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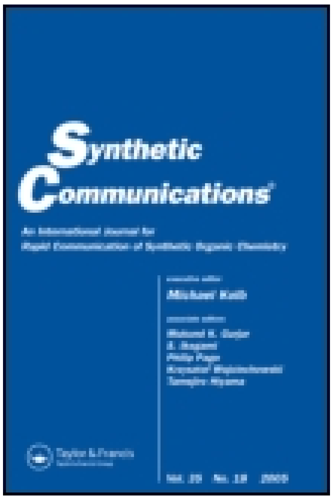

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INDIUM-MEDIATED ALLYLATION OF 1,2-DIKETONES

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INDIUM-MEDIATED ALLYLATION OF 1,2-DIKETONES

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ABSTRACT

Indium-mediated allylation of 1,2-dicarbonyl compounds with indium and allylic bromides was achieved in the presence of $n\mathrm{Bu_4NI}$ or NH_4Cl as additive to afford mono- and/or diallylated products in good yields.

Carbon–Carbon bond formation promoted by allyl metals is one of the fundamental process in organic synthesis.[1] Recently indium-mediated Barbier-type allylation of variety of ketones and aldehydes in aqueous medium received much attention.[2] Li et al.[3] reported the indium-mediated allylation of enolizable 1,3-dicrabonyl compounds under aqueous medium. However, to the best of our knowledge, allylation of 1,2-dicarbonlyl compounds has not been known. Here we wish to report indium-mediated allylation of 1,2-carbonyl compounds in aqueous medium or methanol.

We selected phenylglyoxal as a substrate for allylation of 1,2-diketones and reacted with indium and allylic bromides. As solvents, H_2O, DMF, DMF/H_2O (1:1), THF, THF/H_2O (1:1) were used, but the reactions were sluggish. The addition of the additive was crucial. Thus by adding $n\mathrm{Bu_4NI}$

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(5 mol%) in H_2O, we could get the monoallylated product **3a** in 76% yield (entry 1 in Table 1). With crotyl bromide, the mono-allylated product **3b** was afforded (entry 2). When NH_4Cl was used as an additive in the reaction of phenylglyoxal with allyl bromide in MeOH we could successfully get the diallylated product **3c** in 86% yield (entry 3). Crotyl bromide **2b** and methallyl bromide **2c** were also treated with indium followed by glyoxal **1a** to give the diols **3b** and **3e** (entries 4 and 5). When this method was applied to 1,2 diketones, 1-phenyl-1,2-propandione (**1b**), a separable mixture of mono- and diallylation products **3f** (33%) and **3g** (66%) were afforded (entry 6). For benzil (**1c**) as a source of 1,2-diketones the reaction with allylic bromide and indium provided mono-allylated product **31** as a sole product in 93% yield (entry 9). With crotyl bromide and indium, the reaction of **1c** provided a mixture of unseparable *cis* and *trans* (79 : 21) adduct in 84% yield (entry 10).[4] Finally, treatment of afforded **1c** with indium and methallyl bromide afforded **3n** in 81% yield (entry 11). In summary we have successfully carried out the reaction of 1,2-diketones with indium and allylic bromides by adding additives to afford mono- and/or diallylated products.

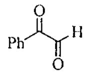
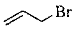
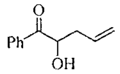
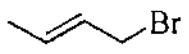
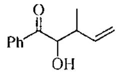
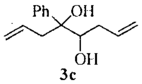
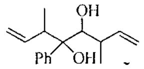
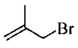
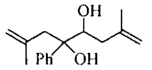
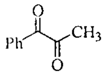
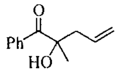
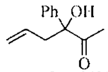
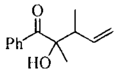
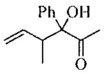
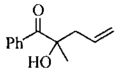
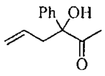
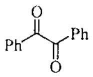
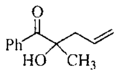
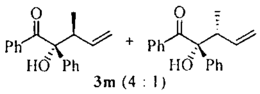
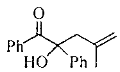
EXPERIMENTAL SECTION

Typical Procedures

Method **A**: Preparation of 2-Hydroxy-1-phenyl-pent-4-en-1-one (**3a**). To a stirred solution of nBu$_4$NI (6.0 mg, 5 mol%) and indium (76 mg, 1.23 mmol) in H_2O (10 mL) was added allyl bromide (120 mg, 1.82 mmol) followed by phenylglyoxal (**1a**) (50 mg, 0.61 mmol) at room temperature under N_2 and the mixture was stirred at rt for 4 h. The reaction mixture was extracted with ether (20 mL) and the organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo. The crude product was separated by SiO_2 column chromatography (EtOAc:hexanes = 1:10, $R_f = 0.21$) to afford the coupled product **3a** (85 mg, 76%). TLC, SiO_2, EtOAc : hexanes, $R_f = 0.29$. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37 (m, 1H), 2.70 (m, 1H), 3.74 (d, 1H, $J = 7.0$ Hz), 5.00 (dd, 1H, $J = 1.3$, 17.0 Hz), 5.18 (m, 1H), 5.80 (m, 1H), 7.25 (m, 2H), 7.63 (m, 1H), 7.92 (m, 1H). IR (neat) 3355, 1265, 1115 cm^{-1}. MS (EI): *m/e* (relative intensity) = 177 (0.37), 176 (M^+, 2), 135 (25), 105 (100), 77 (30).

Method **B**: Preparation of 4-Phenyl-octa-1,7-diene-4,5-diol (**3c**). To a stirred solution of NH_4Cl (33 mg, 0.61 mmol) and indium (76 mg, 1.23 mmol) in MeOH (10 mL) was added allyl bromide (120 mg, 1.82 mmol) followed by phenylglyoxal (**1a**) (50 mg, 0.61 mmol) at room temperature under N_2 and the mixture was stirred at reflux for 6 h. The reaction mixture was extracted with

Table 1. Indium-Mediated Allylation of 1,2-Dicarbonyl Compounds[a]

Entry	Substrate	Allyl halide	Product	Yield(%)
1	 1a	 2a	 3a	76[b]
2	1a	 2b	 3b	72[b]
3	1a	2a	 3c	86
4	1a	2b	 3d	80
5	1a	 2c	 3e	77
6	 1b	2a	 3f (33%) +  3g (66%)	91
7	1b	2b	 3h (34%) +  3i (51%)	85
8	1b	2c	 3j (36%) +  3k (46%)	82
9	 1c	2a	 3l	93
10	1c	2b	 3m (4 : 1)	84
11	1c	2c	 3n	81

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[a] The reactions were run with allylic bromide (3equiv), indium (2 equiv), NH_4Cl (1 equiv) in 10mL MeOH at 60 °C for 6 h. [b] The reactions were run with allylic bromide (3 equive), $n\mathrm{Bu}_4\mathrm{NI}$ (5 mol %) in 10 mL H_2O at rt for 6 h.

ether (20 mL) and the organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo. The crude product was separated by SiO_2 column chromatography (EtOAc : hexanes = 1:10, $R_f = 0.16$) to afford the coupled product **3c** (85 mg, 86%). TLC, SiO_2, EtOAc : hexanes, $R_f = 0.29$. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.94 (m, 1H), 2.10 (m, 1H), 2.20 (br, 1H), 2.53 (br, 1H), 2.83 (m, 1H), 2.87 (m, 1H), 3.80 (d, 1H, $J = 7.0$ Hz), 5.00 ~ 5.47 (m, 4H), 5.51 (m, 1H), 5.76 (m, 1H), 7.25 (m, 1H), 7.40 (m, 4H). IR (KBr) 3055, 1265, 1115 cm^{-1}. MS (EI): *m/e* (relative intensity) = 177 (M^+-C_3H_5, 9), 147 (17), 105 (100), 77 (12).

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