Friedel-Crafts Coordinated Processes: Highly Selective Synthesis of Hydroxynaphthoquinones

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Simple preparation of ethyl 3-hydroxy-1,4-naphthoquinone-2-carboxylates **2** including heterocyclic analogs is accomplished by C-regioselective bis-acylation of aromatic and heteroaromatic β-keto esters **1**. Compounds **2** are readily hydrolyzed and decarboxylated to the corresponding 2-hydroxy-1,4-naphthoquinone derivatives **3**.

Hydroxylated and methoxylated quinones, including heterocyclic analogs, that have a hydroxy or methoxy group attached directly to the quinone moiety are found commonly in nature[1] and vary in structural complexity from the simple Lawsone[2] to the more elaborate fredericamycins[3] and mitomycins.[4] Considerable attention has been paid to the synthesis of these compounds due to their impressive biological activities.[1] However, the methods for their preparation remain limited. Although the oxidation of available aromatic substrates with a wide series of oxidizing reagents provides a convenient route to these compounds,[5] the process fails in the synthesis of heterocyclic quinones such as furano-, thieno-, and carbazoloquinones.

An alternative method is the Michael-like addition of alcohols to the quinones.[6] The main disadvantage of this method is the limited applicability and the lack of selectivity when substituted quinones are utilized.

As part of our continuing work on the metal-template electrophilic bis-acylation of aromatic substrates,[7] we have recently devised a method for hydroxyquinone synthesis that only requires readily available β-keto esters **1** and provides the products **2** and **3** in high yields and complete selectivity.

Results and Discussion

We have previously reported on the utility of aromatic β-dicarbonyl compounds as versatile intermediates from which 1,3-indandione derivatives can be easily synthesized via a cycliacylation reaction even if the process involves aromatic substrates highly deactivated toward electrophilic substitution.[8]

On the basis of these results we decided to extend this reaction to a wider range of electrophilic reagents. Our working hypothesis was that metal chelates of aromatic β-keto esters could give rise to a selective aliphatic-aromatic bis-acylation with oxalyl chloride (Figure 1).

When metal salts of β-dicarbonyl compounds are allowed to react with acid chlorides, it is possible to obtain products resulting from attack at the carbon or oxygen atom. Moreover, on the basis of numerous reports from literature there appears to be a great tendency for C-acylation to occur with magnesium chelates.[9] Because it was the aim of this study to look for a method which would yield the quinones **2** (Scheme I) via selective double C-acylation of substrates **1**, we originally planned to utilize the magnesium chelate of the ethyl benzoylacetate **1a** chosen as the model reagent.

Thus, the magnesium salt of the substrate **1a**[10] was allowed to react with oxalyl chloride in the presence of a stoichiometric amount of aluminum trichloride in nitromethane at 80 °C for 2 h (see β-Keto Ester Oxaloylation. General Procedure in Experimental Section). Unfortunately the reaction gave only poor yield (15%) of the desired quinone **2a**. Probably under these conditions, the oxalyl chloride decomposes giving carbonyl chloride and carbon monoxide.[11]

Therefore, we employed the more reactive dichloroaluminum chelate **4a** which could be easily obtained by reaction of the substrate **1a** with ethyl aluminum dichloride in THF and replacing nitromethane as the reaction solvent. Under these conditions the product **2a** was obtained in 70% yield (Scheme II).

Seeking a more useful and efficient method to synthesize the quinone **2a**, we tried a typical Friedel-Crafts approach. Thus treating directly a solution of **1a** and aluminum trichloride in dry nitromethane with oxalyl chloride (molecular ratio 1:3:1.5) and heating at 80 °C for 3 h resulted in the production of the compound **2a** in 85% yield (Scheme II).

According to early reports on the reaction of β-dicarbonyl compounds with different aluminum salts,[12] the enolized β-keto ester **1a** can react with aluminum trichloride to

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0022-3263/93/1958-0840$04.00/0

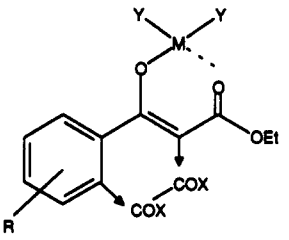
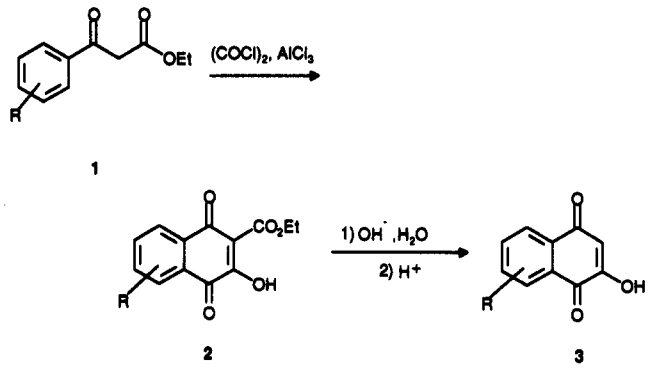
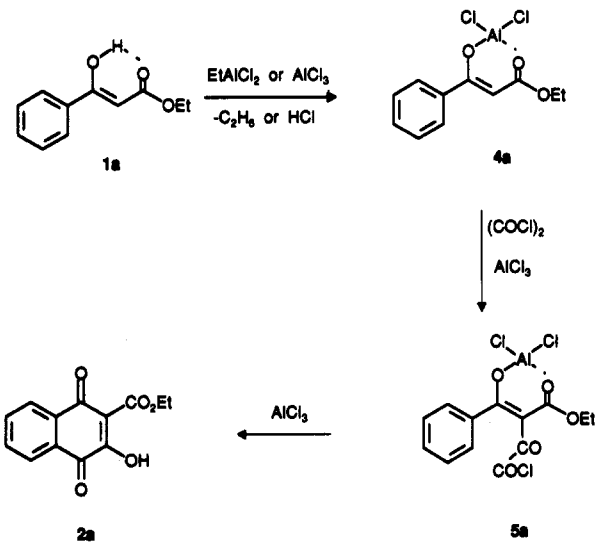


Figure 1.

Scheme I



Scheme II



give the chelate **4a** which has a significant influence on the mode of acylation. C-Selective oxaloylation of the ambident system occurs affording the tetracarbonyl intermediate **5a** which undergo further aluminum trichloride-promoted cycliacylation to the quinone **2a**.[13]

Replacing aluminum trichloride with different Lewis acids ($ZnCl_2$, $MgCl_2$, BF_3–Et_2O, $FeCl_3$, $TiCl_4$) resulted in lower yields and selectivity or complete inhibition of the process.

The same procedure can be performed on various substituted aromatic and heteroaromatic β-keto esters to give the corresponding quinones **2** in good yield as shown in the Table I. On the other hand, benzoylacetone under similar experimental conditions afforded an intractable mixture of products. It is noteworthy that an electron enrichment of the aromatic nucleous results in an increase of the reactivity of the substrate according to a typical electrophilic substitution process.

Finally, we have attempted to decarbethoxylate the compounds **2** to the more important quinones **3** (Scheme III). This was best effected by a workup involving heating of the product **2** at 60 °C for 8 h in a 20% aqueous NaOH solution followed by acidification with 10% HCl and heating at 80 °C for 30 min. The yields are almost quantitative based on the compounds **2**. Some representative results are shown in the Table I.

In conclusion we have presented a new and efficient method for the selective synthesis of hydroxylated quinones **2** and **3**. The utility of the present methodology is also indicated by the mild reaction conditions and by the easy access to the starting β-keto esters.[14-19]

Experimental Section

Melting points are uncorrected. ^1H NMR spectra were recorded at 200 MHz. Mass spectra were obtained in EI mode at 70 eV. TLC analyses were performed on Stratochrom SIF silica gel plates (Carlo Erba) developed with hexane–ethyl acetate or methylene chloride–ethyl acetate–acetic acid mixtures. Column chromatography was performed with 60 PF_{254} silica gel (Merck).

All the reagents were of commercial quality from freshly opened containers. $AlCl_3$ was sublimed and $(COCl)_2$ was distilled before use.

Ethyl 3-oxo-3-(4-methylphenyl)propionate (1b),[14] ethyl 3-oxo-3-(4-methoxyphenyl)propionate (1c),[15] ethyl 3-oxo-3-(4-chlorophenyl)propionate (1d),[15] ethyl 3-oxo-3-(2,5-dimethoxyphenyl)propionate (1e),[16] ethyl 3-oxo-3-(2-thienyl)-propionate (1f),[17] and ethyl 3-oxo-3-(1-furyl)propionate (1g)[18] were prepared as described.

Ethyl 3-oxo-3-[2-(*N*-methylpyrrolyl)]propionate (1h) was prepared according to the general method previously reported in the literature:[15] light yellow oil, yield 60%; bp 140 °C/2 mmHg; ^1H NMR ($CDCl_3$) δ 6.96 (1 H, dd, J = 4.2, 1.7 Hz, H-5), 6.85 (1 H, dd, J = 2.5, 1.7 Hz, H-3), 6.13 (1 H, dd, J = 4.2, 2.5 Hz, H-4), 4.20 (2 H, q, J = 7.1 Hz, OCH_2CH_3), 3.93 (3 H, s, CH_3), 3.79 (2 H, s, CH_2), 1.27 (3 H, t, J = 7.1 Hz, OCH_2CH_3); IR (liquid film) cm^{-1} 1740, 1640; MS (m/z) ($M^{\cdot+}$) 195 (25%).

Ethyl 3-oxo-3-[3-(*N*-allylindolyl)]propionate (1i) was prepared according to the method previously reported in the literature[19] by condensing 1-allyl-3-carbethoxyindole with ethyl acetate. The product **1i** was purified by flash chromatography: overall yield 60%, yellow oil; ^1H NMR ($CDCl_3$) δ 8.5–8.3 (1 H, m, H_{arom}), 7.80 (1 H, s, $H_{arom.}$), 7.4–7.1 (3 H, m, $H_{arom.}$), 6.3–5.8 (1 H, m, $CH{=}CH_2$), 5.29 (1 H, dd, $^1/_2$-CH_2, J = 10.0, 1.1 Hz), 5.15 (1 H, dd, $^1/_2$-$CH_2{=}C$, J = 17.0, 1.1 Hz), 4.74 (2 H, d, CH_3N, J = 5.3 Hz), 4.20 (2 H, q, J = 7.1 Hz, OCH_2CH_3), 3.91 (2 H, s, CH_2), 1.27 (3 H, t, J = 7.1 Hz, OCH_2CH_3); IR (liquid film) cm^{-1} 1745, 1655; MS (m/z) ($M^{\cdot+}$ 271 (75%).

β-Keto Ester Oxaloylation. General Procedure. The selected β-keto ester (0.01 mol) and $AlCl_3$ (4 g, 0.03 mol) were dissolved in dry nitromethane (60 mL) under nitrogen. After stirring for 15 min, oxalyl chloride (0.82 mL, 0.01 mol) in dry nitromethane (40 mL) was added dropwise. After 15 min the solution was heated to 80 °C for 3 h. A solution of 10% aqueous oxalic acid was added under stirring at rt. The resulting mixture was extracted with Et_2O (3 × 70 mL). The combined extracts

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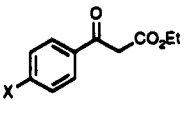
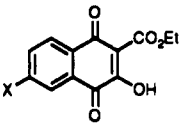
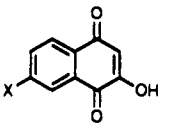
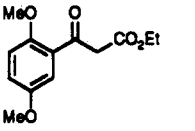
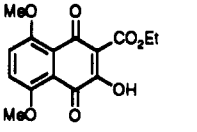
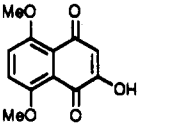
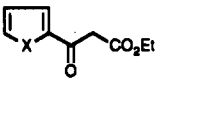
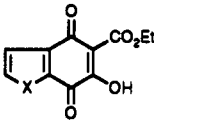
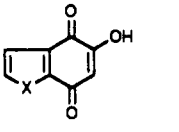
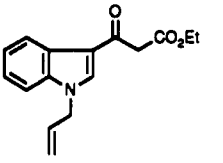
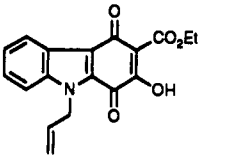
Table I. Oxaloylation of Aroylacetates to Hydroxynaphthoquinones

entry	substrate (1)	product (2)	yield (%)	product (3)	yield (%)
					
a	X = H		85		97
b	X = Me		88		98
c	X = OMe		76		95
d	X = Cl		65		
e			84		90
					
f	X = S		85		95
g	X = O		57		
h	X = N-Me		80		
i			56		

were treated with 10% aqueous Na_2CO_3 (2 × 70 mL). The aqueous layer was washed with Et_2O (50 mL) and acidified with 10% aqueous HCl, and the resulting mixture was extracted with Et_2O (3 × 70 mL). The ethereal solution was dried (Na_2SO_4), the ether was distilled off, and the residue was chromatographed on silica gel plates with CH_2CL_2–$CH_3COOC_2H_5$ mixtures to give the products.

Decarbethoxylation of Carbethoxynaphthoquinones 2 to Hydroxynaphthoquinones 3. General Procedure. A solution of the compound 2 (0.005 mol) in 5% aqueous NaOH (50 mL) was stirred at 60 °C for 8 h. A solution of 10% aqueous HCl (50 mL) was added, and heating was continued for 30 min. After cooling to rt, the mixture was extracted with ether (2 × 50 mL) and dried (Na_2SO_4). Distillation of the solvent and purification (preparative TLC, eluent CH_2Cl_2–$CH_3COOC_2H_5$–CH_3COOH = 63:30:7) yielded the product 3.

2-Ethyl 3-hydroxy-1,4-naphthoquinone-2-carboxylate (2a): yield 2.09 g (85%), orange crystals; mp 108–109 °C (lit.[20] mp 109–110°C); ^{1}H NMR ($CDCl_3$) δ 13.30 (1 H, br s, OH), 8.14 (2 H, m, H-5 and H-8), 7.81 (2 H, m, H-6 and H-7), 4.52 (2 H, q, J = 7.1 Hz, OCH_2CH_3), 1.48 (3 H, t, J = 7.1 Hz, OCH_2CH_3); IR (KBr) 3450, 1670, 1600, 1240 cm^{-1}; MS (m/z) (M$^+$) 246 (3%), 201 (9%), 174 (60%), 133 (14%), 105 (39%).

2-Ethyl 3-hydroxy-6-methyl-1,4-naphthoquinone-2-carboxylate (2b): yield 2.29 g (88%), yellow crystals; mp 148–150 °C (EtOH); ^{1}H NMR ($CDCl_3$) δ 8.05 (1 H, d, J = 7.4 Hz, H-8), 7.89 (1 H, br s, H-5), 7.59 (1 H, dd, J = 7.4, 1.0 H, H-7), 4.51 (2 H, q, J = 7.1 Hz, OCH_2CH_3), 2.49 (3 H, s, CH_3), 1.48 (3 H, t, J = 7.1 Hz, OCH_2CH_3); IR (KBr) 1700, 1670, 1650, 1610, 1260 cm^{-1}; MS (m/z) (M$^+$) 260 (4%), 215 (12%), 188 (74%), 147 (2%), 118 (100%). Anal. Calcd for $C_{14}H_{12}O_5$: C, 64.61; H, 4.65. Found: C, 64.44; H, 4.68.

2-Ethyl 3-hydroxy-6-methoxy-1,4-naphthoquinone-2-carboxylate (2c): yield 2.10 g (76%), red crystals; mp 154–156 °C (EtOH); ^{1}H NMR ($CDCl_3$) δ 8.81 (1 H, d, J = 8.6 Hz, H-8), 7.52 (1 H, br s, H-5), 7.26 (1 H, dd, J = 8.6, 3.0 Hz, H-7), 4.40 (2 H, q, J = 7.1 Hz, OCH_2CH_3), 3.94 (3 H, s, OCH_3), 1.46 (3 H, t, J = 7.1 Hz, OCH_2CH_3); IR (KBr) 3100, 1675, 1600, 1240 cm^{-1}; MS (m/z) (M$^+$) 276 (10%), 202 (100%), 162 (2%), 134 (50%). Anal. Calcd for $C_{14}H_{12}O_6$: C, 60.87; H, 4.38. Found: C, 60.95; H, 4.42.

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2-Ethyl 3-hydroxy-6-chloro-1,4-naphthoquinone-2-carboxylate (2d): yield 1.82 g (65%), yellow crystals; mp 122–124 °C (EtOH); ^{1}H NMR ($CDCl_3$) δ 15.0 (1 H, br s, OH), 8.2–7.3 (3 H, m, H_{arom}), 4.52 (2 H, q, J = 7.1 Hz, OCH_2CH_3), 1.47 (3 H, t, J = 7.1 Hz, OCH_2CH_3); IR (KBr) 3450, 1700, 1670, 1640, 1595, 1220 cm^{-1}; MS (m/z) (M + 2) 282 (2%), (M$^+$) 280 (6%), 235 (11%), 208 (100%), 163 (6%), 138 (83%). Anal. Calcd for $C_{13}H_9ClO_5$: C, 55.63; H, 3.23; Cl, 12.63. Found: C, 55.55; H, 3.30; Cl, 12.69.

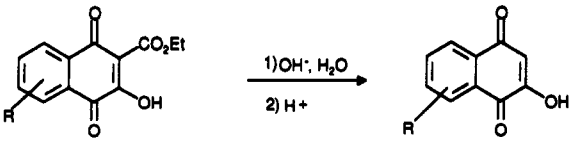
2-Ethyl 3-hydroxy-5,8-dimethoxy-1,4-naphthoquinone-2-carboxylate (2e): yield 2.57 g (84%), red crystals; mp 98–100 °C (EtOH–water); ^{1}H NMR ($CDCl_3$) δ 7.41 (1 H, d, J = 9.6 Hz, H_{arom}), 7.26 (1 H, d, J = 9.6 Hz, H_{arom}), 4.46 (2 H, q, J = 7.1 Hz, OCH_2CH_3), 3.98 (3 H, s, OCH_3), 3.95 (3 H, s, OCH_3), 1.42 (3 H, t, J = 7.1 Hz, OCH_2CH_3); IR (KBr) 3300, 1740, 1675, 1650, 1595, 1230 cm^{-1}; MS (m/z) (M$^+$) 306 (52%), 260 (62%), 232 (50%), 203 (100%), 163 (14%). Anal. Calcd for $C_{15}H_{14}O_7$: C, 58.82; H, 4.61. Found: C, 59.03; H, 4.58.

Ethyl 5-hydroxy-4,7-dioxobenzo[*b*]thiophene-6-carboxylate (2f): yield 2.14 g (85%), orange crystals; mp 128–130 °C (EtOH); ^{1}H NMR ($CDCl_3$) δ 7.66 (1 H, d, J = 5.0 Hz, H_{arom}), 7.58 (1 H, d, J = 5.0 Hz, H_{arom}), 4.49 (2 H, q, J = 7.1 Hz, OCH_2CH_3), 1.46 (3 H, t, J = 7.1 Hz, OCH_2CH_3); IR (KBr) 1700, 1670, 1665, 1250 cm^{-1}; MS (m/z) (M$^+$) 252 (100%), 207 (17%), 178 (93%), 138 (6%), 111 (13%). Anal. Calcd for $C_{11}H_8O_5S$: C, 52.37; H, 3.20; S, 12.71. Found: C, 52.25; H, 3.12; S, 12.80.

Ethyl 5-hydroxy-4,7-dioxobenzo[*b*]furan-6-carboxylate (2g): yield 1.35 g (57%), red crystals; mp >178 °C dec (EtOH); ^{1}H NMR (CD_3OD) δ 7.81 (1 H, d, J = 1.8 Hz, H-2), 6.82 (1 H, d, J = 1.8 Hz, H-3), 4.31 (2 H, q, J = 7.1 Hz, OCH_2CH_3), 1.31 (3 H, t, J = 7.1 Hz, OCH_2CH_3); IR (KBr): 3420 (b), 1660, 1595, 1260 cm^{-1}; MS (m/z) (M$^+$) 236 (100%), 192 (15%), 162 (83%), 122 (11%), 94 (48%). Anal. Calcd for $C_{11}H_8O_6$: C, 55.94; H, 3.41. Found: C, 55.80; H, 3.45.

Ethyl *N*-methyl-5-hydroxy-4,7-dioxobenzo[*b*]pyrrole-6-carboxylate (2h): yield 1.99 g (80%), red crystals; mp 112–113 °C (CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 6.83 (1 H, d, J = 2.7 Hz, H-2); 6.63 (1 H, d, J = 2.7 Hz, H-3), 4.48 (2 H, q, J = 7.1 Hz, OCH_2CH_3), 3.99 (3 H, s, CH_3), 1.46 (3 H, t, J = 7.1 Hz, OCH_2CH_3); IR (KBr) 3400 (b), 1650, 1580, 1280, 1240 cm^{-1}; MS (m/z) (M$^+$) 249 (37%),

Scheme III



2 3

204 (19%), 175 (100%), 135 (4%), 107 (50%). Anal. Calcd for $C_{12}H_{11}NO_5$: C, 57.83; H, 4.45; N, 5.62. Found: C, 57.78; H, 4.49; N, 5.73.

Ethyl 9-allyl-2-hydroxy-1,4-dioxo-1,4-dihydrocarbazole-3-carboxylate (2i): yield 1.82 g (56%), dark-red crystals; mp 141–144 °C (EtOH); ^{1}H NMR ($CDCl_3$) δ 8.6–8.1 (1 H, d, $H_{arom.}$), 7.7–7.2 (3 H, m, $H_{arom.}$), 6.2–5.8 (1 H, m, CH=CH_2), 5.5–4.9 (2 H, m, CH_2=C), 4.7–4.5 (2 H, m, CH_2N), 4.31 (2 H, q, J = 7.1 Hz, OCH_2CH_3), 1.31 (3 H, t, J = 7.1 Hz, OCH_2CH_3); IR (KBr) 1675, 1660, 1590, 1280, 1260 cm^{-1}; MS (m/z) (M^+) 325 (63%), 279 (50%), 251 (100%), 211 (81%), 183 (43%). Anal. Calcd for $C_{18}H_{15}NO_5$: C, 66.45; H, 4.65; N, 3.41. Found: C, 66.54; H, 4.70; N, 3.35.

2-Hydroxy-1,4-naphthoquinone (3a): yield 0.84 g (97%), orange crystals; mp 191–192 °C (EtOH) (lit.[21] mp 190–191 °C).

2-Hydroxy-7-methyl-1,4-naphthoquinone (3b): yield 0.92 g (98%), orange crystals; mp 205–206 °C dec EtOH) (lit.[22] mp 206 °C dec).

2-Hydroxy-7-methoxy-1,4-naphthoquinone (3c): yield 0.97 g (95%), orange crystals; mp 115–116 °C (EtOH) (lit.[23] mp 116–117 °C).

2-Hydroxy-5,8-dimethoxy-1,4-naphthoquinone (3e): yield 1.05 g (90%), red crystals; mp 195–196 °C (EtOH) (lit.[24] mp 194 °C).

5-Hydroxy-4,7-dioxobenzo[*b*]thiophene (3f): yield 0.86 g (95%), yellow crystals; mp 152–154 °C dec EtOH; ^{1}H NMR ($CDCl_3$) 7.64 and 7.55 (2 H, 2 d, J = 5.1 Hz), 6.21 (1 H, s); IR (KBr) 1680, 1640 cm^{-1}; MS (m/z) (M^+) 180 (100), 152 (24), 111 (62). Anal. Calcd for $C_8H_4SO_3$: C, 53.33; H, 2.24; S, 17.80. Found: C, 53.22; H, 2.32; S, 17.71.

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