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A New Synthesis of 1,5-Dicarbonyl Compounds under Neutral Conditions

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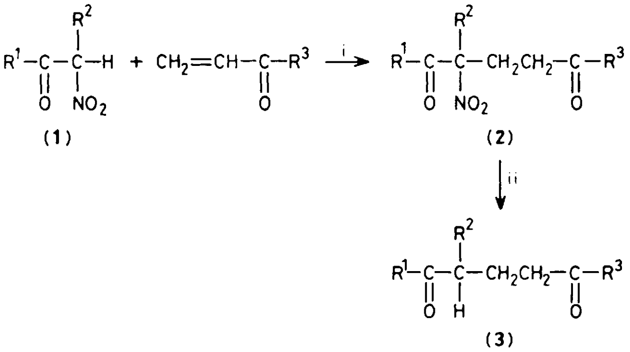
Michael addition of α-nitroketones to methyl vinyl ketone or acrylaldehyde followed by denitration with Bu_3SnH affords 1,5-dicarbonyl compounds in good yields.

1,5-Dicarbonyl compounds (**3**) are an important class of compounds especially as intermediates for the preparation of cyclohexenones.[1] The available routes to (**3**) include 1,4-addition of enolates or enolate equivalents to α,β-unsaturated carbonyl compounds,[2] or alkylation of ketones with a 3-oxoalkyl halide equivalent.[3] Most of these routes are lengthy, require multistep preparation of a special reagent, or give low overall yields. These difficulties are serious in the preparation of δ-oxo-aldehydes owing to the instability of acrylaldehyde under basic conditions. We have found a short route using readily available starting materials which gives high yields of 1,5-dicarbonyl compounds including δ-oxo-aldehydes, as outlined in Scheme 1.

The requisite α-nitroketones (**1**) were prepared by acylation of nitroalkanes[4]† or by oxidation of β-nitroalcohols.[5] Michael addition of (**1**) to methyl vinyl ketone or acrylaldehyde proceeded in the presence of a catalytic amount (0.1 equiv.) of triphenylphosphine to give the adduct (**2**) in good yields.[6] Denitration of (**2**) was carried out by heating a stirred mixture of (**2**), Bu_3SnH (1.3 equiv.), and AIBN (0.3 equiv.) in benzene at 80 °C for 2 h to give the desired 1,5-dicarbonyl compounds



Scheme 1. Reagents: i, Ph_3P, THF, room temperature; ii, Bu_3SnH, AIBN, benzene, 80 °C. THF = tetrahydrofuran, AIBN = azoisobutyronitrile.

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† Reaction of the potassium salt of nitroalkanes with *N*-acylimidazoles in dimethyl sulphoxide at room temperature gave (**1**) in 70—90% yields.

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Table 1. Michael addition of α-nitroketones (**1**) to methyl vinyl ketone or acrylaldehyde, and preparation of 1,5-dicarbonyl compounds (**3**).

R^1	R^2	R^3	Time/h (**1**)→(**2**)	Yield/% (**2**)	Yield/% (**3**)
Ph	H	Me	24	81	78
n-C_7H_{15}	Me	Me	24	91	80
n-C_7H_{15}	H	Me	24	85	90
Pr^i	H	Me	24	77	82
$-[CH_2]_4-$		Me	24	94	90
Ph	Me	H	1	84	76
Pr^n	Et	H	1	87	71
n-C_7H_{15}	Me	H	1	87	87
n-C_4H_9	Et	H	1	90	76
$-[CH_2]_4-$		H	1	92	77

(**3**), where ketone and aldehyde functions were not affected under these conditions.[7] The results are summarized in Table 1. Thus, the present method consists of genuinely simple procedures and requires neither acidic nor basic conditions, so it affords some advantages over the conventional methods.[1]

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