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SYNTHESIS OF α-DIKETONES FROM α,β-DIHYDROXY KETONES

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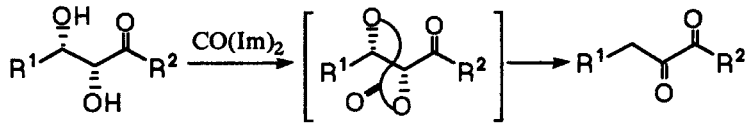
ABSTRACT: Treatment of α,β-dihydroxy ketones with carbonyldiimidazole resulted in the formation of α-diketones based on the elimination of the cyclic carbonates formed *in situ*.

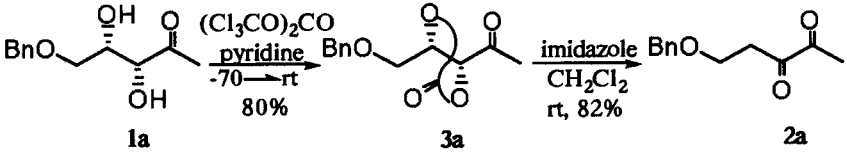
α-Diketones **2** have attracted considerable interest because of their utility as synthetic intermediates[1] to undergo a variety of reactions, for example, the benzil-benzilic acid rearrangement[2] and dioxaphospholene formation[3] and etc., Several methods for preparation of α-diketones have been reported which include oxidation of acetylenes,[4] selenium dioxide oxidation of various monoketones,[5] acyloin condensation of esters followed by subsequent oxidation,[6] acylation of acyl anions or acyl anion equivalents,[7] coupling of acyl chlorides mediated by SmI_2 and $SmCp_2$,[8] and others.[9] Here we wish to report a convenient one-pot procedure for the synthesis of α-diketones **2** from α,β-dihydroxy ketones **1** based on the elimination of the carbonates **3** formed *in situ* by treating with carbonyldiimidazole (Scheme 1).



1 3 2

Scheme 1

The results are summarized in Table 1. Treatment of **1a** with carbonyldiimidazole (1.5 equiv) in CH_2Cl_2 at room temperature for 0.5 h gave a mixture of the diketone **2a** and the cyclic carbonate **3a** by checking tlc, which was subjected to prolonged stirring for 2 h to afford the diketone **2a** as the only isolated product in 89% yield (entry 1). As indirect evidence for the formation of the cyclic carbonate **3a** in the above reaction, reaction of **1a** with triphosgene (0.5 equiv)[10] in the presence of 6 equiv of pyridine at -70°C ⟶ rt gave pure cyclic carbonate **3a** in 80% yield, which was treated with 2 equiv of imidazole in CH_2Cl_2 to afford the diketone **2a** (Scheme 2).



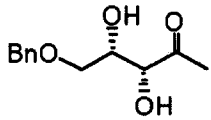
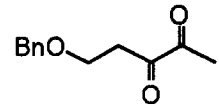
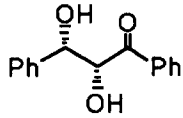
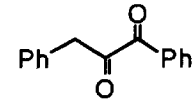
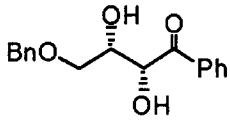
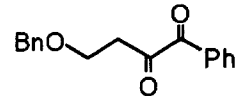
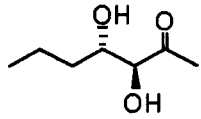
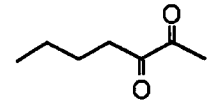
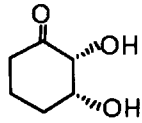
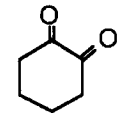
1a **3a** **2a**

Scheme 2

This methodology was also applied to prepare α-diketones **2b-c**, which is shown in Table 1 (entries 2 and 3). For the *threo*-dihydroxy ketone **1d**, reaction with carbonyldiimidazole at room temperature for 10 min gave the cyclic carbonate **3d** (checked by tlc) and a mixture of the carbonate and the diketone **2d** after stirring for 2 h, which without separation was refluxed for 24 h to afford **2d** (entry 4). For the cyclic dihydroxy ketone **1e**, stirring for 0.5 h provided the cyclic carbonate **3e** and stirring for 5 h afforded the diketone **2e**[11] (entry 5), which was an equilibrium mixture of keto and enol form.

In summary, α-diketones were synthesized by mild and one-pot dehydration of α,β-dihydroxy ketones.

Table 1. Systhesis of α-Diketones from α,β-Dihydroxy Ketones

Entry	Substrate	Reaction Conditions	Product	Yield(%)
1	 **1a**	$CO(Im)_2$, CH_2Cl_2 rt, 2 h	 **2a**	89%
2	 **1b**	$CO(Im)_2$, EtOAc rt, 6 h	 **2b**[12]	68%
3	 **1c**	$CO(Im)_2$, EtOAc rt, 12 h	 **2c**	71%
4	 **1d**	$CO(Im)_2$, CH_2Cl_2 40°C, 24 h	 **2d**[7a]	60%
5	 **1e**	$CO(Im)_2$, CH_2Cl_2 rt, 5 h	 **2e**[11]	74%

EXPERIMENTAL

5-Benzyloxy-2,3-pentanedione (2a) : General procedures :

To a stirred solution of $CO(Im)_2$ (290 mg, 1.8 mmol) in dry CH_2Cl_2 (3 ml) was added the diol **1a** (270 mg, 1.2 mmol) in dry CH_2Cl_2 (1.5 ml) at room temperature. The reaction mixture was stirred for 2 h. The mixture was quenched with 5% HCl (10 ml) and then extracted with ether (15 ml) for three times. The organic layer was washed with water three times and dried over anhydrous $MgSO_4$ and then concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel using EtOAc/hexanes 1 : 3 as eluent to afford **2a** (219 mg, 89%). TLC ; SiO_2, EtOAc/hexanes 1 : 3 R_f = 0.70. IR (neat) : 1711 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$) δ 2.30 (s, 3H), 3.01 (t, 2H, J = 6Hz), 3.78 (t, 2H, J = 6Hz), 4.52 (s, 2H), 7.15 (s, 5H). GC-MS (HP-1, 0.2mm X 25m, oven temp 200 - 280°C, carrier gas : N_2), retention time: 3.20 min. MS (m/e) 206 (M^+), 163 (6), 100 (22), 91 (base peak), 77 (11), 65 (16), 55 (12), 43 (39). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88 ; H, 6.84. Found: C, 70.06 ; H, 6.97.

(3*R*,4*S*)-5-Benzyloxy-3,4-dihydroxy-2-pentanone 3,4-cyclic carbonate (3a) :

To a stirred solution of triphosgene (200 mg, 0.68 mmol) in dry CH_2Cl_2 (3 ml) was added dropwise to a solution of pyridine (641 mg, 8.10 mmol) and the diol **2a** (300 mg, 1.35 mmol) in dry CH_2Cl_2 (5 ml) cooled to -70°C. Once addition was complete the reaction was then allowed to warm room temperature. The reaction mixture was qunched with saturated aqueous ammonium chloride and the aqueous portion was separated and extracted with CH_2Cl_2 (15 ml). The organic layer was washed with 1N HCl, saturated aqueous $NaHCO_3$, brine, dried over anhydrous $MgSO_4$ and then concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel using EtOAc/hexanes 1 : 1 as eluent to afford **3a** (270 mg, 80%). TLC ; SiO_2, EtOAc/hexanes 1 : 1 R_f = 0.49. IR (neat) : 1800, 1717 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.35 (s, 3H), 3.65 (dd, 1H, J = 9, 8 Hz), 3.85 (dd, 1H, J = 9, 3 Hz), 4.6 (m, 2H), 4.79 (m, 1H), 4.86 (m, 1H), 7.3 (m, 5H). GC-MS (HP-1, 0.2mm X 25m, oven temp 220 - 280 °C, carrier gas : N_2), retention time: 8.22 min. MS (m/e) 250 (M^+), 162 (13), 105 (base peak), 91 (54), 79 (12), 77 (64), 51 (23). Anal. calcd for $C_{13}H_{14}O_5$: C, 61.65 ; H, 5.73. Found : C, 63.39 ; H, 5.64.

5-Benzyloxy-2,3-pentanedioneb (2a) :

To a stirried solution of the carbonate **3a** (225 mg. 0.9 mmol) in CH_2Cl_2 (3 ml) was added imidazole (123 mg, 1.8 mmol). and stirred at room temperature for 2 h. The mixture was quenched with 5% HCl (9 ml) and then extracted with ether (15 ml) for three times. The organic layer was washed with water and dried over anhydrous $MgSO_4$ and then concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel using 1 : 3 as eluent to afford **2a** (152 mg, 82%). TLC ; SiO_2, EtOAc/hexanes 1 : 3 R_f = 0.70, IR (neat) : 1711 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$) δ 2.31 (s, 3H), 3.01 (t, 2H, J = 6 Hz), 3.78 (t, 2H, J = 6 Hz), 4.52 (s, 2H), 7.15 (s, 5H).

1,3-Diphenyl-1,2-propanedione (2b) :

TLC ; SiO_2, EtOAc/hexanes 1 : 3 R_f = 0.56. IR (neat) : 1714, 1672, 1667 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 4.20 (s, 2H), 7.20 - 7.89 (m, 10H).

4-Benzyloxy-1-phenyl-1,2-butanedione (2c) :

TLC ; SiO_2, EtOAc/hexanes 1 ; 1 R_f = 0.79. IR (neat) : 3400, 1720, 1707 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 3.16 (t, 2H, J = 6 Hz), 3.88 (t, 2H, J = 6 Hz) 4.46 (s, 2H), 7.29 - 7.85 (m, 10H) MS (m/e) 268 (M^+), 91 (base peak).

2,3-Heptanedione (2d) :

TLC ; SiO_2, EtOAc/hexanes R_f = 0.71. IR (neat) : 1714 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$) δ 0.95 (t, 3H), 1.65 (m, 4H), 2.32 (s, 3H), 2.7 (t, 2H).

1,2-Cyclohexanedione(2e) :

TLC ; SiO_2, EtOAc R_f = 0.71. IR (neat) : 3380, 1720, 1660 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$) δ 2.1 (m, 3H), 2.45 (m, 4H), 6.18 (t, 1H).

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