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

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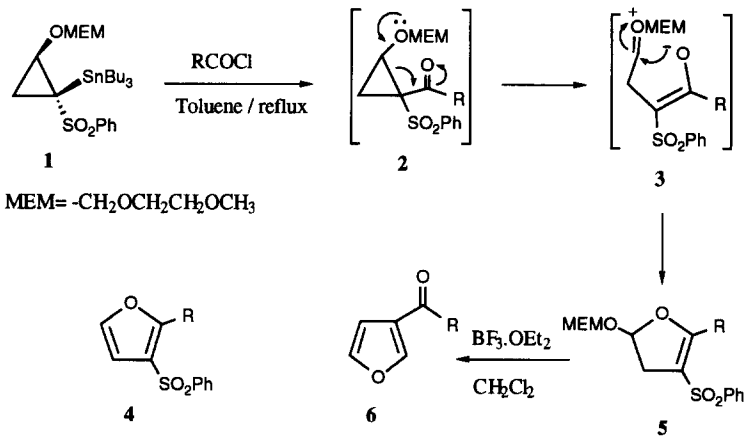
Abstract: Destannylative acylation of 1-[(2-methoxyethoxy)methoxy]-2-(phenylsulfonyl)-2-(tributylstannyl)cyclopropane (**1**) provided dihydrofurans **5** in good yields, which upon treatment with $BF_3.OEt_2$ in CH_2Cl_2 led to the formation of 3-acylfurans **6** in moderate yields. The reaction was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

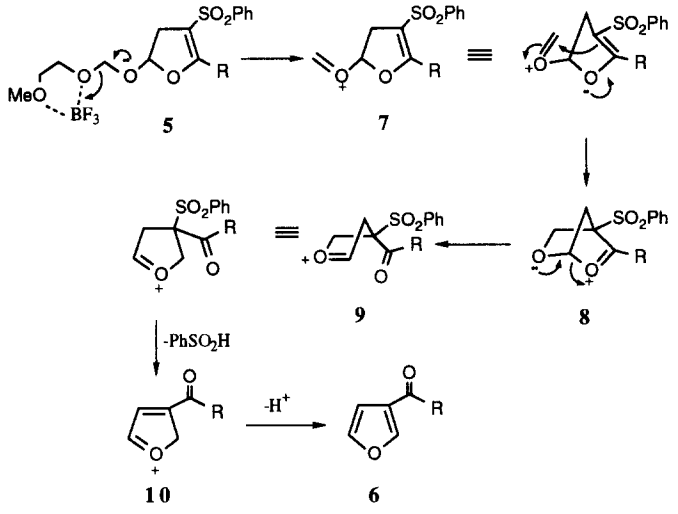
RCOCl	Dihydrofuran 5 (%)[a]	3-Acylfuran 6 (%)[a]
PhCOCl	**5a**, R= Ph (83)	**6a**, R= Ph (45%)
p-$CH_3C_6H_4COCl$	**5b**, R= *p*-$CH_3C_6H_4$ (74%)	**6b**, R= *p*-$CH_3C_6H_4$ (44%)
t-BuCOCl	**5c**, R= *t*-Bu (72%)	**6c**, R= *t*-Bu (34%)
n-BuCOCl	**5d**, R= *n*-Bu (70%)	**6d**, R= *n*-Bu (30%)
CH_3COCl	**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.

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REFERENCES

1. (a) Donnelly, D.M.X.; Meegan, M.J. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A.R., Reese, C.W., Eds.; Pergamon Press: Oxford, **1984**; Vol. 4, Part 3, p 657. (b) Katritzky, A.R. *Adv. Heterocycl. Chem.* **1982**, *30*, 167. (c) Lipshutz, B.H. *Chem. Rev.* **1986**, *86*, 795. (d) Bolvin, T.L.B. *Tetrahedron* **1987**, *43*, 3309. (e) Padwa, A.; Murphree, S.S. *Org. Prep. Proc.* **1991**, *23*, 545.
2. Piancatelli, G.; D'Auria, M.; D'Onofrio, F. *Synthesis* **1994**, 867.
3. See for examples, (a) Kratritzky, A.R.; Li, J. *J. Org. Chem.* **1995**, *60*, 638. (b) Trost, B.M.; Flygare, J.A. *ibid.* **1994**, *59*. 1078. (c) Dulce're, J.P.; Baret, N.; Rodriguez, J. *J. Chem. Soc. Chem. Commun.* **1994**, 303. (d) Aurrecoechea, J.M.; Solay-Ispizua, M. *Heterocycles* **1994**, *37*, 223. (e) Marshall, J.A.; Bennett, C.E. *J. Org. Chem.* **1994**, *59*, 6110 and references cited therein. (f) Bhat, L.; Ila, H.; Junjappa, H. *J. Chem. Soc. Perkin Trans I*, **1994**, 1749. (g) Kratritzky, A.R.; Li, J.; Gordeev, M.F. *J. Org. Chem.* **1993**, *58*, 3038. (h) Craig, D.; Etheridge, C.J. *Tetrahedron Lett.* **1993**, *34*, 7487. (i) Frey, H. *Synlett* **1993**, 905. (j) Tiecco, M.; Testafferi, L.; Tingoli, M.; Marini, F. *Synlett* **1994**, 373. (k) Gray, M.; Parsons, P.J.; Neary, A.P. *Synlett* **1992**, 597. (l) Chan, W.H.; Lee, A.W.M.; Chan, E.T.T. *J. Chem. Soc. Perkin Trans I* **1992**, 945. (m) Shu, H.G.; Shiu, L.H.; Wang, S.L.; Lee, G.H.; Peng, S.M.; Liu, R.S. *J. Am. Chem. Soc.* **1996**, *118*, 530 and references cited therein. (n) Hashmi, A.S.K. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1581. (o) Trost, B.M.; McIntosh, M.C. *J. Am. Chem. Soc.***1995**, *117*, 7255. (p) McDonald, F.E.; Schultz, C.C. *ibid.* **1994**, *116*, 9363. (q) Marson, C.M.; Harper, S.; Wrigglesworth, R. *J. Chem. Soc. Chem. Commun.* **1994**, 1879. (r) Ji, J.; Lu, X. *ibid.* **1993**, 764. (s) O' Connor, J. M.; Ji, H.L.; Rheingold, A.L. *J. Am. Chem. Soc.* **1993**, *115*, 9846.
4. (a) Reissis, H.-U. *Top. Curr. Chem.* **1988**, *144*, 73. (b) Horiguchi, Y.; Suehiro, I.; Sasaki, A.; Kuwajima, I. *Tetrahedron Lett.* **1993**, *34*, 6077. (c) Saigo, K.; Shimada, S.; Hashimoto, Y.; Hasegawa, M. *Chem. Lett.* **1989**, 1293: Saigo, K.; Shimada, S.; Shibasaki, T.; Hasegawa, M. *Chem. Lett.* **1990**, 1093: Saigo, K.; Shimada, S.; Hasegawa, M. *Chem. Lett.* **1990**, 1101: Shimada, S.; Saigo, K.; Hashimoto, Y.; Maekawa, Y.; Yamashita, T.; Yamamoto, T.; Hasegawa, M. *Chem. Lett.* **1991**, 1475. (d) Horiguchi, Y.; Suehiro, I.; Sasaki, A.; Kuwajima, I. *Tetrahedron Lett.* **1993**, *34*, 6077. (e) Davies, H.M.L.; Hu, B. *J. Org. Chem.* **1992**, *57*, 3186, 4309. (f) Lee, P.H.; Kim, J.S.; Kim, Y.C.; Kim, S. *Tetrahedron Lett.* **1993**, *34*, 7583. (g) Barluenga, J.; Tomas, M.; Lo'pez-Pelegrin, J.A.; Rubio, E. *J. Chem. Soc. Chem. Commun.* **1995**, 665. (h) Marino, J. P.; Long, J. K.; *J. Am. Chem. Soc.* **1988**, *110*, 7916. (i) Pirrung, M.; Zhang, J.; Lackey, K.; Sternbach, D.D.; Brown, F. *J. Org. Chem.* **1995**, *60*, 2112 and references cited therein. (j) Lund, E.A.; Kennedy, I.A.; Fallis, A.G. *Tetrahedron Lett.* **1993**, *34*, 6841.
5 Pohmakotr, M.; Pisutjaroenpong, S. *Tetrahedron Lett.* **1985**, *26*, 3613.
6. Pohmakotr, M.; Ratchataphusit, J. *Tetrahedron* **1993**, *49*, 6473.
7. Pohmakotr, M.; Takampon, A.; Ratchataphusit, J. *Tetrahedron* **1996**, *52*, in press.
8. (a) Pohmakotr, M.; Sithikanchanakul, S.; Khosavanna, S. *Tetrahedron* **1993**, *49*, 6651. (b) Pohmakotr, M.; Sithikanchanakul, S. *Tetrahedron Lett.* **1989**, *30*, 6773.
9. Pohmakotr, M.; Khosavanna, S. *Tetrahedron* **1993**, *49*, 6483.
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).
11. (a) For a review, see: Snider, B.B. "The Prins and Carbonyl Ene Reactions", In *Comprehensive Organic Synthesis*, Trost, B.M., Ed.; Pergamon: Oxford, **1991**; *Vol. 2*, p 527. (b) Overman, L.E.; Castaneda, A.; Blumenkopf, T.A. *J. Am. Chem. Soc.* **1986**, *108*, 1303. (c) Hopkins, M.H.; Overman, L.E. *ibid.* **1987**, *109*, 4748. (d) Blumenkopf, T.A.; Bratz, M.; Castaneda, A.; Look, G.C.; Overman, L.E.; Rodiguez, D.; Thompson, A.S. *ibid.* **1990**, *112*, 4386. (e) Blumenkopf, T.A.; Look, G.C.; Overman, L.E. *ibid.* **1990**, *112*, 4399. (f) Bratz, M.; Bullock, W.H.; Overman, L.E.; Takemoto, T. *ibid.* **1995**, *117*, 5958.
12. (a) Inomata, K.; Sumita, M.; Kotake, H. *Chem. Lett.* **1979**, 109. (b) Bailey, T. R. *Synthesis* **1991**, 242. (c) Cahiez, G.; Chavant, P.Y.; Metais, E. *Tetrahedron Lett.* **1992**, *33*, 5245. (d) Satoh, T.; Itaya, T.; Okuro, K,; Miura, M.; Nomura, M. *J. Org. Chem.* **1995**, *60*, 7267.

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