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

## *A NEW SYNTHESIS OF SESQUIROSE FURAN*

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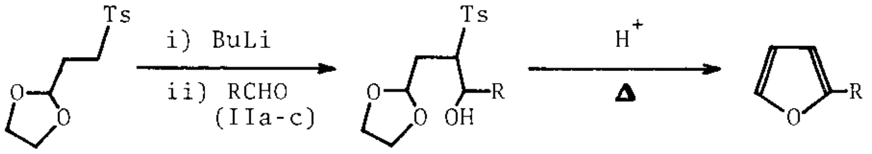
Various 2-substituted and 2,3-disubstituted furans were prepared starting from 3-tosylpropanal ethylene acetal in two and three steps, respectively. Sesquirose furan was readily synthesized by the present method.

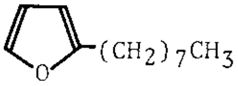
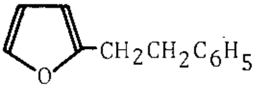
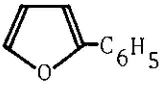
In the previous paper,[1] it was reported that 3-tosylpropanal ethylene acetal (I) is useful starting material for the preparation of 3-substituted furans such as dendrolasin [3-(4,8-dimethyl-3,7-nonadienyl)furan]. In this paper we wish to show that I is also useful for the preparation of 2-substituted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

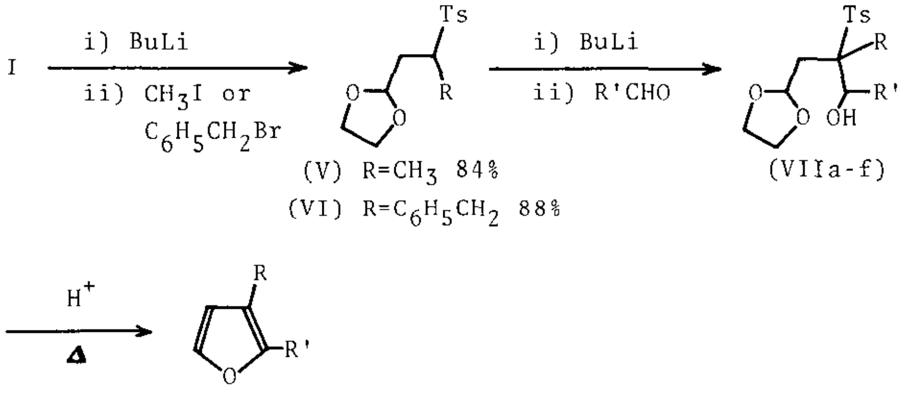


(I) (IIIa-c) (IVa-c)

| RCHO | Isolated yield (%)[a]<br>IVa-c | |
|---|---|---|
| IIa, $CH_3(CH_2)_7CHO$ |  | 64 |
| IIb, $C_6H_5CH_2CH_2CHO$ |  | 66 |
| IIc, $C_6H_5CHO$ |  | 58 |

a) Based on I.

The combination of the synthetic method of 3-substituted furan reported previously[1] 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.



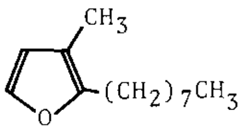
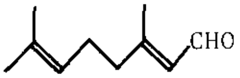
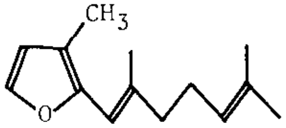
(V) $R=CH_3$ 84%

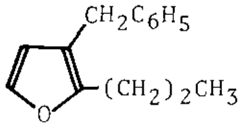
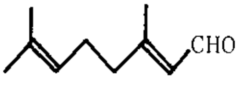
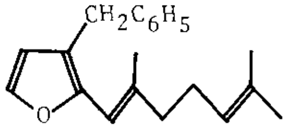
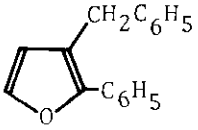
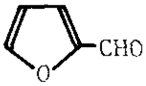
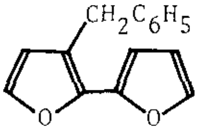
(VI) $R=C_6H_5CH_2$ 88%

(VIIa-f)

(VIIIa-f)

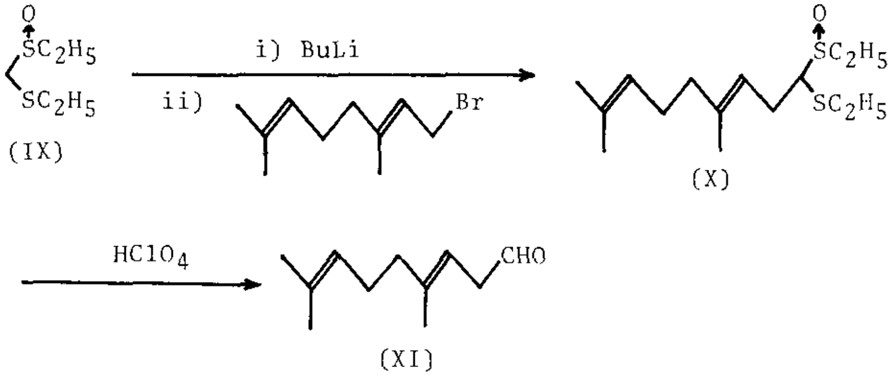
TABLE 2. SYNTHESIS OF 2,3-DISUBSTITUTED FURANS

| | R'CHO | Isolated yield (%)$^{a)}$<br>VIIIa-f | |
|---|---|---|---|
| V | $CH_3(CH_2)_7CHO$ | VIIIa,  | 72 |
| |  | VIIIb,  | 78 |

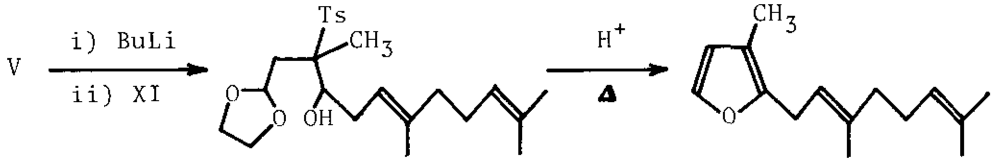
| | | | |
|---|---|---|---|
| VI | $CH_3(CH_2)_2CHO$ | VIIIc,  | 76 |
| |  | VIIId,  | 78 |
| | $C_6H_5CHO$ | VIIIe,  | 70 |
| |  | VIIIf,  | 69 |

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 others[2] according to the following scheme. However, it was



required to use the crude solution[3] 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 follows[4]:



(XII) 61%

(XIII) 64%

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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