# Synthesis of 4-Alkylfuran-2-acetates and 4-Alkylthiophene-2-acetates Using 2-(Chloromethyl)-3-(tributylstannyl)propene†

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Furanoid units are found in many natural products[1] and biologically active compounds.[2] Furans also served as synthetic intermediates[3] and building blocks in material science.[4] Functionalization of available furan precursors and formation of new furan rings by cyclization of acyclic precursors[5] are the two fundamental approaches used to prepare substituted furans. Introduction of substituents into a furan ring has been exclusively investigated. Nevertheless, the preference for lithiation[6] and electrophilic addition[7] at C-2 or C-5 positions of furan rings makes the synthesis of some furans, especially for 2,4-disubstituted furans, difficult.[8] Cyclization method looks suitable for some specific compounds. However, to synthesize a series of compounds, a lengthy sequential reactions has to be carried out for each individual member of the series.

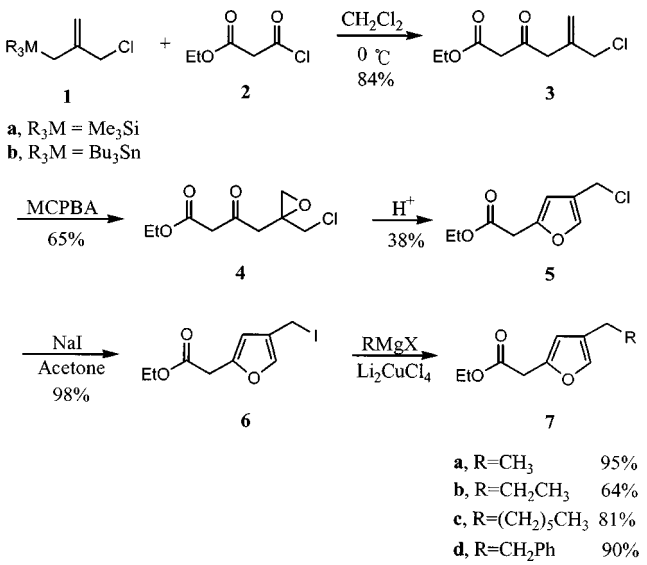
For some projects, we had to prepare a series of 4-alkyl substituted furan-2-acetic acids, the synthesis of which is rare in the literature. In a patent, 4-methylfuran-2-acetic acid was prepared from 2-formyl-4-methylfuran by a 5-step reaction sequence.[9] 2-Formyl-4-methylfuran, in turn, was prepared as a minor product (less than 1/15 of total formylated products) from Vielsmeir-Haack-Arnold formylation of 3-methylfuran. Undesired 2-formyl-3-methylfuran was the major product. In another report, 4-methyl- and 4-benzylfuran-2-acetic acids were prepared by cyclizing acylic precursors. They were obtained in less than 6% overall yield from the individual 6-step reaction sequence starting from $\alpha$-chloroketones.[10] Both procedures suffer from lengthy reaction sequences and low yields.

Here we wish to report an easy access to a variety of 4-alkylfuran- and 4-alkylthiophene-2-acetic acids *via* cyclization of an acyclic precursor followed by side chain modification. $\beta,\gamma$-Epoxycarbonyl compounds were proved by us to be useful precursors of furans[11] and thiophenes.[12] The whole synthetic sequence is denoted in Scheme 1.

Ethoxycarbonyl-attached $\beta,\gamma$-epoxycarbonyl compound **4**, a key intermediate for furan **5**, can be obtained by epoxidation of the allylic ketone **3**. Most allylic ketones were successfully prepared from the Lewis acid-mediated reactions of allylsilanes with acid chlorides.[11,12a] If the same method was utilized, the reaction of ethyl malonyl chloride with (2-chloromethyl)-3-(trimethylsilyl)propene (**1a**)[13] should have produced the allylic ketone **3**. Unfortunately, all attempts failed, regardless of the reaction conditions and the Lewis acids employed ($TiCl_4$, $BF_3$ etherate, etc).

On the contrary, the reaction of the allylstannane, (2-chloromethyl)-3-(tributylstannyl)propene (**1b**), with ethyl malonyl chloride (**2**) proceeded smoothly and in good yield at 0 °C even without any catalytic activation to afford allylic ketone **3**. Though allylstannanes are more reactive than allylsilanes toward several electrophiles such as acid chlorides and aldehydes,[14] allylstannanes normally couple with acid chlorides in the presence of palladium catalyst or Lewis acid.[15] Due to the presence of electron-withdrawing ethoxycarbonyl group, ethyl malonyl chloride is considerably more reactive than simple acid chlorides. This explains why the reaction of allylstannane **1b** with ethyl malonyl chloride occurs smoothly.

Epoxidation of **3** with 2.5 equivalents of *m*-chloroperoxybenzoic acid (MCPBA) in dichloromethane at 0 °C ~ ambient temperature gave the $\beta,\gamma$-epoxycarbonyl compound **4** in 65% yield after purification ($SiO_2$, $CH_2Cl_2$). When a benzene solution of the epoxide **4** was refluxed in the presence of a catalytic amount of *p*-toluenesulfonic acid, ethyl 4-




**Scheme 1**

†This paper is dedicated to the late Professor Sang Chul Shim for his distinguished achievements in chemistry.

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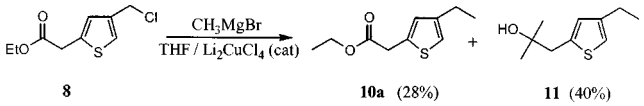
(chloromethyl)furan-2-acetate (**5**) was produced. The chloride **5** was transformed to the iodide **6** by halide exchange reaction using NaI in acetone. The modification of iodomethyl group in **6** were achieved by treating with Grignard reagents in the presence of a catalytic amount of the Kochi's catalyst ($Li_2CuCl_4$).[16] Ethyl esters of furan-2-acetic acid of different alkyl side chain (**7**) were obtained in good yields. By introducing the alkyl side chain in the last step, various alkyl substituted furans can be synthesized easily without repeating the whole 5-step sequence.

The synthesis of 4-alkylthiophene-2-acetic acids also appears rare in spite of their biological activities. 4-Methylthiophene-2-acetic acid having both anti-inflammatory and analgesic activity was prepared from 4-methylthiophene-2-carboxylic acid by the Arndt-Eistert synthesis.[17] Saponification and decarboxylation of the adducts prepared from manganese (III)-induced addition of ethyl methanetricarboxylate to 3-methyl-thiophene produce a mixture of 3-methylthiophene-2-acetic acid and 4-methylthiophene-2-acetic acid in 1:2 ratio.[18]

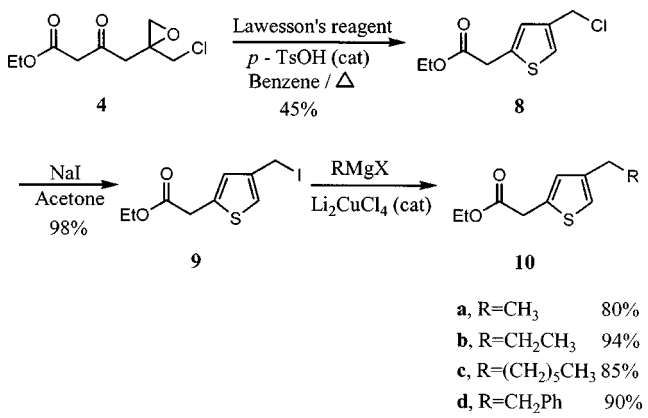
The synthetic scheme for furan derivatives can be slightly modified for the general synthesis of 4-alkylthiophene-2-acetic acids. It differs from the synthesis of furan derivative, only in the fourth step in Scheme 1. The use of Lawesson's reagent enables the cyclization to thiophene derivatives instead of furan (Scheme 2). In the reaction with Lawesson's reagent in the presence of a catalytic amount of *p*-toluenesulfonic acid, the epoxide **4** was transformed to ethyl 4-(chloromethyl)thiophene-2-acetate (**8**).[12] To avoid the cyclization to furan ring, *p*-toluenesulfonic acid must be added only after complete stirring with Lawesson's reagent. If *p*-toluenesulfonic acid was added prior to Lawesson's reagent, the furan **5** was formed in some extent along with the thiophene **8**.

Ethyl 4-(iodomethyl)thiophene-2-acetate (**9**) was obtained from transhalogenation of the chloride **8** with NaI in acetone. Ethyl esters of 4-alkylthiophene-2-acetic acid **10** were also prepared similarly from the reactions of the iodide **9** with Grignard reagents in the presence of a catalytic amount of $Li_2CuCl_4$.

The chloromethyl group has to be converted to the more reactive iodomethyl group. When the cross-coupling was performed with the chloride **8** omitting the halogen exchange, the cross coupled product **10a** was obtained in a mere 28% yield, along with 40% of unwanted **11**.




In summary, the present reaction sequence provides a facile and regioselective synthesis of various 4-alkylfuran-2-acetates and 4-alkylthiophene-2-acetates. The sequential steps are fewer and the yields are higher than any previous reports. A more important feature of our procedure is that alkyl substituent at 4-position can be easily modified in the last step, by the copper (II) catalized cross-coupling reactions of the iodide with Grignard reagents.




**Scheme 2**

## Experimental Section

$^1$H-NMR spectra were recorded on a Varian Gemini-200 (200 MHz) and Varian Inova (500 MHz) spectrometer using chloroform as an internal standard. The instruments were also used for recording $^{13}$C NMR spectra in $CDCl_3$ as the solvent and internal reference. GC-MS analyses were performed with a Kratos Profile HV-3 spectrometer using a HP-5 column.

**2-(Chloromethyl)-3-(tributylstannyl)propene (1b)**. To a carbon tetrachloride (100 mL) solution of 2-(tributylstannylmethyl)-2-propen-1-ol (14.5 g, 40.0 mmol),[19] were added triethylamine (4.86 g, 48.0 mmol) and triphenylphosphine (12.6 g, 48.0 mmol). The mixture was refluxed for 18 h. After being cooled to room temperature petroleum ether (100 mL) was added. The combined organic phase was washed with brine, concentrated, and chromatographed on silica gel (hexane : ether = 15 : 1) to afford 13.9 g (91%) of **1b**. $^1$H-NMR $\delta$ 0.80-1.56 (27H, m), 1.88 (2H, s), 3.95 (2H, s), 4.71 (1H, s), 4.83 (1H, s); $^{13}$C NMR $\delta$ 9.7, 13.7, 15.8, 27.3, 29.0, 50.1, 109.8, 145.7.

**Preparation of allylic ketone 3 from the reaction of allylstannane 1b with ethyl malonyl chloride (2)**. Ethyl malonyl chloride (**2**, 3.46 g, 23.0 mmol) and 2-(chloromethyl)-3-(tributylstannyl)propene (**1b**, 10.13 g, 26.7 mmol) were dissolved in dichloromethane (25 mL), and stirred at 0 $^o$C for 3 h. The reaction was quenched with sat. sodium bicarbonate solution and an aqueous layer was extracted with dichloromethane. The combined organic extract was washed with brine, dried over $Na_2SO_4$, and concentrated. The residue was chromatographed on silica gel (hexane : ether = 3 : 1) to give 3.95 g (84%) of allylic ketone **3**. $^1$H-NMR $\delta$ 1.27 (3H, t, $J$ = 7.3 Hz), 3.45 (2H, s), 3.49 (2H, s), 4.10 (2H, s), 4.15 (2H, q, $J$ = 7.3 Hz), 5.07 (1H, s), 5.34 (1H, s); $^{13}$C NMR $\delta$ 14.0, 46.7, 47.8, 48.8, 61.5, 119.5, 138.0, 166.8, 199.9.

**Preparation of $\beta,\gamma$-epoxycarbonyl compound 4 by oxidation of allylic ketone 3 with MCPBA**. *m*-Chloroperoxybenzoic acid (MCPBA, 50%, 2.40 g, 6.95 mmol) was

added to a dichloromethane (10 mL) solution of allylic ketone **3** (0.71 g, 3.47 mmol) and stirred for 24 h at room temperature. The mixture was washed with sat. aq $NaHCO_3$ solution, and the aqueous solution was extracted with dichloromethane. The combined organic extracts were dried ($Na_2SO_4$), concentrated, and chromatographed on silica gel (hexane : ether = 2 : 1) to give $\beta,\gamma$-epoxycarbonyl compound **4** (0.50 g, 65%). $^1$H-NMR 1.27 (3H, t, *J* = 7.3 Hz), 2.87 (1H, d, *J* = 4.2 Hz), 2.94 (1H, d, *J* = 4.2 Hz), 3.40 (1H, d, *J* = 19.4 Hz), 3.49 (2H, s), 3.54 (1H, d, *J* = 11.7 Hz), 3.73 (1H, d, *J* = 19.4 Hz), 3.84 (1H, d, *J* = 19.4 Hz), 4.18 (2H, q, *J* = 7.3 Hz); $^{13}$C NMR $\delta$ 14.1, 44.7, 45.0, 48.2, 49.7, 52.7, 61.7, 64.2, 166.7, 199.0.

**Synthesis of ethyl 4-(chloromethyl)furan-2-acetate (5)**. A benzene (5 mL) solution of $\beta,\gamma$-epoxycarbonyl compound **4** (0.50 g, 2.27 mmol) and *p*-toluenesulfonic acid (5 mg) was refluxed for 1 h. The reaction mixture was partitioned between sat. aq $NH_4Cl$ solution and ether, and the aqueous layer was separated and extracted with ether. The combined organic phases were washed with water and dried over $Na_2SO_4$, filtered, concentrated and chromatographed (silica gel, hexane : ether = 15 : 1) to afford 175 mg (38%) of ethyl 4-(chloromethyl)furan-2-acetate (**5**). $^1$H-NMR $\delta$ 1.26 (3H, t, *J* = 7.3 Hz), 3.65 (2H, s), 4.18 (2H, q, *J* = 7.3 Hz), 4.44 (2H, s), 6.30 (1H, s), 7.38 (1H, s); $^{13}$C NMR $\delta$ 14.1, 34.2, 37.2, 61.3, 108.8, 123.3, 140.1, 149.2, 169.1.

**Copper(II) catalyzed cross-coupling reaction of the iodide 6 with Grignard reagents-Synthesis of ethyl 4-alkylfuran-2-acetate 7**. The chloride **5** (175 mg, 0.87 mmol), NaI (150 mg, 1.00 mmol), and 9 mL of dry acetone were mixed and the resulting heterogeneous mixture was stirred for 1 day at room temperature and extracted with ether. After removal of acetone, the residue was treated with aqueous $Na_2S_2O_3$ solution. The organic layer was dried ($Na_2SO_4$) and concentrated to give 250 mg (98 %) of **6**. $^1$H-NMR $\delta$ 1.26 (3H, t, *J* = 7.3 Hz), 3.62 (2H, s), 4.16 (2H, q, *J* = 9.3 Hz), 4.22 (2H, s), 6.25 (1H, s), 7.40 (1H, s).

Dilithium tetrachlorocuprate ($Li_2CuCl_4$) solution was prepared by reacting lithium chloride (85 mg, 2.0 mmol) and copper (II) chloride (99 mg, 1.0 mmol) in THF (10 mL). To a THF (3 mL) solution of the iodide **6** (250 mg, 0.85 mmol) containing $Li_2CuCl_4$ (0.1 M THF solution, 0.5 mL, 0.05 mmol), methylmagnesium bromide (1.0 mmol, 0.34 mL of 3M solution) was slowly added at -78 $^o$C. After stirring 1 h at -78 $^o$C, the reaction mixture was poured into ice-water and extracted with ether. The organic extract was dried ($Na_2SO_4$), concentrated, and chromatographed on silica gel (hexane : ether = 15 : 1) to give **7a** (147 mg, 95%).

The compounds **7b-7d** were similarly prepared.

**7a**: $^1$H-NMR $\delta$ 1.15 (3H, t, *J* = 7.3 Hz), 1.26 (3H, t, *J* = 7.3 Hz), 2.40 (2H, q, *J* = 7.3 Hz), 3.62 (2H, s), 4.18 (2H, q, *J* = 7.3 Hz), 6.12 (1H, s), 7.12 (1H, s); $^{13}$C NMR $\delta$ 14.1, 18.2, 34.3, 61.1, 109.3, 127.9, 137.7, 147.7, 169.6; MS m/z 182 ($M^+$, 34), 109 (100%). **7b**: $^1$H-NMR $\delta$ 0.92 (3H, t, *J* = 7.3 Hz), 1.26 (3H, t, *J* = 7.0 Hz), 1.55 (2H, q, *J* = 7.0 Hz), 2.34 (2H, t, *J* = 7.3 Hz), 3.62 (2H, s), 4.19 (2H, q, *J* = 7.3 Hz), 6.09 (1H, s), 7.11 (1H, s); $^{13}$C NMR $\delta$ 13.9, 14.2, 23.0, 27.0, 34.3, 61.1, 109.6, 126.2, 138.2, 147.6, 169.6; MS m/z 196 ($M^+$, 28), 168 (21), 123 (100%). **7c**: $^1$H-NMR $\delta$ 0.87 (3H, t, *J* = 7.0 Hz), 1.23-1.56 (13H, m), 2.35 (2H, t, *J* = 7.3 Hz), 7.11 (1H, s); $^{13}$C NMR $\delta$ 14.1, 22.7, 24.9, 29.1, 29.3, 29.8, 31.8, 34.3, 61.1, 109.6, 126.4, 138.1, 147.6, 169.6; MS m/z 252 ($M^+$, 10), 181 (17), 179 (12), 168 (100%). **7d**: $^1$H-NMR $\delta$ 1.27 (3H, t, *J* = 7.0 Hz), 2.68 (2H, t, *J* = 8.8 Hz), 2.85 (2H, t, *J* = 9.5 Hz), 3.62 (1H, s), 4.18 (2H, q, *J* = 7.0 Hz), 6.10 (1H, s), 7.10 (1H, s), 7.16-7.31 (5H, m); $^{13}$C NMR $\delta$ 14.2, 26.9, 34.3, 36.2, 61.2, 109.5, 125.5, 125.9, 128.3, 128.4, 138.4, 141.7, 147.8, 169.5; MS m/z 258 ($M^+$, 23), 185 (20), 167 (100), 91 (51), 77 (5%).

**Synthesis of ethyl 4-(chloromethyl)thiophene-2-acetate (8)**. Lawesson's reagent (1.1 g, 2.7 mmol) was added to a benzene (7 mL) solution of epoxycarbonyl compound **4** (0.50 g , 2.27 mmol) and the mixture was slowly heated to reflux. After 30 minutes, *p*-toluenesulfonic acid (5 mg) was added. After an hour reflux, the reaction mixture was partitioned between sat. aq $NaHCO_3$ and ether, and the aqueous layer was extracted with ether. The combined organic extracts were washed with brine and dried over anhydrous $Na_2SO_4$. Purification by chromatography on silica gel (hexane : ether = 30 : 1) gave 221 mg (45%) of **8**. $^1$H-NMR $\delta$ 1.28 (3H, t, *J* = 7.0 Hz), 3.79 (2H, s), 4.19 (2H, q, *J* = 7.0 Hz), 4.54 (2H, s), 6.96 (1H, s), 7.16 (1H, s); $^{13}$C NMR $\delta$ 14.1, 35.6, 40.9, 61.3, 123.7, 127.2, 136.7, 137.6, 170.1.

**Synthesis of ethyl 4-alkylthiophene-2-acetates (10)**. Chloride **8** (220 mg, 1.0 mmol), NaI (165 mg, 1.1 mmol) and 9 ml of dry acetone were mixed and stirred for 1 day at room temperature. Acetone was evaporated and the residue was treated with aqueous $Na_2S_2O_3$ solution. The product was extracted with ether. The organic phase was dried ($Na_2SO_4$) and concentrated to give 301 mg (98%) of **9**. To a THF (5 mL) solution of the iodide **9** (301 mg, 0.98 mmol) containing $Li_2CuCl_4$-THF solution (0.1 M, 0.5 mL) methylmagnesium bromide (1.0 mmol, 0.33 mL of 3 M solution) was slowly added at -78 $^o$C. After 1 h stirring at -78 $^o$C, the reaction mixture was poured into ice-water and extracted with ether. The organic extracts were dried ($Na_2SO_4$), concentrated, and chromatographed on silica gel (hexane : ether = 15 : 1) to afford 153 mg (80%) of **10a**. The compounds **10b-10d** were similarly prepared.

**10a**: $^1$H-NMR $\delta$ 1.16-1.30 (6H, m), 2.61 (2H, q, *J* = 7.3 Hz), 3.76 (2H, s), 4.18 (2H, q, *J* = 7.0 Hz), 6.79 (2H, s); $^{13}$C NMR $\delta$ 14.2, 14.5, 23.6, 35.7, 61.2, 118.8, 127.9, 135.0, 144.4, 170.6; MS m/z 198 ($M^+$, 26), 125 (100%). **10b**: $^1$H-NMR $\delta$ 0.93 (3H, t, *J* = 7.4 Hz), 1.27 (3H, t, *J* = 7.0 Hz), 1.52-1.67 (2H, m), 2.52 (2H, t, *J* = 7.2 Hz), 3.76 (2H, s), 4.18 (2H, q, *J* = 7.0 Hz), 6.77 (1H, s), 6.78 (1H, s); $^{13}$C NMR $\delta$ 13.9, 14.1, 23.5, 32.5, 35.7, 61.1, 119.5, 128.2, 134.8, 142.8, 170.6; MS m/z 212 ($M^+$, 37), 184 (30), 139 (100), 111 (15%). **10c**: $^1$H-NMR $\delta$ 0.87 (3H, t, *J* = 6.6 Hz), 1.24-1.59 (3H, m), 2.54 (2H, q, *J* = 7.4 Hz), 3.76 (2H, s), 4.18 (2H, q, *J* = 7.0 Hz), 6.77 (2H, s); $^{13}$C NMR $\delta$ 14.1, 14.1, 22.6, 29.1, 29.3, 30.3, 30.5, 31.8, 35.7, 61.1, 119.3, 128.2, 134.8, 143.0, 170.6; MS m/z 268 ($M^+$, 12), 184 (100%). **10d**: $^1$H-NMR $\delta$ 1.28 (3H, t, *J* = 7.4 Hz), 2.90 (4H, s), 3.77 (2H, s), 4.19 (2H,

q, $J$ = 7.4 Hz), 6.79 (2H, s), 7.16-7.29 (5H, m); $^{13}$C NMR $\delta$ 14.1, 32.4, 35.7, 36.7, 61.2, 119.9, 125.9, 128.1, 128.3, 128.4, 135.0, 141.7, 141.9, 170.5; MS m/z 274 ($M^+$, 93), 197 (33), 91 (100), 77 (67%).

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