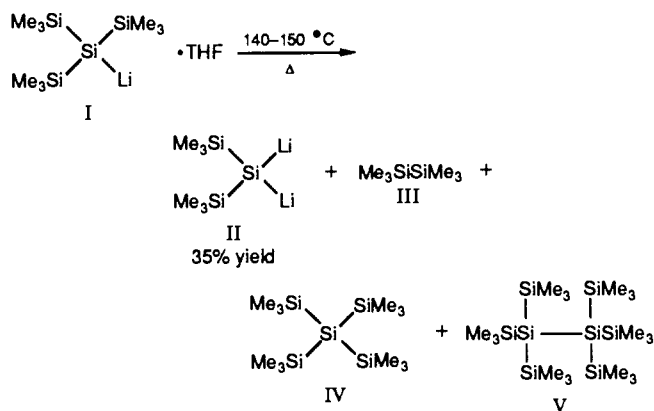
Synthesis of the First Organodilithiosilane by Thermal Rearrangement

S. K. Mehrotra, H. Kawa, J. R. Baran, Jr., M. M. Ludvig, and R. J. Lagow*

Department of Chemistry, University of Texas
Austin, Texas 78712

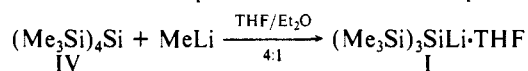
Received May 2, 1990

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 dilithio-methanes.^{1,2} We have found that we can extend this Kawa-Lagow modified Ziegler synthetic technique³ 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 SiLi₄ 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 SF₄ are forecast for both species. It was also calculated that the potential energy surface is flat for SiLi₄. In 1977 our laboratory succeeded in preparing tetralithiosilane (SiLi₄) 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 methyl lithium using a Et₂O/THF (1:4) solvent mixture.⁸ The product was purified by recrystallization⁹ 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.



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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