

An Alternative Route to 1,3-Diketones Promoted By Samarium Diiodide

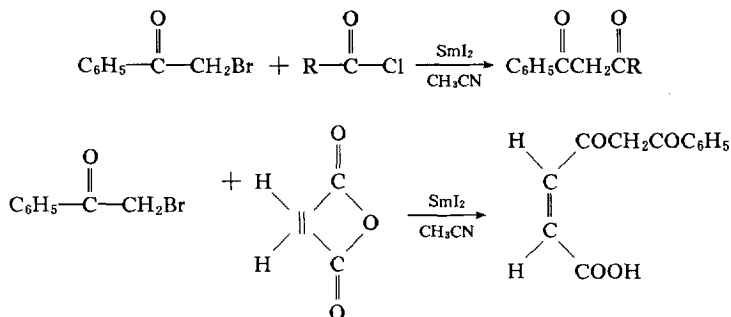
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ABSTRACT; SmI₂ promoted condensation of α-haloketones with carboxylic acid chlorides or anhydrides leads to 1,3-diketones. Copyright © 1996 Elsevier Science Ltd

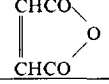
As a superior one-electron transfer reducing agent and coupling agent, samarium (II) iodide has been extensively used in organic synthesis in the last decade.¹ Most of the coupling reactions promoted by SmI₂ are carbonyl addition reactions, including Barbier-Type reactions and Pinacolic couplings, in which at least one of the carbonyl groups is opened to become such groups as hydroxyl or a carbon-carbon double bond group etc. Wurtz-type coupling reactions promoted by SmI₂ can be carried out effectively, but the regioselectivity is low.^{1,2}

Here we wish to report that α-haloketones can reductively couple with carboxylic acid halides or anhydrides mediated by SmI₂ to give 1,3-diketones:



As far as we know, this was the first example of a 1,3-diketone synthesis using SmI₂. The mechanism of the reaction may be through the samarium enolates as we have already suggested in our previous work,³ which is somewhat different from Molander's.⁴ In the classical procedures, 1,3-diketones may be synthesized by condensation of ketones, having an α-hydrogen atom, with acid chlorides, but the reaction is usually effected by means of a strong basic reagent such as sodium amide,⁵ with acid anhydrides a Lewis acid such as boron trifluoride is generally used.⁶ O-Acyl derivatives are also formed in these reactions.⁷ In

our methodology synthesizing 1,3-diketones, both acid chlorides and anhydrides can be used as the substrates, the ratio of O-acyl derivatives is neglectedly small (less than 5%).

No	Acid Chlorides	Reaction Times (h)	Yields (%)	Acid Anhydrides	Reaction Times (h)	Yields (%)
1	CH ₃ COCl	0.5	83	(CH ₃ CO) ₂ O	1	89
2	CH ₃ CH ₂ COCl	0.5	77		1.5	90
3	CH ₃ CH ₂ CH ₂ COCl	0.5	82	(CH ₃ CH ₂ CO) ₂ O	1	85
4	(CH ₃) ₂ CHCH ₂ COCl	0.5	80	(CH ₃ CH ₂ CH ₂ CO) ₂ O	1	89
5	CH ₃ (CH ₂) ₄ COCl	1	79	[(CH ₃) ₂ CHCH ₂ CO] ₂ O	1	81
6	PhCOCl	1	85	[CH ₃ (CH ₂) ₄ CO] ₂ O	1.5	79
7	CH ₃ (CH ₂) ₇ COCl	1	71	(PhCO) ₂ O	1.5	85

The reactions were carried out at room temperature and in neutral, mild conditions with satisfactory yields. But the reaction must be conducted in the strict absence of active hydrogen in order to avoid a reduction product (acetophenone).

Typical procedure: The solvents were thoroughly dried. The acid chlorides and acid anhydrides were freshly distilled before use. The reactions were performed in a Schlenk apparatus and under a nitrogen atmosphere.

α -Halo ketone (2mmol) was added to SmI₂ (4mmol, in 40ml CH₃CN) at room temperature. After stirring for 0.5 hr, acid chloride or acid anhydride (2mmol) was added. The reaction mixture was stirred for 2 hrs and then the solvent was evaporated under vacuum. The residue was added to HCl (0.1M, 1ml) and extracted with ether. After usual work-up, the product was purified by chromatography.

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