HETEROCYCLES, Vol. 75, No. 12, 2008, pp. 2973 - 2980. © The Japan Institute of Heterocyclic Chemistry
Received, 3rd June, 2008, Accepted, 14th July, 2008, Published online, 17th July, 2008. COM-08-11458

A SIMPLE AND PRACTICAL SYNTHESIS OF METHYL BENZO[*b*]FURAN-3-CARBOXYLATES

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Abstract – A simple and practical two-step procedure for the preparation of 2-unsubstituted 1-benzo[*b*]furan-3-carboxylic acid methyl esters is described. The procedure uses the copper-catalyzed intramolecular C–O bond formation and provides an efficient route to the title compounds in good to excellent yields.

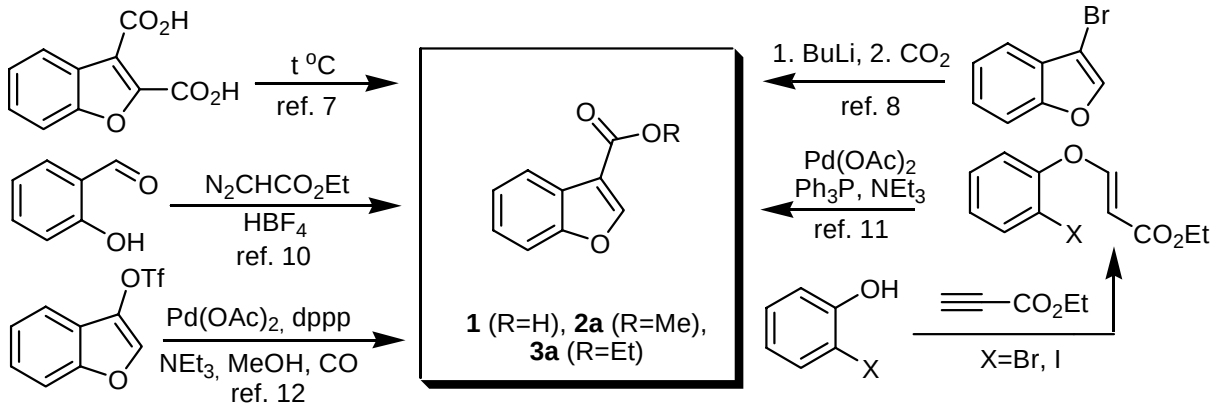
INTRODUCTION

Benzo[*b*]furan derivatives are an important class of heterocyclic compounds widely presented in nature.[1] Substituted benzo[*b*]furans are known to possess important biological properties and find application as pharmaceuticals, agricultural chemicals and in other fields of chemistry.[2] For this reason, numerous methods for the synthesis of benzo[*b*]furan derivatives[1-3] have been developed over the years and the majority of methods for selectively constructing benzo[*b*]furan ring system includes the transition metal-catalyzed transformations.[4]

1-Benzo[*b*]furan-3-carboxylic acids (**1**) and their derivatives have found significant use as building blocks for the synthesis of pharmaceutically important molecules.[5] Moreover, lithium 2-lithiobenzo[*b*]furan-3-carboxylate which readily generated from acid **1** is a useful synthetic intermediate for 2-substituted derivatives of acid **1** *via* reactions with a number of electrophiles.[6] Although several synthetic routes to benzo[*b*]furan-3-carboxylic acid (**1**) and its esters have been reported (Scheme 1), all of these methods suffer from significant drawbacks which include: low-yielding or lengthy in terms of steps; the use of expensive or hazardous starting materials or catalysts, reactions can be performed only on gram to mg scale, drastic reaction conditions.

Historically, acid **1** was prepared by decarboxylation of benzo[*b*]furan-2,3-dicarboxylic acid[7] or *via* lithiation/carboxylation of 3-bromobenzo[*b*]furan.[8] Both these methods are difficult to operate on a multi-gram scale and complicated by side-reactions.[9] Recently, the synthesis of ethyl benzo[*b*]furan-3-carboxylate (**3a**) from salicylaldehyde and ethyl diazoacetate in the presence of $HBF_4 \times Et_2O$ as a catalyst has been reported.[10] Although the method is high-yielding and simple to operate,

the use of diazoacetate as a reagent makes this protocol less attractive for medium and large scale. Several methods for the preparation of benzo[*b*]furan-3-carboxylic acid esters include the palladium-catalyzed transformations: the intramolecular Heck reaction of (2-bromo(iodo)phenoxy)acrylate[11] and carbonylation of the triflates derived from 3-coumaranones (Scheme 1).[12] Both these approaches use relatively expensive (or not easily achievable) starting materials and/or catalysts. Several other reactions leading to acid **1** or the corresponding esters have also been described,[13] but all of these approaches cannot be regarded as a general method. Thus, a simple and efficient route to benzo[*b*]furan-3-carboxylic acids is still of current interest to synthetic organic chemists. Therefore, our efforts have been focused on the development of a simple and efficient procedure for the preparation of acid **1** or the corresponding esters. Herein we report a practical means of the medium-scale synthesis of methyl benzo[*b*]furane-3-carboxylates via a copper-catalyzed intramolecular C–O bond-forming reaction.



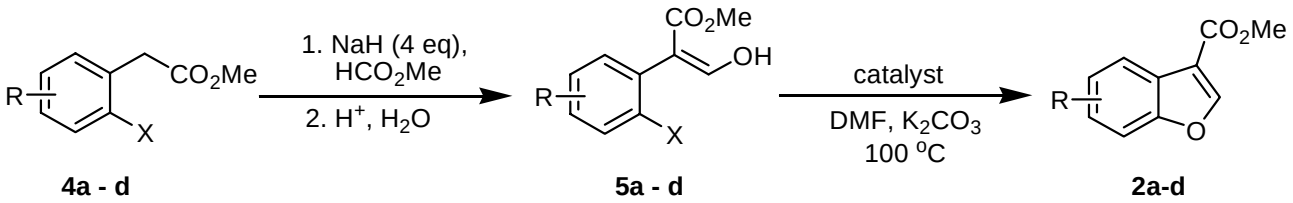
Scheme 1. Literature routes to benzo[*b*]furan-3-carboxylic acid and corresponding esters.

RESULTS AND DISCUSSION

In the course of our ongoing medicinal chemistry programs, we required an operationally simple method for the preparation of benzo[*b*]furan-3-carboxylic acid (**1**) in a multi-gram scale. In recent research, the copper-catalyzed C–O bond formation reactions[14] has been demonstrated to be among the most promising ways for the construction of the benzo[*b*]furan ring system. This useful synthetic tool has been successfully applied to the synthesis of a wide variety of 2-, 3- and 2,3-substituted benzo[*b*]furans[15] via a ring closure of 2-haloaromatic ketones and esters 2-substituted benzo[*b*]furan-3-carboxylic acid from 1-bromo-2-iodobenzene and β-ketoesters.[16] In recent years, the copper-catalyzed C–C and C–X (X = N, O, S) bond formation reactions have widely been applied to the synthesis and transformation of various other heterocyclic compounds as well.[14, 17] Recently, we described a new protocol for the assembly of *N*-alkyl- and *N*-aryl-1*H*-indole-3-carboxylic acid derivatives based on the copper(I)-catalyzed intramolecular amination of aryl bromides.[18] This catalytic process is simply performed and provides good to high yields of the desired products even under an air atmosphere. We therefore focused our efforts on the development a scaleable synthesis of methyl benzo[*b*]furan-3-carboxylate (**2a**) via the copper-catalyzed intramolecular

C–O bond formation since we believed that this methodology could offer distinctive advantages over other approaches to date.

Our synthetic pathway to methyl benzo[*b*]furan-3-carboxylate (**2a**) is depicted in Scheme 2 and based on an elegant and highly efficient synthesis of benzo[*b*]furans via a copper-catalyzed ring closure of 2-halo aromatic ketones reported by Chen and Dormer.[15a] The starting materials **5a-d** were easily synthesized in one step from corresponding methyl phenylacetates **4a-d** by a known procedure.[19] The following furan ring-closure reaction was first investigated using copper (I) iodide (10 mol%) as the catalyst. The reaction was performed in DMF as the solvent without any ligand added. Catalytic cyclization of substrate **5a** turned out to give 87% of ester **2a** after as little as 1.5 h at 100 °C (bath temperature hereafter) with quantitative conversion of the starting material (Table 1, entry 1). Advantageously, no column chromatography is necessary for the product, after standard work-up it was obtained in high purity (≥95% by GC and ^{1}H NMR).



4a - d **5a - d** **2a-d**

Scheme 2.

The reaction with 5 and even 1 mol% catalyst loadings gave essentially the same result for slightly longer reaction times (entries 2 and 3). At the rt a complete conversion was reached after 12 h and product was obtained with excellent yield (92%, entry 2). Other copper sources such as $Cu(OAc)_2$ and $CuSO_4\times5H_2O$ were demonstrated to be similarly effective, though with $CuSO_4\times5H_2O$ as the catalyst precursor ester **2a** was obtained in slightly lower yield (entry 5), probably because of the hydrolysis of the ester group.

We also investigated the use of $FeCl_3$ as an alternative catalyst for the benzo[*b*]furan ring construction via the catalytic C–O bond-forming reaction. Recently several new practical methods of the C–C, C–N and C–O bond formations using iron salts as a catalyst have been described.[20] Iron-catalyzed reactions are very attractive because of extremely low price of iron and its environmentally benign features. Unfortunately, in our case $FeCl_3$ has proved to be much less effective than any copper catalyst used. The reaction with 10 mol% of $FeCl_3$ gave ester **2a** in only 51% yield with quantitative conversion of the starting material after 24 h at 100 °C (entry 6). When a higher catalyst loading was employed no significant improvement was achieved and ester **2a** was obtained in only 53% yield after 10 h.

Using the optimal reaction conditions (5 mol% CuI, 100 °C) we prepared methyl 5-methoxy- (**2b**) and 6-fluorobenzofuran-3-carboxylates (**2c**) in high yields (entries 8 and 9). Chloride **5d** seemed to be much

less reactive under these reaction conditions and the corresponding ester **2d** was isolated in a poor yield (entries 10 and 11), though the conversion in both cases was nearly quantitative.

Table 1. Synthesis of benzo[*b*]furan-3-carboxylic acid derivatives

#	R	X	Y	Yield, %	Catalyst (mol%)	Time, h	Yield, %[a]
1	H	Br	CO_2Me	**5a** 90	CuI (10)	1.5	**2a** 87
2					CuI (5)	2 (12[b])	88 (92[b])
3					CuI (1)	4	87
4					$Cu(OAc)_2$ (10)	2	88
5					$CuSO_4 \times 5H_2O$ (10)	2	75
6					$FeCl_3$ (10)	24	51
7					$FeCl_3$ (20)	10	53
8	5-MeO	Br	CO_2Me	**5b** 85	CuI (5)	2	**2b** 78
9	4-F	Br	CO_2Me	**5c** 82	CuI (5)	2	**2c** 82
10	4-Cl	Cl	CO_2Me	**5d** 86	CuI (10)	24	**2d** 33[c]
11					$Cu(OAc)_2$ (10)	24	31[c]

[a] Yields are given for isolated products with purity ≥95% (GC and ^{1}H NMR). [b] Reaction was carried out at rt. [c] Isolated yield after column chromatography.

CONCLUSION

In conclusion, we have provided a simple and practical means for the preparation of methyl benzo[*b*]furan-3-carboxylates starting from methyl *o*-bromophenylacetates using a copper-catalyzed intramolecular C–O bond-forming reaction as the key step. The procedure can be performed under an air atmosphere and allows synthesizing the title compounds with high yields and purity even without column chromatography purification. This process is significantly improved compared to the literature methods mentioned above.

EXPERIMENTAL

General. All chemicals and solvents were purchased from commercial suppliers and used as received. All reactions were performed under an air atmosphere. ^{1}H and ^{13}C NMR spectra were obtained at 400 and 100 MHz correspondingly with $CDCl_3$ or DMSO-d_6 as a solvent and internal standard. Chemical shift values are expressed in δ and *J* values are in Hz. Splitting patterns are indicated as s (singlet), d (doublet), dd (doublet of doublets), t (triplet), td (triplet of doublets), m (multiplet), b (broad signal). Compounds described in the literature were characterized by comparing their ^{1}H and ^{13}C NMR spectra to the previously

reported data and all new compounds were further characterized. IR spectra were recorded for neat compounds (liquid) or for suspension in Nujol (solid) and only noteworthy absorptions are listed. Mass spectra were recorded in electron impact mode at 70 eV. Melting points were determined by open capillary method and are uncorrected. Analytical samples were prepared by flash chromatography on silica gel (230-400 mesh) using a mixture of hexane/EtOAc (20:1) as eluent. TLC was carried out on silica gel 60 F_{254} plates, and the spots were located with UV light.

Methyl 2-(2-bromophenyl)-2-formylacetate (5a).[19]

To a stirred solution of methyl 2-bromophenylacetate (71.1 g, 0.31 mol) in methyl formate (500 mL) a suspension of sodium hydride (60%, 49.89 g, 1.24 mol) was slowly added over a period of 1 h at 10-15 ^{o}C. After the mixture was stirred for an additional hour it was treated with iced water (600 mL) and two layers were separated. The aqueous layer was acidified with 10% HCl and then extracted (3 x 300 mL) with EtOAc. The organic layers were combined, washed successively with water (2 x 300 mL), saturated aqueous $NaHCO_3$ (2 x 300 mL) and saturated brine and then dried over anhydrous Na_2SO_4. Filtration and evaporation gave the title compound as the only tautomer (71.1 g, 90%). Mp 123-125 ^{o}C (hexane). ^{1}H NMR ($CDCl_3$): δ 3.78 (s, 3H), 7.19 (s, 1H), 7.20–7.26 (m, 2H), 7.33 (td, J = 8.0, 1.4 Hz, 1H), 7.63 (dd, J = 8.0, 1.2 Hz, 1H), 11.91 (d, J = 12.8 Hz). ^{13}C NMR ($CDCl_3$): δ 51.9, 108.4, 126.6, 127.4, 129.4, 132.3, 132.6, 134.7, 163.4, 171.3. MS, *m/z* (I, %): 258, 256 (M^+; 5, 5), 228, 230 (8, 8), 224, 226 (6, 6), 177 (43), 145 (100), 134 (10), 121 (17), 105 (7), 88 (23), 89 (80), 77 (15), 63 (25), 50 (10), 39 (15). IR (film, ν, cm^{-1}): 1615, 1670, 1740, 2935.

The above procedure was followed to afford the following compounds.

Methyl 2-(2-bromo-5-methoxyphenyl)-2-formylacetate (5b). Yield 85% as the only tautomer. Pale yellow solid. Mp 110-115 ^{o}C (toluene/hexane). ^{1}H NMR ($CDCl_3$): δ 3.78 (s, 3H), 3.81 (s, 3H), 6.75–6.85 (m, 2H), 7.19 (d, J = 12.9 Hz, 1H), 7.49 (d, J = 8.6 Hz, 1H), 11.89 (d, J = 12.9 Hz). ^{13}C NMR (DMSO-d_6): δ 51.5, 55.8, 109.9, 115.1, 115.9, 118.8, 133.0, 136.2, 156.9, 158.7, 167.5. MS, *m/z* (I, %): 288, 286 (M^+; 3, 3), 207 (100), 175 (42), 119 (26), 77 (24), 76 (20), 75 (17), 65 (16), 63 (18), 62 (15), 51 (27), 50 (25). IR (film, ν, cm^{-1}) 1620, 1680, 1745, 2930. Anal. Calcd for $C_{11}H_{11}BrO_4$: C, 46.02, H, 3.86. Found: C, 46.03, H, 3.84%.

Methyl 2-(2-bromo-4-fluorophenyl)-2-formylacetate (5c). Yield 82%. Pale yellow amorphous solid. This compound was obtained as a mixture of three tautomers. ^{1}H NMR ($CDCl_3$): δ 3.73 (s, 0.9H), 3.77 (s, 1.8H), 3.83 (s, 0.3H), 5.04 (s, 0.1H), 6.76 (bs, 0.3H), 6.99–7.45 (m, 3.6H), 7.78 (bs, 0.3H), 9.99 (s, 0.1H), 11.96 (d, J = 12.9 Hz, 0.6H). ^{13}C NMR (DMSO-d_6): δ 51.5, 108.9, 114.9 (d, $J_{C\text{-}F}$ = 20.5 Hz), 119.6 (d, $J_{C\text{-}F}$ = 24.2 Hz), 125.7 (d, $J_{C\text{-}F}$ = 10.3 Hz), 131.7 (d, $J_{C\text{-}F}$ = 3.7 Hz), 134.4 (d, $J_{C\text{-}F}$ = 8.1 Hz), 157.3, 161.4 (d, $J_{C\text{-}F}$ = 247.4 Hz), 167.4. MS, *m/z* (I, %): 276, 274 (M^+; 3, 3), 244, 242 (4, 4), 203, 201 (4, 4), 195 (19), 163 (55),

108 (23), 107 (100), 81 (20), 57 (32). IR (film, ν, cm^{-1}) 1610, 1670, 1735, 2940. Anal. Calcd for $C_{10}H_8BrFO_3$: C, 43.66, H, 2.93. Found: C, 43.70, H, 2.94 %.

Methyl 2-(2,4-dichlorophenyl)-2-formylacetate (5d).[21] Yield 86%. Yellow liquid. This compound was obtained as a mixture of three tautomers with more than 80% of major tautomer. ^{1}H NMR ($CDCl_3$, major tautomer): δ 3.78 (s, 3H), 7.16 (d, *J* = 8.2, 1H), 7.19 (d, *J* = 12.8 Hz, 1H), 7.26 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.45 (d, *J* = 2.2 Hz, 1H), 11.95 (d, *J* = 12.8 Hz, 1H). ^{13}C NMR (DMSO-d_6): δ 51.5, 106.8, 127.4, 128.9, 132.3, 133.0, 134.6, 135.5, 157.7, 164.3. MS, *m/z* (I, %): 248, 246 (M^+; 8, 14), 216, 214 (16, 26), 181 (41), 179 (100), 160 (24), 159 (35), 158 (36), 125 (55), 124 (20), 123 (93), 111 (25), 97 (29), 89 (35), 87 (4), 86 (29), 85 (26), 75 (41), 74 (22), 73 (48), 63 (45), 62 (43), 61 (41), 57 (27), 55 (27), 50 (25), 43 (40), 41 (28), 39 (24). IR (film, cm^{-1}) 1610, 1670, 1735, 2940. Anal. Calcd for $C_{10}H_8Cl_2O_3$: C, 48.61, H, 3.26. Found: C, 48.63, H, 3.26.

Methyl 1-benzofuran-3-carboxylate (2a).[12] To a stirred solution of methyl 2-(2-bromophenyl)-2-formylacetate (**5a**) (71.1 g, 0.275 mol) in DMF (300 mL) CuI (21.7 g, 0.114 mol, 5 mol%) and K_2CO_3 (130.9 g, 0.55 mol) were added. The reaction mixture was heated at 100°C (bath temperature) for 2 h and allowed to cool to rt. Solvent was evaporated to dryness under reduced pressure. Water (300 mL) was added to the residue, the mixture was extracted (3 x 150 mL) with EtOAc. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo to yield 42.6 g (88%) of the crude product as pale yellow liquid with purity ≥95%. ^{1}H NMR ($CDCl_3$): δ 3.96 (s, 3H), 7.36–7.41 (m, 2H), 7.52–7.58 (m, 1H), 8.07–8.12 (m, 1H), 8.28 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 51.6, 111.7, 114.5, 122.0, 124.2, 124.6, 125.3, 151.0, 155.6, 163.4. MS, *m/z* (I, %): 176 (M^+; 37), 145 (50), 90 (19), 89 (100), 88 (22), 87 (21), 86 (20), 77 (25), 72 (16), 63 (99), 62 (97), 61 (43), 53 (16), 51 (40), 50 (56), 45 (16), 44 (17), 43 (22), 39 (97), 38 (40), 37 (29). IR (film, ν, cm^{-1}) 1060, 1130, 1730.

The above procedure was followed to afford the following compounds.

Methyl 5-methoxy-1-benzofuran-3-carboxylate (2b). Yield 78%. Tan liquid. ^{1}H NMR ($CDCl_3$): δ 3.89 (s, 3H), 3.93 (s, 3H), 6.96 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.41 (d, *J* = 9.1 Hz, 1H), 7.51 (d, *J* = 2.5 Hz, 1H), 8.21 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 51.5, 55.9, 103.7, 112.2, 114.3, 114.6, 125.3, 150.5, 151.5, 157.0, 163.8. MS, *m/z* (I, %): 206 (M^+; 78), 191 (21), 175 (100), 147 (19), 120 (16), 119 (38), 104 (19), 91 (16), 89 (18), 88 (17), 87 (27), 86 (17), 82 (32), 77 (37), 76 (71), 75 (37), 74 (35), 65 (58), 63 (40), 62 (44), 61 (17), 59 (47), 54 (42), 53 (31), 51 (26), 50 (87), 39 (27), 38 (21). IR (film, ν, cm^{-1}) 1060, 1180, 1725. Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.07, H, 4.89. Found: C, 64.10, H, 4.85.

Methyl 6-fluoro-1-benzofuran-3-carboxylate (2c). Yield 82%. Of-white solid. Mp 63-65 °C (toluene/hexane). ^{1}H NMR ($CDCl_3$): δ 3.94 (s, 3H), 7.07–1.19(m, 1H), 7.21–7.30 (m, 1H), 7.95–8.05 (m,

1H), 8.24 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 51.7, 99.4 (d, $J_{C\text{-}F}$ = 27.1 Hz), 112.6 (d, $J_{C\text{-}F}$ = 24.2 Hz), 114.4, 120.8, 122.5 (d, $J_{C\text{-}F}$ = 10.3 Hz), 151.4 (d, $J_{C\text{-}F}$ = 3.7 Hz), 155.4 (d, $J_{C\text{-}F}$ = 13.2 Hz), 161.2 (d, $J_{C\text{-}F}$ = 243.7 Hz), 163.5. MS, *m/z* (I, %): 194 (M^+; 25), 163 (61), 107 (85), 81 (33), 63 (23), 62 (27), 57 (100), 50 (23), 43 (20), 41 (21). IR (Nujol, cm^{-1}) 1060, 1140, 1735. Anal. Calcd for $C_{10}H_7FO_3$: C, 61.86, H, 3.63. Found: C, 61.85, H, 3.61.

Methyl 6-chloro-1-benzofuran-3-carboxylate (2d). Yield 33% (after chromatography purification). Yellow solid. Mp 67 °C. ^{1}H NMR ($CDCl_3$): δ 3.95 (s, 3H), 7.34 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.54 (d, *J* = 1.3 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 8.23 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 51.7, 112.2, 114.4, 122.6, 123.3, 125.0, 131.3, 151.4, 155.5, 163.3. MS, *m/z* (I, %): 212, 210 (M^+; 8, 25), 181, 179 (15, 46), 125 (19), 123 (40), 111 (21), 97 (37), 95 (23), 87 (20), 83 (40), 81 (29), 75 (18), 73 (20), 71 (52), 70 (22), 69 (60), 67 (30), 63 (20), 62 (25), 57 (92), 56 (33), 55 (90), 43 (100), 42 (25), 41 (97), 39 (29). IR (Nujol, cm^{-1}) 1060, 1130, 1730. Anal. Calcd for $C_{10}H_7ClO_3$: C, 57.03, H, 3.35. Found: C, 57.01, H, 3.34.

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