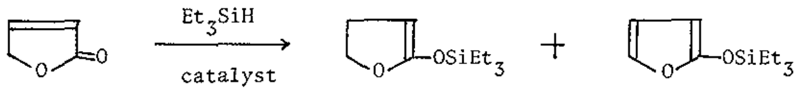
HETEROCYCLES, Vol. 4, No. 10, 1976

PREPARATION AND SOME REACTIONS OF 2-TRIMETHYLSILYLOXYFURANS

Eiichi Yoshii*, Toru Koizumi, Eitaro Kitatsuji, Toshiji Kawazoe, and Tomie Kaneko
Faculty of Pharmaceutical Sciences, University of Toyama, Toyama 930, Japan

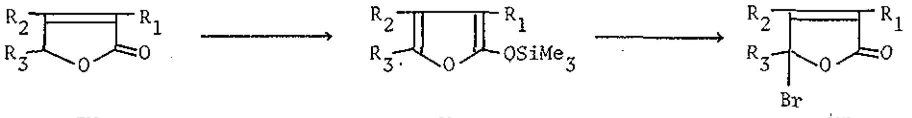
Synthetically useful 2-trimethylsilyloxyfurans were prepared by silylation of but-2-enolides. Some of their reactions —— bromination, dichlorocarbene addition, and a Diels-Alder reaction —— were also reported.

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-hydroxyfuran[2] directed us to establish the more effective preparative method of 2-silyloxyfurans from but-2-enolides and also to examine their chemical reactivity.



I II III

Catalytic dehydrogenation between triethylsilane and I using various catalysts was not fruitful, resulting *in unacceptable yields(maximum yield of* ca. 40% by $PdCl_2$-C_6H_5SH[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 crotonaldehyde*[4] and trans-



IV V VI

	R_1	R_2	R_3
a	H	H	H
b	CH_3	H	H
c	H	CH_3	H
d	H	H	CH_3

Table 1. Physical and Pmr Data of 2-Trimethylsilyloxyfurans

Compd.	bp, °C(Torr)	pmr: δ_{ppm}(J, Hz) in CCl_4 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.

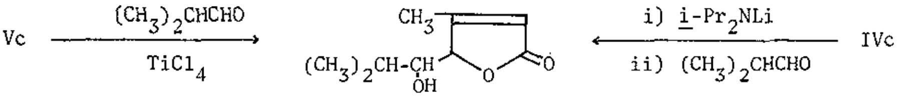
b) Bath temperature(short path distillation).

c) This compound was also prepared from α-angelic lactone with bistrimethylsilylacetamide 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-trimethylsilyoxyfuran(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.

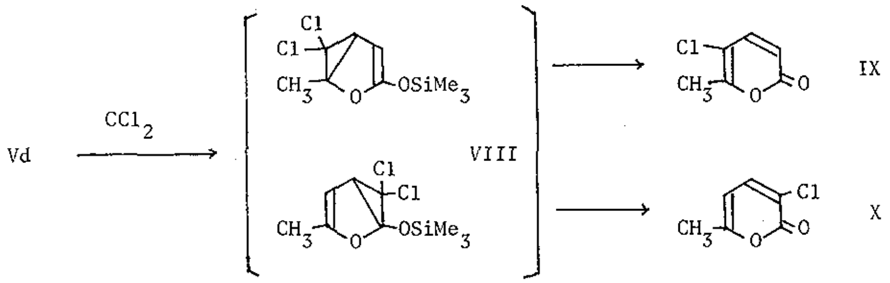
Bromine addition to Va-d in carbon tetrachloride afforded the corresponding 5-bromobut-2-enolides(VIa-d)[7-10] in quantitative yields, establishing the similar reactivity of V to 2-acetoxyfuran. The present synthetic method of 5-bromobut-2-enolides[11] through this silylation-bromination sequence would 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 condensation[12] 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 aldehyde[14] 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.



VII

2-Silyloxyfurans also entered in the addition reaction with dichlorocarbene. Refluxing the benzene solution of Vd and $C_6H_5HgCBrCl_2$ 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-acetoxyfuran or 2-alkoxyfuran,[19] they could be potentially useful as synthetic intermediates.

REFERENCES AND NOTES

1 E. Yoshii, Y. Kobayashi, T. Koizumi, and T. Oribe, *Chem. Pharm. Bull.* (Tokyo), 1974, **22**, 2767.

2 B. Maume, W.E. Wilson, and E.C. Horning, *Anal. Letters*, 1968, 401. These authors, based on mass spectroscopic evidence, have reported the formation of a 2-silyloxyfuran derivative from digitoxigenin under the silylation condition using bistrimethylsilylacetamide, trimethylchlorosilane, and pyridine. However, we were unable to reproduce their result.

3 Y. Nagai, K. Uetake, and T. Yoshikawa, *Yuki Gosei Kagaku Kyokai Shi*, 1973, **31**, 759. For other catalyst systems employed for dehydrogenative condensation between enolizable ketones and triethylsilane, see E. Frainnet, V. Martel-

Siegfried, E. Brousse, and J. Dedier, *J. Organometal. Chem.*, 1975, **85**, 297.

4 P. Cazeau and E. Frainnet, *Chem. Abstr.*, 1968, **68**, 49733.

5 S. Danishefsky and T. Kitahara, *J. Am. Chem. Soc.*, 1974, **96**, 7807.

6 The moderate yields might be attributable to the high volatility of the products.

7 All new compounds gave satisfactory elemental analyses and spectral data.

8 VId was thermally unstable, producing protoanemonin on distillation.

9 C.B. Chaples, K.L. Svanholt, R. Martin, and A.S. Dreiding, *Helv. Chim. Acta*, 1976, **59**, 100.

10 T.C. McMorris, R. Seshadri, and T. Arunachalam, *J. Org. Chem.*, 1974, **39**, 669.

11 5-Bromobut-2-enolides have been most commonly prepared by bromination of 2-acetoxyfurans. N. Elming, *Acta Chem. Scand.*, 1952, **6**, 578, and literatures cited therein.

12 T. Mukaiyama, K. Banno, and K. Narasaka, *J. Am. Chem. Soc.*, 1974, **96**, 7503.

13 Pmr spectra in CDCl$_3$(δ_{ppm}). *threo*-VII(mp 126-9°): 1.06, 1.00(isopropyl, d, J=6 Hz). 4.90(-$\overset{|}{\text{C}}$HOCO, br. s), 3.76(-$\overset{|}{\text{C}}$HOH, br. d, J=8 Hz). *erythro*-VII(oil): 0.90(isopropyl, d, J=6 Hz), 4.73(-$\overset{|}{\text{C}}$HOCO, br. d, J=7 Hz), 3.44(-$\overset{|}{\text{C}}$HOH, dd, J= 7 and 5 Hz).

14 For similar reaction, see ref. 10.

15 Pmr spectra in CDCl$_3$(δ_{ppm}). IX(mp 86.5-7°): 2.37(s), 6.16 and 7.27(d, J= 10 Hz). X(mp 86-8°): 2.25(s), 5.97 and 7.37(d, J=7 Hz).

16 E. Yoshii, T. Koizumi, and T. Kawazoe, *Chem. Pharm. Bull.*(Tokyo), 1976, **24**, 1957.

17 Use of sodium trichloroacetate in dimethoxyethane-tetrachloroethylene at 120° produced a comparable result.

18 M.P. Cava, C.L. Wilson, and C.J. Williams, Jr., J. Am. Chem. Soc., 1956, **78**, 2303.

19 These compounds have been prepared usually by several step sequence starting from furan derivatives. G.F. D'Alelio, C.J. Williams, Jr., and C.L. Wilson, J. Org. Chem., 1960, **25**, 1025, 1028; D.G. Manly and E.D. Amstuts, ibid., 1956, **21**, 516.

Received, 14th August, 1976