

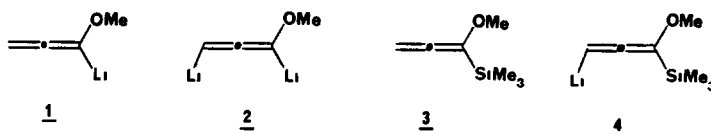
SILICON IN SYNTHESIS 1-TRIMETHYLSILYL-1-METHOXY ALLENE; A REAGENT FOR THE
DIRECT CONVERSION OF ALIPHATIC ALDEHYDES INTO 2-TRIMETHYLSILYL FURANS

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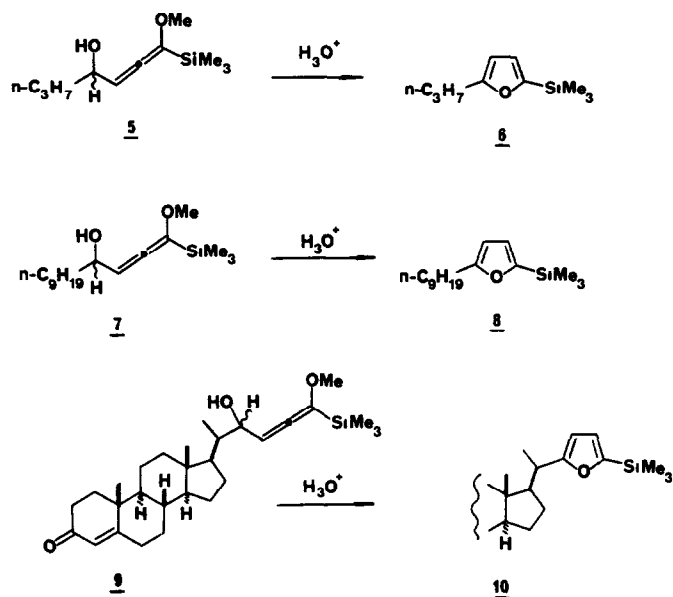
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Abstract 3-Lithio 1-trimethylsilyl-1-methoxy allene **4** reacts with aldehydes to give adducts that are readily transformed into 2-trimethylsilyl furans.

Recently we described some additions of lithio methoxyallene **1** to aldehydes and ketones,² and have tried to extend this reagent to the generation of the dilithio species **2** without success. Consequently we treated **1** with chlorotrimethylsilane to give 1-trimethylsilyl-1-methoxyallene **3**, (81% b.p. 40-43°C/28mm).³ When **3** was treated with t-BuLi in THF at -78°C the lithio species **4** was formed.⁴ Treatment of n-butyraldehyde with **4** gave the adduct **5** (95%),⁵ as a mixture of

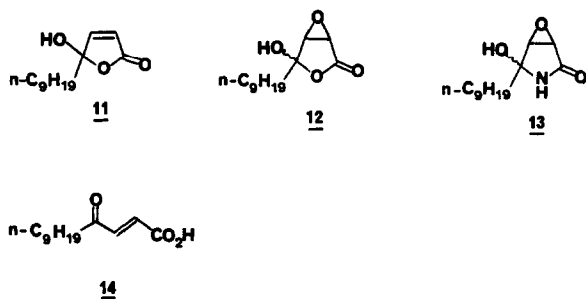


diastereomers. Mild acid hydrolysis of **5** gave the 2-trimethylsilyl furan **6**. n-Decanal, on treatment with **4**, gave the adduct **7** (97% crude yield) which was hydrolysed (HClO₄/20% aqueous THF at 0°C for 20 min.) to give the furan **8** in overall 25% yield after chromatography. The conditions for this hydrolysis are crucial since it is well known that 2-trimethylsilyl furan is extremely susceptible to protodesilylation.⁶ The steroid adduct **9** on standing in chloroform is slowly converted into **10**, albeit in low yield. The adducts of aromatic aldehydes with **4** gave complex mixtures on exposure to acid with only traces of furan

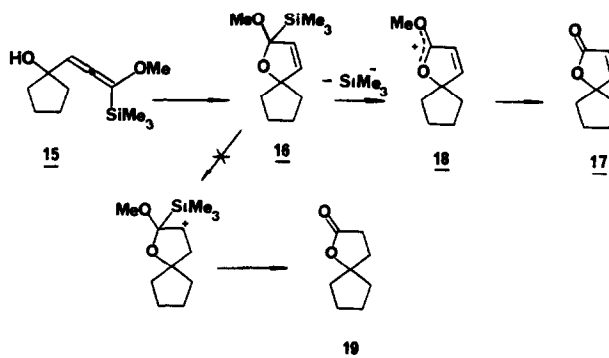


products being discernible. It should be noted that the only previous method for the synthesis of 2-trimethylsilyl furans involves the silylation of 2-lithiofuran.⁶

2-Trimethylsilyl furans are very susceptible to electrophilic substitution, although this has not been exploited in synthesis. 2-Trimethylsilyl-5-nonylfuran **8** was exposed to singlet oxygen ($O_2/h\nu$ /rose bengal in methanol)⁷ for a few minutes at 20°C to give, directly, the δ -hydroxy butenolide **11** (90%). Treatment of **11** with NaOH/H₂O₂/aq. MeOH gave the epoxide **12**, which was



converted into the amide **13** (m.p. 110°C) by exposure to $\text{NEt}_3/\text{ClCO}_2\text{Et}/\text{NH}_3$. Thus these reactions convert, in a direct manner, the 2-trimethylsilyl furan **8** into the cerulenin model system **13**⁸. Interestingly attempted distillation of **11** gave only the trans- ketoenoic acid **14** (m.p. 111-112°C). Surprisingly the adduct **15**,



between **4** and cyclopentanone, on mild acid hydrolysis gave the spiro-butenolide **17**. The adduct **15** slowly converted into **16**, on standing in CH_2Cl_2 at room temperature, and further aqueous acid treatment of **16** gave **17**. Formally this represents an oxidation where the $-\text{SiMe}_3$ group has functioned as a leaving group. While this is unprecedented under these acidic conditions, it is thermodynamically favorable since the oxonium ion **18** dominates any build-up of electrophilic character β - to silicon, which would have produced the saturated lactone **19**.

In summary, the reagent **3** provides a direct method for making 2-trimethylsilylfurans from aliphatic aldehydes. To date the butenolide formation has not proven general, but in the example given it proceeds in good yield (70%).

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References and notes

1. Address correspondence to the author at Indiana University, Department of Chemistry, Bloomington, Indiana 47405.
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3. While this work was in progress the alkylation of **4** was reported J-C Clinet, and G. Linstrumelle, Tetrahedron Letters, 3987 (1980). For dianions of substituted allenes see - Y. Leroux, and R. Mantione, Ibid, 591 (1971); Y. Leroux, and C. Roman, Ibid, 2585 (1973).
4. n-BuLi will form the species **4**, but in general the use of t-BuLi gave considerably cleaner reactions.
5. NMR(CCl₄, benzene as internal standard) **5**, δ 5.71(1H,d J=5Hz), 3.42(3H,s), 1.8-0.8(3H,m), 0.20(9H,s), **6**, 6.32(1H,d J=3Hz), 5.76(1H,d J=3Hz), 2.6(2H, t J=7Hz), 0.91(5H,m), 0.1(9H,s); **7**, 5.70(1H,d), 3.36(3H,s), 2.35(1H,s), 1.22(17H, bs), 0.93(3H,d), 0.10(9H,s); **8**, 6.47(1H,d J=3Hz), 5.90(1H,d J=8Hz), 2.55 (2H,t J=7Hz), 1.27(17H,bs), 0.90(3H, bd), 0.23(9H,s); **10**, 6.30(1H,d J=3Hz), 5.70(1H,d J=3Hz), 5.55(1H,bs), 1.1(3H,s), 0.75(3H,s), 0.15(9H,s), and the broad methylene envelope, **11**, 7.23(1H,d J=4.5Hz), 6.10(1H,d J=4.5Hz), 5.35(1H,s), 2.0(2H,bm), 1.4(14H,bs), 0.98(3H,bm), **12**, 9.52(1H,bs), 3.55(2H,dd J=4.5Hz), 2.27(2H,t J=5Hz), 1.2(14H,bs), 0.81(3H,m); **13**, 3.55(2H,bs), 2.46(2Hbs), 1.31(14H,bs), 0.91(3H,m), **14**, 7.08(1H,d J=12Hz), 6.57(1H,d J=12Hz), 2.57(2H,t J=5.5Hz), 1.20(14H,bs), 0.80(3H,m); **15**, 5.80(1H,s), 3.39(3H,s), 1.70(8H,bs), 0.12(9H,s), **16**, 6.65(2H,q J=5.5Hz), 1.90(8H,s).
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