Pergamon

Tetrahedron Letters, Vol. 37, No. 26, pp. 4585-4588, 1996

0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)00852-0

Destannylative Acylation of 1-[(2-Methoxyethoxy)methoxy]-2-(phenylsulfonyl)-2-(tributylstannyl)cyclopropane: A Novel Route to 3-Acylfurans

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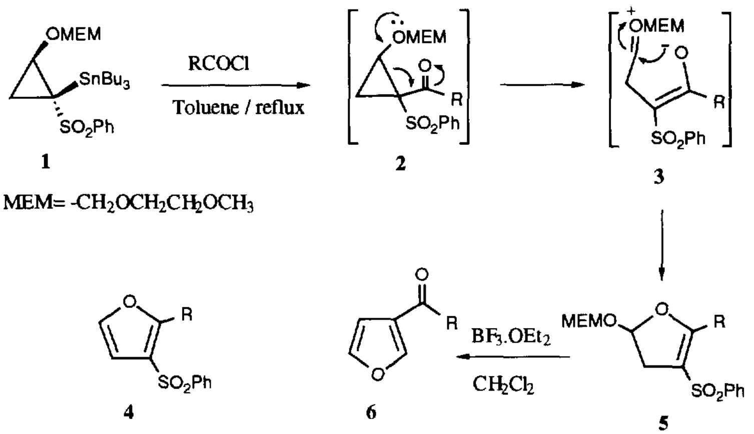
Abstract: Destannylative acylation of 1-[(2-methoxyethoxy)methoxy]-2-(phenylsulfonyl)-2-(tributylstannyl)cyclopropane (**1**) provided dihydrofurans **5** in good yields, which upon treatment with $BF_3.OEt_2$ in CH_2Cl_2 led to the formation of 3-acylfurans **6** in moderate yields. The reaction was proposed to proceed via the intramolecular Prins-type reaction of the oxonium intermediate **7**.

Five-membered oxygenated heterocycles including dihydrofurans and furans are important structural units in organic molecules.[1] Additionally, furans serve as diverse intermediates in synthetic organic chemistry.[1c,2] Consequently, the construction of the furan rings and derivatives continues to be of interest to organic chemists for the development of new synthetic methods.[1e,3] Recently, the synthetic utilization of vicinally donor-acceptor substituted cyclopropanes in organic synthesis has been extensively investigated.[4] We have successfully demonstrated that 1-[(2-methoxethoxy)methoxy]-2-(phenylsulfonyl)cyclopropane and 1,1-diphenoxy-2-(phenylsulfonyl)cyclopropane can be employed as useful three-carbon building blocks for the preparation of α,β-unsaturated aldehydes[5] and esters[6] as well as substituted furans.[7] These results and our recent reports concerning the *stanna*-Pummerer rearrangement of α-stannyl sulfoxides[8] and the destannylative acylation of α-stannyl sulfones[9] led us to study the possibilities of using 1-[(2-methoxyethoxy)methoxy]-2-(phenylsulfonyl)-2-(tributylstannyl)cyclopropane (**1**) as a three-carbon furan annulating agent. In this communication, we describe a new general strategy for the synthesis of 3-acylfurans in which involves destannylative acylation of **1** followed by sequential hydrolysis of the MEM-group and the intramolecular Prins type reaction (or a [3.3]-sigmatropic rearrangement) of the resulting oxonium intermediate as illustrated in Scheme I

Treatment of α–stannyl (phenylsulfonyl)cyclopropane **1**[10] with freshly distilled benzoyl chloride (2 equiv) in refluxing toluene for 5 h afforded the expected dihydrofuran **5a** (R = Ph) in 83% yield after workup with aqueous potassium fluoride followed by chromatography. The reaction of **1** with other acid chlorides under the same conditions provided good yields of the products of type **5** (Table 1). Scheme I shows a mechanism for the formation of the dihydrofuran **5**. Thus it is anticipated that the initially formed donor-acceptor substituted cyclopropane **2**, occurred by destannylative acylation of **1**, would undergo ring-opening reaction to afford the zwitterion intermediate **3**. Cyclization of **3** was then expected to lead to **5**.



Scheme I

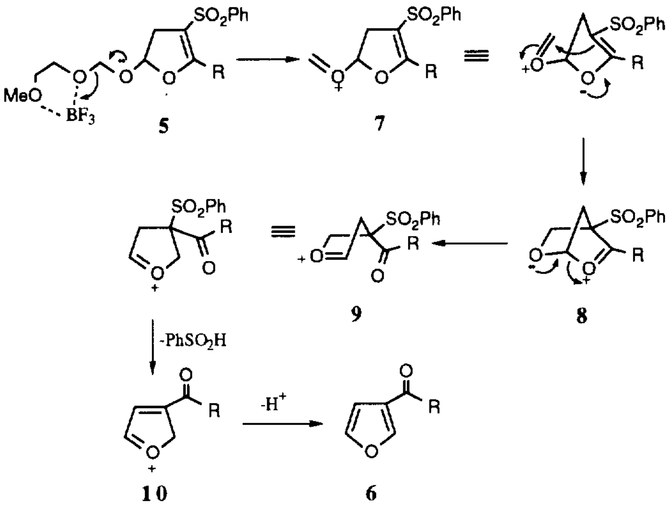
Table 1. Preparation of dihydrofurans **5** and 3-acylfurans **6**.

RCOCl	Dihydrofuran 5 (%)[a]	3-Acylfuran 6 (%)[a]
PhCOCl	**5a**, R= Ph (83)	**6a**, R= Ph (45%)
p-$CH_3C_6H_4COCl$	**5b**, R= *p*-$CH_3C_6H_4$ (74%)	**6b**, R= *p*-$CH_3C_6H_4$ (44%)
t-BuCOCl	**5c**, R= *t*-Bu (72%)	**6c**, R= *t*-Bu (34%)
n-BuCOCl	**5d**, R= *n*-Bu (70%)	**6d**, R= *n*-Bu (30%)
CH_3COCl	**5e**, R= CH_3 (77%)	---[b]
i-PrCOCl	**5f**, R= *i*-Pr (72%)	---[b]
n-PrCOCl	**5g**, R= *n*-Pr (70%)	---[b]
	5h[c], R= 2-Furyl (64%)	**6e**, **R**= 2-Furyl (62%)

a) Yields were of isolated products and unoptimized. All products were characterized by spectroscopic methods (IR, ^1H NMR, MS and elemental analysis).
b) The reactions were not performed.
c) **5h** (64 %) was prepared by reacting the lithio derivative generated from 1-[(2-methoxethoxy)methoxy]-2-(phenylsulfonyl)cyclopropane (n-BuLi , -78 °C) with 2-furoyl imidazole at -78 °C in THF.

Our extensive investigation for making efforts to accomplish the preparation of furan **4** from **5** under various conditions was disappointingly unsuccessful. Fortunately, treatment of **5a** with $BF_3.OEt_2$ (1.2 equiv) in dry dichloromethane at -78 °C followed by slowly warming up to room temperature within 12-14 h provided a crystalline product (mp 37-38 °C) which showed a strong IR-absorption peak at 1650 cm^{-1} due to the carbonyl group and exhibited the molecular ion peak in the MS-spectrum at m/e 172. The ^1H NMR (60 MHz) spectrum of this product revealed the characteristic peaks of furan protons at δ 6.89 (dd, *J*= 1,2 Hz, 1H) and 7.51-8.15 (m, 2H). It could be concluded from the data above that this product was 3-benzoylfuran **6a** (R= Ph; 45% yield). This conclusion was finally confirmed by the elemental analysis. In order to test the generality of this useful hydrolytic rearrangement, investigation was extended to dihydrofurans **5b**, **5c**, **5d**, and **5h**. As expected, the reactions of these dihydrofurans with $BF_3.OEt_2$ under the standard conditions furnished the desired 3-acylfurans **6b**, **6c**, **6d** and **6e** in moderate yields (Table 1). We believe that the actual yield is considerably higher (judging by thin-layer chromatography) since loss occurred during isolation due to the volatility of the products.

A mechanism for the formation of **6** from **5** could be envisaged as depicted in Scheme II. Complexation of the MEM-moiety of **5** with $BF_3.OEt_2$ results in cleavage to give an oxonium ion intermediate **7** which undergoes an intramolecular Prins-type reaction [11] to afford an oxonium ion **8** followed by ring cleavage to **9**. The oxonium ion intermediate **9** may arise from a [3.3]-sigmatropic type rearrangement of **7**. Elimination of benzenesulfinic acid followed by aromatization of the oxonium ion **9** yields 3-acylfuran **6**.



Scheme II

In summary, our method described herein provides a new useful, general entry for the synthesis of 3-acylfurans[12] by employing the α–stannyl (phenylsulfonyl)cyclopropane **1**. Extension of this novel hydrolytic rearrangement is in progress and the results will be reported in due course.

Acknowledgement. Generous financial support for this research by grants from the Thailand Toray Science Foundation and the Faculty of Science, Mahidol University is gratefully acknowledged.

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10. The starting compound **1** could be readily obtained as a colorless liquid in 59% yield by reacting the lithio derivative derived from 1-[(2-methoxethoxy)methoxy]-2-(phenylsulfonyl)cyclopropane (*n*-BuLi, THF, -78 °C) with tributyltin chloride at -78 °C to room temperature (overnight).
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(*Received in UK* 15 *April* 1996; *revised* 30 *April* 1996; *accepted* 3 *May* 1996)