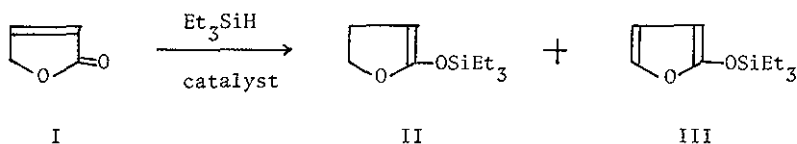


PREPARATION AND SOME REACTIONS OF 2-TRIMETHYLSILYLOXYFURANS

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Synthetically useful 2-trimethylsilyloxyfurans were prepared by silylation of but-2-enolides. Some of their reactions ----- bromination, dichlorocarbene addition, and a Diels-Alder reaction ----- were also reported.

As an extension of our study on the hydrosilation of α,β -unsaturated esters we subjected but-2-enolide(I) to Rh(I) complex catalyzed reaction with triethylsilane.¹ The reaction afforded the expected 1,4-addition product(II) along with ca. 10% yield of 2-triethylsilyloxyfuran(III). The first isolation of a silyl trapped 2-hydroxyfuran² directed us to establish the more effective preparative method of 2-silyloxyfurans from but-2-enolides and also to examine their chemical reactivity.



Catalytic dehydrogenation between triethylsilane and I using various catalysts was not fruitful, resulting in unacceptable yields (maximum yield of ca. 40% by $\text{PdCl}_2\text{-C}_6\text{H}_5\text{SH}^3$) and difficulty in separating III from II. The best preparative method was found to be the direct silylation (trimethylchlorosilane/triethylamine/zinc chloride) which has been reported for crotonaldehyde⁴ and trans-

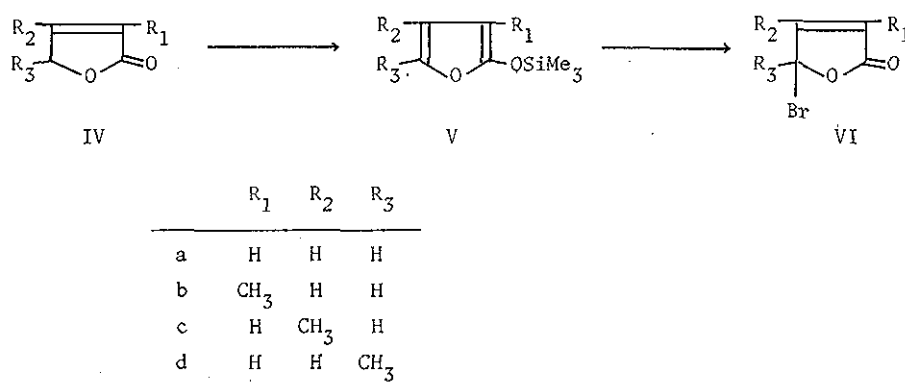


Table 1. Physical and Pmr Data of 2-Trimethylsilyloxyfurans

Compd.	bp, °C(Torr)	pmr: δ_{ppm} (J, Hz) in $\text{CCl}_4^{\text{a)}$			
		3-H	4-H	5-H	CH_3
Va	42-50(17) ^{b)}	4.90(dd 1,3)	6.00(t, 3)	6.60(diff. s)	
Vb	50-60(17) ^{b)}		5.95(d, 2)	6.64(d, 2)	1.83
Vc	60-65(7) ^{b)}	4.83(br. s)		6.47(diff. s)	1.90
Vd ^{c)}	66-68(22)	4.77(d, 3)	5.57(diff. s)		2.03

a) Determined by Jeol PMX-60(60MHz). s=singlet, d=doublet, t=triplet, dd=doublet of doublets, br.=broad, diff.=diffused.

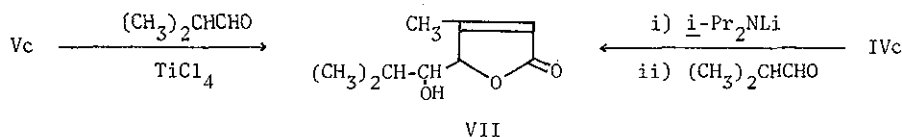
b) Bath temperature(short path distillation).

c) This compound was also prepared from α -angelic lactone with bistrimethylsilyl-acetamide and trimethylchlorosilane in pyridine(89% yield).

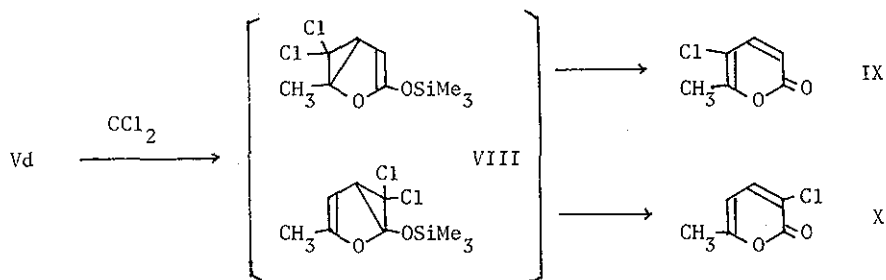
4-methoxybuten-2-one.⁵ Using tetrahydrofuran solvent instead of benzene and reacting at 65° for 3 hr, 2-trimethylsilyloxyfuran(Va) and its three monomethyl derivatives(Vb-d) were obtained in the yields of 55-60%.⁶ The pmr data which supported their structures are given in Table 1.

Bromine addition to Va-d in carbon tetrachloride afforded the corresponding 5-bromobut-2-enolides(VIa-d)⁷⁻¹⁰ in quantitative yields, establishing the similar reactivity of V to 2-acetoxymfuran. The present synthetic method of 5-bromobut-2-enolides¹¹ through this silylation-bromination sequence would be specifically useful in the case of alkyl substituted but-2-enolides whose NBS bromination are known to favor on the side chain.^{9,10}

A titanium chloride induced condensation¹² of Vc with isobutyraldehyde took place smoothly in dichloromethane at -78°, at the 5-position again and giving VII(erythro/threo ratio=1/4).¹³ The stereochemical result obtained here was reversed in the reaction of the enolate anion of IVc with the same aldehyde¹⁴ where erythro isomer was predominantly formed. The stereoselectivity of the former reaction could be rationalized by assuming a directed coordination of the reactants with titanium ion.



2-Silyloxyfurans also entered in the addition reaction with dichlorocarbene. Refluxing the benzene solution of Vd and $\text{C}_6\text{H}_5\text{HgCBrCl}_2$ gave methylchloro-2-pyrones (IX and X in the ratio of 2:1).¹⁵ The conversion should be interpreted as proceeded via dichlorocyclopropane intermediates(VIII) followed by thermal loss of trimethylchlorosilane.^{16,17}



Furthermore, the reaction of Vd with maleic anhydride gave a Diels-Alder adduct which gave 2-hydroxy-5-methylphthalic anhydride after acid treatment.¹⁸ The high reactivity of 2-silyloxyfurans towards electrophiles due to the ketene silyl acetal structure and the furan ring itself has been demonstrated. Since 2-silyloxyfurans are now more easily accessible than 2-acetoxymethoxyfuran or 2-alkoxyfuran,¹⁹ they could be potentially useful as synthetic intermediates.

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- 14 For similar reaction, see ref. 10.
- 15 Pmr spectra in CDCl_3 (δ_{ppm}). IX (mp 86.5-7⁰): 2.37(s), 6.16 and 7.27(d, J=10 Hz). X (mp 86-8⁰): 2.25(s), 5.97 and 7.37(d, J=7 Hz).
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