

A GENERAL METHOD FOR THE PREPARATION OF
2-SUBSTITUTED AND 2,3-DISUBSTITUTED FURANS.

A NEW SYNTHESIS OF SESQUIROSE FURAN

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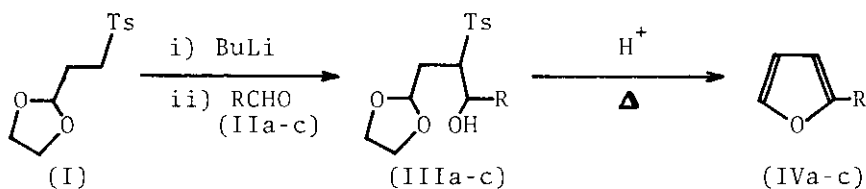
Various 2-substituted and 2,3-disubstituted furans were prepared starting from 3-tosylpropanal ethylene acetal in two and three steps, respectively. Sesquirose furan was readily synthesized by the present method.

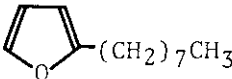
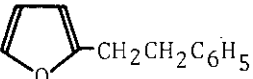
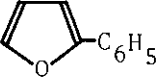
In the previous paper,¹ it was reported that 3-tosylpropanal ethylene acetal (I) is useful starting material for the preparation of 3-substituted furans such as dendrolasin [3-(4,8-dimethyl-3,7-nonadienyl)furan]. In this paper we wish to show that I is also useful for the preparation of 2-substituted and 2,3-disubstituted furans.

2-Substituted furans were readily prepared in two steps according to the accompanying scheme from I as follows: in the first

place I was lithiated by stirring with an equimolar amount of butyllithium in THF at -78°C for 10 min under nitrogen atmosphere. Treatment of the lithiated I with aldehydes(II) at -78°C and then at room temperature gave the corresponding alcohols(III) in approximately 80% yield. A benzene solution of III was refluxed in the presence of a catalytic amount of p-toluenesulfonic acid for 3.5 h to give the expected 2-substituted furans(IV) in fairly good yield as listed in Table 1.

TABLE 1. SYNTHESIS OF 2-SUBSTITUTED FURANS



RCHO	Isolated yield (%) ^{a)} IVa-c
IIa, $\text{CH}_3(\text{CH}_2)_7\text{CHO}$	 64
IIb, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CHO}$	 66
IIc, $\text{C}_6\text{H}_5\text{CHO}$	 58

a) Based on I.

The combination of the synthetic method of 3-substituted furan reported previously¹ and that of 2-substituted furan may afford a new method for the preparation of 2,3-disubstituted furans through the sequence of reactions shown below. Actually various 2,3-disubstituted furans were readily prepared by the method in good yields as listed in Table 2.

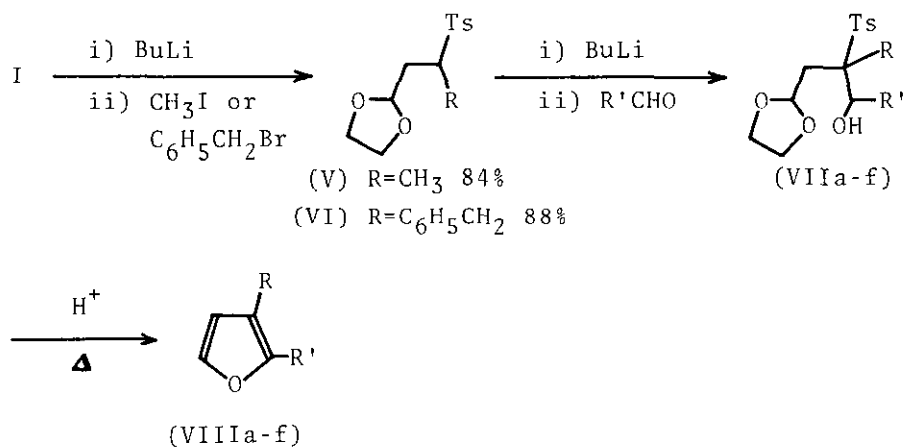
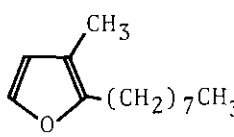
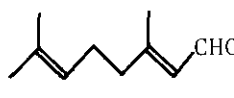
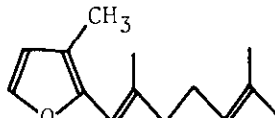
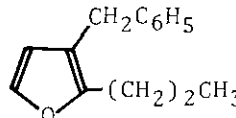
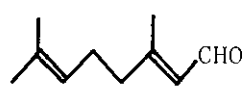
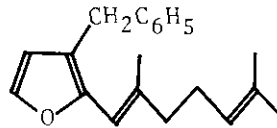
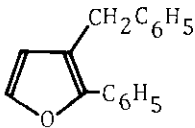
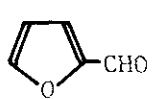
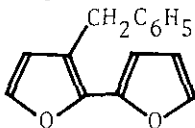


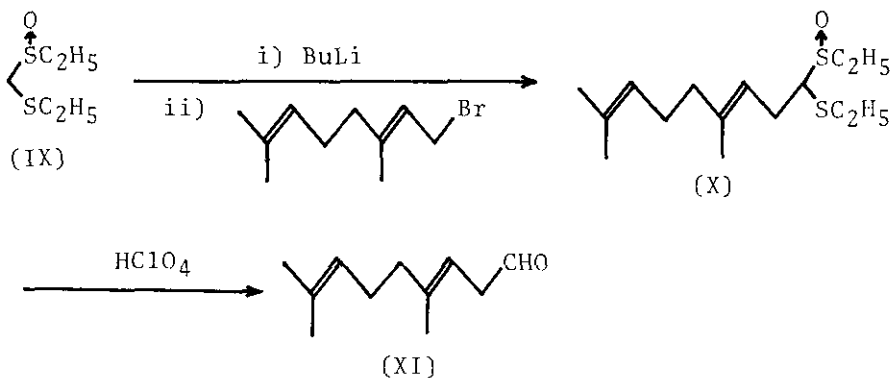
TABLE 2. SYNTHESIS OF 2,3-DISUBSTITUTED FURANS

	R'CHO	Isolated yield (%) ^{a)} VIIIa-f
V	$\text{CH}_3(\text{CH}_2)_7\text{CHO}$	VIIIa,  72
		VIIIb,  78

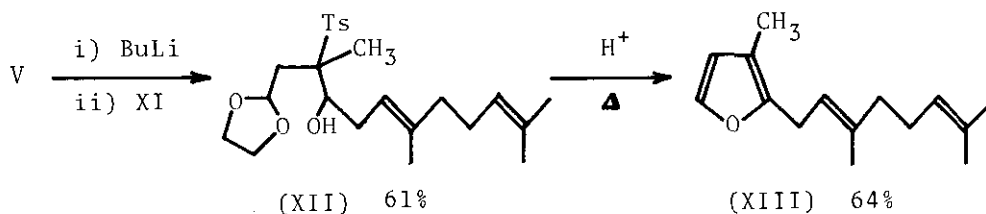
VI	$\text{CH}_3(\text{CH}_2)_2\text{CHO}$	VIIIc,		76
		VIIIId,		78
	$\text{C}_6\text{H}_5\text{CHO}$	VIIIe,		70
		VIIIIf,		69

a) Based on V or VI.

In order to demonstrate the utility of this route, we tried to synthesize sesquirose furan [2-(3,7-dimethyl-2,6-heptadienyl-3-methylfuran, XIII], which is a typical 2,3-disubstituted furan occurring in nature, starting from V and 4,8-dimethyl-3,7-nonadienal (XI). The aldehyde XI was prepared by the procedure of Richman and others² according to the following scheme. However, it was



required to use the crude solution³ of XI obtained by acidic hydrolysis of X because of its instability. The desired sesquirose furan (XIII) was consequently synthesized in a similar manner above-mentioned as follows⁴:



IR and NMR spectra of this compound (XIII) were identical with those of authentic sample.

REFERENCES

- 1 K. Inomata, S. Aoyama, and H. Kotake, Bull. Chem. Soc. Jpn., 1978, 51, 930.
- 2 J. E. Richman, J. L. Herrmann, and R. H. Schlessinger, Tetrahedron Lett., 1973, 3267.
- 3 Diethyl disulfide was removed by column chromatography on silica gel.
- 4 The isolated yields shown were not optimized.

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