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A General and Straightforward Approach to α,ω-Ketoesters

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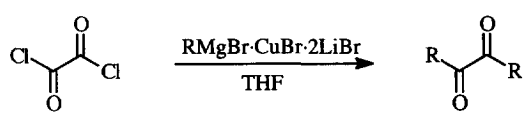
Abstract: Chemoselective cross-coupling reactions of monoesters of dicarboxylic acid chlorides with organocopper reagents derived from Grignard reagents, cuprous bromide, and lithium bromide, provide a simple and straightforward method for synthesizing a variety of ketoesters. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Ketoesters play an important role in organic synthesis as useful intermediates in the preparation of a variety of complex structures.[1] Therefore, a simple procedure leading to this important class of compounds from easily accessible starting materials would result of great usefulness.

Among the various approaches to the synthesis of ketoesters, we believe that in principle the chemoselective cross-coupling reactions of monoesters of dicarboxylic acid chlorides with organometallic reagents probably should be considered the most direct one. A variety of organometallic reagents have been developed[2] to achieve selective carbon-carbon bond formation, such as cuprates[2a,b], Grignard reagents[2b,c], organotin compounds[2d], organomanganese[2e], organoboron[2f] and organovanadium compounds[2g]. However, most of them suffer from a lack of generality and are not free from side reactions.

Recently, we have reported a new synthetic entry into α-diones by means of an efficient cross-coupling reaction of oxalyl chloride and organocopper reagents, derived from Grignard reagents, cuprous bromide, and lithium bromide:[3]

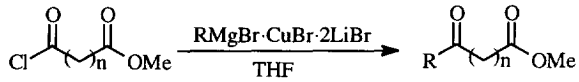


R = alkyl, aryl

The success of this reaction and our continuing interest in this area[4] prompted us to investigate a further application of this strategy.

RESULTS AND DISCUSSION

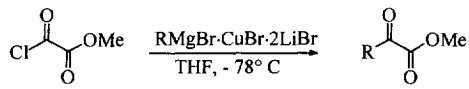
We extended our attention to the coupling reaction between the above mentioned organocopper reagents and easily available monoesters of dicarboxylic acid chlorides, with the aim of developing a straightforward and general route to α,ω-ketoesters:



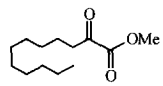
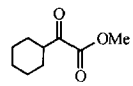
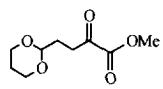
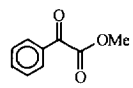
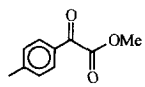
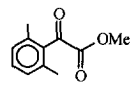
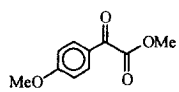
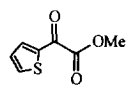
Now we describe the outcome of our attempts toward the realization of this chemistry along with the limitations which define its domain of applicability.

Representative coupling examples are collected in the Tables 1 and 2.

Table 1. Cross-coupling reactions of methyl oxalyl chloride 1 with organocopper reagents derived from RMgBr, CuBr and LiBr (1:1:2).

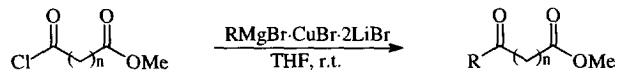


1 **3a-h**

R	Products 3a-h		Yield (%)[a]
n-Decyl		**3a**	89
Cyclohexyl		**3b**	75
2-(1,3-Dioxan-2-yl)ethyl		**3c**	71[c]
Phenyl		**3d**	86
p-Tolyl		**3e**	93
2,6-Dimethylphenyl		**3f**[b]	89
p-Methoxyphenyl		**3g**[b]	68
2-Thienyl		**3h**[b]	87

a) Yields refer to products purified by flash chromatography; all compounds exhibited spectral data consistent with the assigned structure; b) Reactions performed at room temperature; c) Yield determined by G.L.C. analysis.

Table 2. Cross-coupling reactions of monoesters of dicarboxylic acid chlorides **2** with organocopper reagents



2 (n = 2, 3, 7) **4-6**

R	**4a-h** (n=2)	Yield[a] (%)	**5a-h** (n=3)	Yield[a] (%)	**6a-h** (n=7)	Yield[a] (%)
n-Decyl	**4a**	80	**5a**	80	**6a**	76
Cyclohexyl	**4b**	87	**5b**	89	**6b**	91
2-(1,3-Dioxan-2-yl)ethyl	**4c**	95	**5c**	82	**6c**	95
Phenyl	**4d**	91	**5d**	97	**6d**	94
p-Tolyl	**4e**	91	**5e**	98	**6e**	97
2,6-Dimethylphenyl	**4f**	90	**5f**	88	**6f**	96
p-Methoxyphenyl	**4g**	82	**5g**	79	**6g**	74
2-Thienyl	**4h**	93	**5h**	91	**6h**	98

a) Yields refer to products purified by flash chromatography; all compounds exhibited spectral data consistent with the assigned structure.

Data inspection reveals that organocopper reagents, derived from Grignard reagents, cuprous bromide, and lithium bromide, were also the reagents of choice in the cross-coupling reactions with monoesters of dicarboxylic acid chlorides. Indeed, as illustrated in the Table 1, various monoesters of α-dicarboxylic acid chlorides undergo a very simple and efficient chemoselective cross-coupling reaction with a wide range of organocopper reagents to form α-ketoesters in high yields.

One particular aspect of these results is the dependence of the yields on the reaction temperature and on the nature of the organocopper reagent. Indeed in the case of α-ketoesters **3a-c** (see Table 1), derived from aliphatic and functionalized organocopper reagents, and **3d,e**, derived from phenyl and *p*-tolyl organocopper reagents, the coupling reaction, carried out at room temperature, led to a considerable amount of the homocoupling product and to a moderate yield of the cross-coupling product. Nevertheless, when the reaction was performed at -78°C, the yields of α-ketoesters were greatly increased and the undesired homocoupling reactions were almost completely suppressed. However high yields could be achieved at room temperature in the case of compounds **3f-h**.

Unfortunately, this method shares a common limitation with several other reactions involving easily enolizable carbonyl compounds and organometallic reagents.[5] In fact, attempts to apply our methodology to the

synthesis of β-ketoesters, starting with methyl malonyl chloride, failed, giving unacceptably low yields which were not improved by the addition of cerium chloride.[6] This result is very likely due to a greater rate of proton abstraction process versus nucleophilic attack at the carbonyl group, generating an enolate structure which is inert towards nucleophilic attack.[7]

On the contrary all the reactions examined with γ-, δ-, and ω-monoesters of dicarboxylic acid chlorides proceeded very cleanly at room temperature, leading to essentially pure ketoesters contaminated only by small amounts of homocoupling products. Thus, as shown in the Table 2, various γ-, δ-, and ω-ketoesters can be synthesized by this method in high isolated yields.

It is noteworthy that protected aldehydo ketoesters were also prepared successfully, including methyl 9-oxo-11-(1,3-dioxan-2-yl)undecanoate **6c**, which can be considered the parent compound of methyl 7-(5-oxocyclopentenyl)heptanoate, a popular intermediate for prostaglandin synthesis.[8]

In summary, these results offer a general and simple method leading to a wide spectrum of ketoesters. Comparison with other organometallic reagents, used to convert ester chlorides[2] or similar systems[9] into ketoesters, shows that organocopper reagents derived from RMgBr/CuBr/LiBr appear to be more useful particularly when the high yields, the high selectivity and the mild reaction conditions are taken into account.

EXPERIMENTAL

Methyl oxalyl chloride, methyl succinyl chloride and methyl glutaryl chloride were commercially available (Aldrich). Methyl azelayl chloride was prepared from the related commercially available acid (Aldrich). Merck silica gel (60, particle size 0.040-0.063 mm) for flash column chromatography and Merck plastic sheets with silica gel 60 F_{254} for TLC were used. GC analysis was performed on a Hewlett-Packard 5890 series II gas chromatograph equipped with a SE-30 (methylsilicone, 30 m x 0.25 mm id) capillary column. GC/mass-spectrometry analysis was performed on a Hewlett-Packard 5970A equipped with an HP-1 capillary column, 25 m, and HP MSD 5970B. ^{1}H NMR spectra were recorded in deuterochloroform on a Bruker AM 500 spectrometer at 500 MHz and on a Bruker AM 300 spectrometer at 300 MHz.

General procedure for the cross-coupling reactions of monoesters of dicarboxylic acid chlorides with organocopper reagents.

A THF solution of anhydrous LiBr (2.4 equiv.) was added at room temperature (or at -78°C, see Table 1), under nitrogen, to a stirred suspension of CuBr (1.2 equiv.) in THF, and the resulting mixture was stirred at the same temperature until it became homogeneous. A freshly prepared THF solution of Grignard reagent (1.2 equiv.) and soon afterwards monoester of dicarboxylic acid chloride (1.0 equiv.) in THF were quickly added to the stirred solution of salts. The mixture was stirred for 30 min, quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. The organic extracts were dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography leading to ketoesters **3-6**.

The spectral data of unknown compounds are as follows.

Methyl 9-oxo-9-cyclohexylnonanoate (6b). Compound **6b** was prepared from **2** (n=7) (0.50 g, 2.27 mmol) in accordance with general procedure. Purification by flash chromatography (hexane/diethyl ether = 8:2) gave **6b** (0.56 g, 91%). **6b:** ^{1}H-NMR (500 MHz): δ 1.09-1.32 (m, 11H), 1.45-1.65 (m, 5H), 1.69-1.80 (m, 4H), 2.22-2.31 (m, 3H), 2.36 (t, *J* = 7.4 Hz, 2H), 3.61 (s, 3H) ppm; MS *m/z* 268 (M^+, 6), 237 (4), 185 (19), 153 (11), 126 (31), 111 (30), 97 (18), 83 (100), 55 (98), 43 (18), 41 (51), 39 (13).

Methyl 2-oxo-4-(1,3-dioxan-2-yl)butanoate (3c). Compound **3c** was prepared from **1** (0.50 g, 4.08 mmol) in accordance with general procedure in 71% yield (G.L.C. analysis). Spectral data refer to product purified by flash chromatography (petroleum ether/AcOEt = 8:2). **3c:** ^{1}H-NMR (500 MHz): δ 1.25-1.32 (m, 1H), 1.91-2.05 (m, 3H), 2.92 (t, *J* = 7.0 Hz, 2H), 3.65-3.73 (m, 2H), 3.83 (s, 3H), 4.00-4.06 (m, 2H), 4.57 (t, *J* = 4.7 Hz, 1H) ppm; MS *m/z* 201(2), 143 (53), 115 (5), 87 (37), 85 (100), 59 (21), 57 (21), 41 (18).

Methyl 4-oxo-6-(1,3-dioxan-2-yl)hexanoate (4c). Compound **4c** was prepared from **2** (n=2) (0.50 g, 3.32 mmol) in accordance with general procedure. Purification by flash chromatography (petroleum ether/AcOEt = 7:3) gave **4c** (0.73 g, 95%). **4c:** ^{1}H-NMR (500 MHz): δ 1.26-1.32 (m, 1H), 1.85 (dt, *J* = 7.3, 4.9 Hz, 2H), 1.95-2.05 (m, 1H), 2.54 (t, *J* = 7.1 Hz, 4H), 2.70 (t, *J* = 6.6 Hz, 2H), 3.63 (s, 3H), 3.66-3.73 (m, 2H), 4.00-4.07 (m, 2H), 4.52 (t, *J* = 4.9 Hz, 1H) ppm; MS *m/z* 229 (3), 199 (4), 143 (24), 115 (20), 112 (19), 100 (76), 87 (100), 89 (51), 59 (31), 57 (18), 55 (31), 41 (20).

Methyl 5-oxo-7-(1,3-dioxan-2-yl)heptanoate (5c). Compound **5c** was prepared from **2** (n=3) (0.50 g, 3.04 mmol) in accordance with general procedure. Purification by flash chromatography (petroleum ether/ AcOEt = 8:2) gave **5c** (0.61 g, 82%). **5c:** ^{1}H-NMR (500 MHz): δ 1.19-1.25 (m, 1H), 1.71-1.81 (m, 4H), 1.86-1.97 (m, 1H), 2.21 (t, *J* = 7.3 Hz, 2H), 2.37 (t, *J* = 7.3 Hz, 2H), 2.40 (t, *J* = 7.3 Hz, 2H), 3.54 (s, 3H), 3.58-3.66 (m, 2H), 3.91-3.99 (m, 2H), 4.44 (t, *J* = 4.9 Hz, 1H) ppm; MS *m/z* 244 (M^+, 1), 243 (4), 143 (37), 137 (28), 100 (100), 87 (76), 85 (60), 59 (38), 57 (15), 55 (26), 41 (20).

Methyl 9-oxo-11-(1,3-dioxan-2-yl)undecanoate (6c). Compound **6c** was prepared from **2** (n=7) (0.50 g, 2.27 mmol) in accordance with general procedure. Purification by flash chromatography (petroleum ether/AcOEt = 8:2) gave **6c** (0.65 g, 95%). **6c:** ^{1}H-NMR (500 MHz): δ 1.19-1.32 (m, 7H), 1.48-1.62 (m, 4H), 1.83 (dt, *J* = 7.3, 4.9 Hz, 2H), 1.95-2.07 (m, 1H), 2.26 (t, *J* = 7.5 Hz, 2H), 2.36 (t, *J* = 7.4 Hz, 2H), 2.48 (t, *J* = 7.3 Hz, 2H), 3.63 (s, 3H), 3.67-3.74 (m, 2H), 4.01-4.07 (m, 2H), 4.53 (t, *J* = 4.9 Hz, 1H) ppm; MS *m/z* 299 (1), 269 (5), 243 (2), 224 (2), 185 (2), 158 (8), 143 (21), 125 (4), 100 (100), 87 (51), 85 (34), 59 (16), 57 (11), 55 (23), 41 (19).

Methyl 9-oxo-9-(*p*-tolyl)nonanoate (6e). Compound **6e** was prepared from **2** (n=7) (0.50 g, 2.27 mmol) in accordance with general procedure. Purification by flash chromatography (petroleum ether/AcOEt = 8:2) gave **6e** (0.61 g, 97%). **6e:** ^{1}H-NMR (500 MHz): δ 1.21-1.40 (m, 6H), 1.52-1.62 (m, 2H), 1.63-1.73 (m, 2H), 2.25 (t, *J* = 7.5 Hz, 2H), 2.36 (s, 3H), 2.88 (t, *J* = 7.4 Hz, 2H), 3.61 (s, 3H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H) ppm; MS *m/z* 245 (1), 147 (6), 134 (70), 119 (100), 91 (32), 65 (11), 55 (11), 41 (8), 39 (4).

Methyl 2-oxo-2-(2,6-dimethylphenyl)ethanoate (3f). Compound **3f** was prepared from **1** (0.50 g, 4.08 mmol) in accordance with general procedure. Purification by flash chromatography (petroleum ether/AcOEt = 9:1) gave **3f** (0.70 g, 89%). **3f:** ^{1}H-NMR (300 MHz): δ 2.24 (s, 6H), 3.88 (s, 3H), 7.03 (d, *J* = 7.7 Hz, 2H), 7.23 (t, *J* = 7.7 Hz, 1H) ppm; MS *m/z* 192 (M^+, 1), 133 (100), 105 (49), 77 (27), 44 (27), 40 (88).

Methyl 4-oxo-4-(2,6-dimethylphenyl)butanoate (4f). Compound **4f** was prepared from **2** (n=2) (0.50 g, 3.32 mmol) in accordance with general procedure. Purification by flash chromatography (petroleum ether/AcOEt = 9:1) gave **4f** (0.66 g, 90%). **4f:** ^{1}H-NMR (500 MHz): δ 2.20 (s, 6H), 2.68 (t, *J* = 6.4 Hz, 2H), 2.99 (t, *J* = 6.4 Hz, 2H), 3.67 (s, 3H), 6.96 (d, *J* = 7.6 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 1H) ppm; MS *m/z* 220 (M^+, 4), 189 (6), 133 (100), 105 (36), 77 (17).

Methyl 5-oxo-5-(2,6-dimethylphenyl)pentanoate (5f). Compound **5f** was prepared from **2** (n=3) (0.50 g, 3.04 mmol) in accordance with general procedure. Purification by flash chromatography (petroleum ether/AcOEt = 9:1) gave **5f** (0.63 g, 88%). **5f:** ^{1}H-NMR (500 MHz): δ 2.00 (quintet like, *J* = 7.2 Hz, 2H), 2.16 (s, 6H), 2.40 (t, *J* = 7.2 Hz, 2H), 2.73 (t, *J* = 7.2 Hz, 2H), 3.62 (s, 3H), 6.95 (d, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H) ppm; MS *m/z* 234 (M^+, 4), 203 (5), 175 (4), 133 (100), 105 (28), 77 (11).

Methyl 9-oxo-9-(2,6-dimethylphenyl)nonanoate (6f). Compound **6f** was prepared from **2** (n=7) (0.50 g, 2.27 mmol) in accordance with general procedure. Purification by flash chromatography (petroleum ether/AcOEt = 8:2) gave **6f** (0.63 g, 96%). **6f:** ^{1}H-NMR (500 MHz): δ 1.20-1.40 (m, 6H), 1.53-1.62 (m, 2H), 1.63-1.72 (m, 2H), 2.16 (s, 6H), 2.26 (t, *J* = 7.5 Hz, 2H), 2.65 (t, *J* = 7.4 Hz, 2H), 3.61 (s, 3H), 6.95 (d, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H) ppm; MS *m/z* 290 (M^+, 2), 133 (100), 105 (16), 77 (5).

Methyl 9-oxo-9-(*p*-methoxyphenyl)nonanoate (6g). Compound **6g** was prepared from **2** (n=7) (0.50 g, 2.27 mmol) in accordance with general procedure. Purification by flash chromatography (petroleum ether/AcOEt = 8:2) gave **6g** (0.49 g, 74%). **6g:** ^{1}H-NMR (500 MHz): δ 1.20-1.38 (m, 6H), 1.52-1.61 (m, 2H), 1.62-1.73 (m, 2H), 2.24 (t, *J* = 7.5 Hz, 2H), 2.85 (t, *J* = 7.4 Hz, 2H), 3.60 (s, 3H), 3.80 (s, 3H), 6.84-6.89 (m, 2H), 7.85-7.90 (m, 2H) ppm; MS *m/z* 292 (M^+, 1), 261 (2), 163 (8), 150 (73), 135 (100), 107 (9), 92 (11), 77 (18).

Methyl 9-oxo-9-(2-thienyl)nonanoate (6h). Compound **6h** was prepared from **2** (n=7) (0.50 g, 2.27 mmol) in accordance with general procedure. Purification by flash chromatography (petroleum ether/ AcOEt = 8:2) gave **6h** (0.60 g, 98%). **6h:** ^{1}H-NMR (500 MHz): δ 1.23-1.39 (m, 6H), 1.55-1.64 (m, 2H), 1.67-1.75 (m, 2H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.86 (t, *J* = 7.4 Hz, 2H), 3.63 (s, 3H), 7.09 (dd, *J* = 4.9, 3.8 Hz, 1H), 7.59 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.68 (dd, *J* = 3.8, 1.1 Hz, 1H) ppm; MS *m/z* 268 (M^+, 3), 237 (1), 195 (1), 139 (10), 126 (100), 111 (79), 83 (7), 55 (12), 39 (13).

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