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Carbon—Carbon Double Bond Formation Between α—Haloketones And Aldehydes Promoted By Samarium Triiodide

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Abstract: Reaction of α—haloketones with aldehydes in the presence of either SmI_3 or Sm/I_2 formed the carbon—carbon double bond to give α,β—unsaturated ketones in good to excellent yields under mild conditions. Samarium(Ⅲ) enolates formed from the dehalogenation of α—haloketones by SmI_3 were assumed to be the reaction intermediates.

Recently the application of lanthanoid compounds in organic synthesis has been of great interest. In particular, a number of exciting samarium diiodide promoted synthetic transformation have been developed.[1] Trivalent lanthanoid compound have also been applied in organic synthesis. For example, lanthanoid trichlorides were used in combination with NaBH4,[2] $LiAlH_4$,[3] or Grignard reagent[4] for selective reduction or alkylation of carbonyl compounds; and CeI_3 or $CeCl_3/NaI$ was used in the carbon—carbon bond formation between α—haloketones and aldehydes.[5] In our previous work in the reaction of α—haloketones and carbonyl compounds in the presence of samarium diiodide, we assumed that the reaction proceeded via samarium(Ⅲ) enolates, which were formed from the dehalogenation of α— haloketone by both samarium diiodide and samarium(Ⅲ)/I^- species.[6] This presumption has led us to study on the reaction of α—haloketones with carbonyl compounds in the presence of samarium triiodide. Here we wish to report a convenient synthetic method of α,β—unsaturated ketones from α—haloketones and aldehydes promoted by either samarium triiodide or samarium powder/iodine.

We found that the reaction of equimolar phenacyl bromide with benzaldehyde or its derivatives in the presence of one equivalent of SmI_3 gave the ketones in high yields. SmI_3 could be easily prepared from powdered samarium and iodine (molar ratio 1 : 1.5), either stepwise, prior to the reaction (Method A), or in situ, in an one pot reaction (Method B). Similar treatment of phencyl bromide with α,β—unsaturated aldehydes, such as cinnamaldehyde and acrolein gave the corresponding buta—1, 3—dienyl ketones in good yields. However, the reactions of phenacyl bromide with p - N, N dimethylaminobenzaldehyde or ketones, such as cyclohexanone, did not give the corresponding α,β

—unsaturated ketones or α—hydroxy ketones. Besides, treatment of ethyl bromoacetate and benzaldehyde with SmI_3 gave no Reformatsky—type product, starting materials being recovered. In the reaction of aldehydes with steric hindered α—haloketone, such as α—bromocamphor or α—chloro—α—phenylacetophenone the desired products also were not obtained. The results were summarized in Table 1.

Table 1. Carbon—Carbon double Bond formation between α—Haloketones and Aldehydes by SmI_3 or Sm/I_2

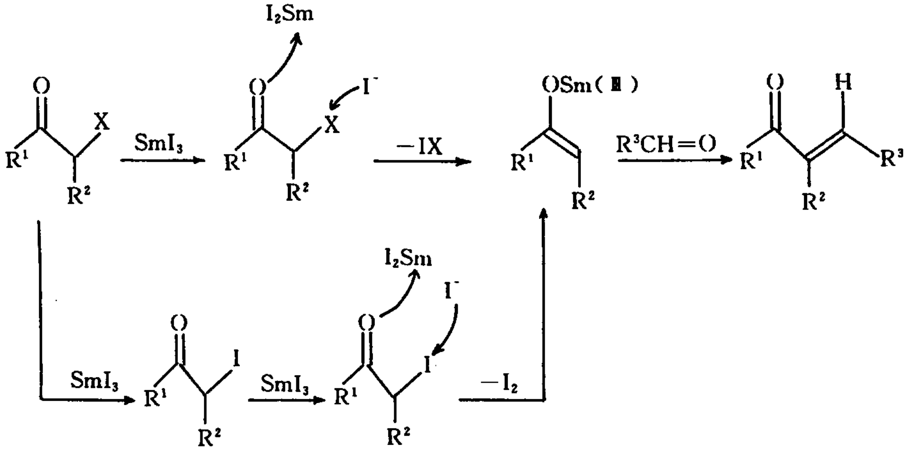
Entry	α—Haloketone	Aldehyde	Product[a]	Yield[b] (%)	m. p. (°C) (lit.)
1	$C_6H_5COCH_2Br$	$p-O_2NC_6H_4CHO$	$p-O_2NC_6H_4CH=CHCOC_6H_5$	94(93)	163—164(164)
2	$C_6H_5COCH_2Br$	$m-O_2NC_6H_4CHO$	$m-O_2NC_6H_4CH=CHCOC_6H_5$	93(92)	143—145(145)
3	$C_6H_5COCH_2Br$	$p-ClC_6H_4CHO$	$p-ClC_6H_4CH=CHCOC_6H_5$	92(90)	103—1047 (103—104)
4	$C_6H_5COCH_2Br$	$p-BrC_6H_4CHO$	$p-BrC_6H_4CH=CHCOC_6H_5$	91(88)	123—124 (123.5)
5	$C_6H_5COCH_2Br$	$C_6H_5CH=CHCHO$	$C_6H_5COCH=CHCH=CHC_6H_5$	75(71)	100—102 (101—102)
6	$C_6H_5COCH_2Br$	$CH_2=CHCHO$	$C_6H_5COCH=CHCH=CH_2$	56(57)	47—47.5 (47—48)
7	$p-BrC_6H_4COCH_2Br$	C_6H_5CHO	$p-BrC_6H_4COCH=CHC_6H_5$	85(87)	112—113 (113)
8	$p-BrC_6H_4COCH_2Br$	$p-O_2NC_6H_4CHO$	$p-BrC_6H_4COCH=CHC_6H_4NO_2$	85(87)	160—162 (159—162)

a. Predominantly trans—isomer

b. Isolated yield in the stepwise reaction (Method A).

The data in parentheses were the isolated yields in the one pot reaction (Method B)

By analogy with the SmI_2—promoted reaction mechanism,[6] SmI_3—promoted carbon carbon double bond formation reaction might also proceed via the samarium(Ⅲ) enolate, which was formed from the dehalogenation of α—haloketone by SmI_3. The dehalogenation of α—haloketone might proceed via the following two pathways: a direct reduction of C—Br bond by the interaction with SmI_3 and/or a halogen exchange leading to the α—iodoketone which was then reduced by I^- /Sm(Ⅲ) species in the similar manner. The observed appearance of I_2 and/or IX, as well as the isolation of α—iodoketone when α—bromoacetophenone was treated with SmI_3 in the absence of aldehyde supported the following mechanism:



In the one—pot reaction, as a possible pathway, direct reaction of α—haloketone with samarium metal was ruled out since the desired product could not be obtained when the one—pot reaction was performed in the absence of iodine under the same conditions.

General procedures are as follows. Method A: Preparation of SmI_3 and reaction of α—haloketones with aldehyde in the presence of SmI_3. Under anhydrous conditions, a mixture of powdered samarium (0.32g, 2mmol) and iodine (0.75g, 3mmol) in dry THF (20ml) was stirred at room temperature until samarium disappeared (ca. 0.5h). To the resulting pale yellow suspension of SmI_3 was added simultaneously a α—haloketone (2mmol) and an aldehyde (2mmol) and stirred for 2h. The reaction mixture become dark red and homogeneous. The solution was quenched with HCl, extracted with ether. The combined organic layer was washed with aqueous $Na_2S_2O_3$, dried over anhydrous $MgSO_4$ and evaporated to give crude product. The crude product was then purified by column chromatography on silica gel eluting with CH_2Cl_2 or recrystallized from ethanol. All ketone products have physical data(m. p.) and spectral characteristics (IR and ^1H NMR) in agreement with literature data.

Method B: One — pot reaction of α — haloketone with aldehydes in the presence of samarium and iodine. Under anhyrdous conditions, a mixture of α—haloketone (2mmol), aldehyde (2mmol), samarium powder (0. 32g, 2mmol) and iodine (0. 75g, 3mmol) in dry THF (20ml) was stirred at room temperature for 2h. and then treated in a similar manner as described in Method A to give the product.

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