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A FACILE ROUTE TO CONVERT ACETYLACETONE INTO OTHER β-DIKETONES WITH ACYL CHLORIDES PROMOTED BY SAMARIUM TRIIODIDE

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ABSTRACT: Reaction of acetylacetone with acyl chlorides in the presence of SmI_3 gave β-diketones $RCOCH_2COCH_3$ (I) or $RCOCH_2COR$ (II) in good yields under mild and neutral conditions.

Recently, lanthanide compounds, in particular samarium diiodide, have been of great interest as versatile reagents in organic synthesis[1]. At the same time, much attention has been devoted to the application of samarium (III) compoudns[2]. For example, we have reported that, promoted by SmI_3, α-haloketones can react with aldehydes to give α,β-unsaturated ketones[3], Sasai reported that 1-hyloro-2-heptanone is able to react with benzaldehyde to form α-chloro-β-hydroxy ketones catalyzed by $Sm(HMDS)_3$[4], in the presence of Sm

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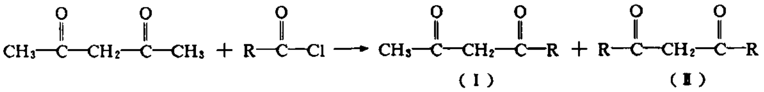
$(OTF)_3$, benzylamine can add to ethyl crotonate to form β-amino esters[5]; Mori reported that, mediated by SmI_2 or SmI_3, α-haloketones may react with α-ketocarboxylates and α-diketones to give α-hydroxy-γ-ketocarboxylates and 2-hydroxy-1,4-diketones respectively[6]. Very recently, we have found that samarium triiodide promoted the reaction of ω-bromoacetophenone with acyl chloride[7]. Now we wish to report that SmI_3, which is considered as a hard Lewis acid, can promote the reaction of acetylacetone with acyl chlorides to give new β-diketones. The reaction is shown in the scheme and the results are summarized in table 1.

We found that the temperature has an important influence on the reaction. When the reaction is carried out at −5℃, the major product is I and the yields are good (75—83%), whereas at 70℃, the major

Scheme



(1) $R=C_6H_5$ (2) $R=p\text{-}IC_6H_4$

(3) $R=p\text{-}CH_3OC_6H_4$ (4) $R=CH_3(CH_2)_{10}$

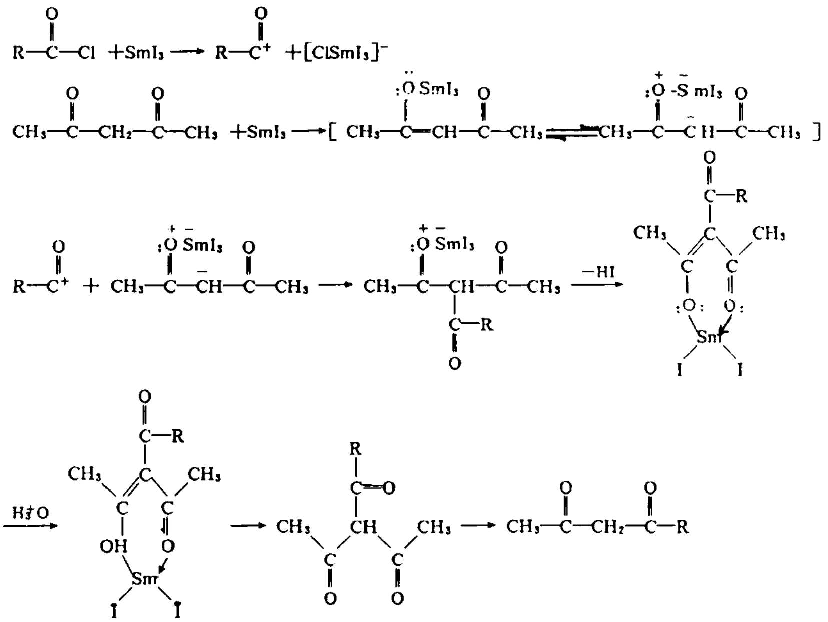
(5) $R=m\text{-}ClC_6H_4$ (6) $R=p\text{-}CH_3C_6H_4$

Table 1. β-diketones prepared at different temperatures

At-5℃		At 70℃	
No. Major Product	Yield(%)	No. Major Product	Yield(%)
1a $C_6H_5COCH_2COCH_3$	75	1b $C_6H_5COCH_2COC_6H_5$	78
2a $p\text{-}IC_6H_4COCH_2COCH_3$	83	2b $(p\text{-}IC_6H_4\text{-}CO)_2CH_2$	73
3a $p\text{-}CH_3OC_6H_4COCH_2COCH_3$	82	3b $(p\text{-}CH_3OC_6H_4\text{-}CO)_2CH_2$	76
4a $CH_3(CH_2)_{10}COCH_2COCH_3$	78	4a $CH_3(CH_2)_{10}COCH_2COCH_3$	74
5a $m\text{-}ClC_6H_4COCH_2COCH_3$	81	5b $(m\text{-}ClC_6H_4CO)_2CH_2$	75
6a $p\text{-}CH_3C_6H_4COCH_2COCH_3$	81	6b $(p\text{-}CH_3C_6H_4CO)_2CH_2$	74

product is II and the yields are 73—78%. But when the reaction is carried out at room temperature, I and II are both formed in a ratio of 3 : 2 and each of the yields is low, even after extended reaction times. Furthermore, we studied the analogous reaction of benzoylacetone with benzyl chloride at 70°C, and dibenzoylmethane was obtained as we expected.

According to the report of Hauser[8], a possible reaction mechanism is as follows:



The SmI$_3$ plays a double role in the reaction. It assists in ionization of the acyl chloride, and converts the acetylacetone into a samarium derivative of the enolate. Then acylium ion react with the carbanion of the enolate to afford a product containing three acyl group on one carbon[9]. The most strongly acidic[10] of these acyl groups is then cleaved[11] and the corresponding β-diketone is obtained.

It is known that usual methods to form β-diketone, such as Claisen condensations of esters with ketones in the presence of NaOC$_2$H$_5$ as catalyst are limited to the condensations of alkyl acetates with methyl ketones to give β-diketones of the structrue R-CO-CH_2-CO-CH_3. Our present reaction could be used for the conversion of these types of β-diketones into others of the structure R-CO-CH_2-CO-R′ under mild and neutral conditions. This makes it a good method for preparation of a number of β- diketones which are not available by direct ester condensation[12].

Experimental

^{1}H-NMR spectra were recorded in CCl_4, $CDCl_3$ or DMSO on a JEOL PMX 60si spectrometer using TMS as internal standard. IR spectra were obtained on a PE-683 spectrometer. Melting points are uncorrected. The solvents were predried according to standard procedures before use. The reactions were performed in a Schlenk type glass apparatus and under a nitrogen atmosphere.

General procedure.

A mixture of powdered samarium (0. 30g, 2mmol) and iodine (0. 75g, 3mmol) in dry acetonitrile (20ml) was stirred at room temperatures until the samarium disappeared. To the resulting brown yellow suspension of SmI_3 was added a mixture of acetylacetone (2mmol, −5℃/ 1mmol, 70℃) and acyl chloride (2mmol) and the resulting mixture was stirred for 3h at −5℃ or 70℃. It was then treated with dilute hydrochloric acid and extracted with ether. The combined organic layers were washed with aqueous sodium thiosulfate, dried over magnesium sulfate, and evaporated. The crude product was purified by column chromatography (silica gel, CH_2Cl_2 : petroleum ether = 1 : 1 as eluant). The spectral and analytical data of the products are as follows:

Benzoylacetone (1a): mp 57—58℃

^{1}H-NMR(CCl_4, TMS): 1. 93(s, 3H), 5. 93(s, 2H), 7. 20—7. 79(d, 5H)

IR(KBr, cm^{-1}, υ): 1620, 1705

Dibenzoylmethane (1b): mp 72—73℃

^{1}H—NMR(CCl_4, TMS): 7. 40—8. 03(m, 10H), 6. 73, 16. 70(s, 2H)

IR(KBr,cm^{-1},υ):1646,1730

p—Iodobenzoylacetone(2a):mp 116—117℃

^{1}H—NMR(CCl_4,TMS):2. 07(s,3H),7. 40—7. 80(m,4H),5. 97, 15. 93(s,2H)

IR(KBr,cm^{-1},υ):1691,1766

Di(p—Iodobenzoyl)methane(2b):mp 175—176℃

^{1}H—NMR(DMSO,TMS):6. 47(s,2H),7. 57—7. 90(m,8H)

IR(KBr,cm^{-1},υ):1707,1782

p-Anisoylacetone (3a):mp 52—53℃

^{1}H—NMR(CCl_4,TMS):2. 03(s,3H),3. 73(s,3H),6. 70—6. 83(d, 2H),7. 70—7. 83(d,2H),5. 93,16. 26(s,2H)

IR(KBr,cm^{-1},υ):1643,1725

Di(p-Anisoyl)methane(3b):mp 105—106℃

^{1}H—NMR(CCl_4,TMS):3. 73(s,6H),6. 70—6. 83(d,4H),7. 70—7. 83(d,4H) 6. 52,17. 12(s,2H)

IR(KBr,cm^{-1},υ):1652,1731

Lauroylacetone(4a):mp 31—32℃

^{1}H —NMR(CCl_4,TMS):0. 83— 1. 33(m,21H),2. 08—2. 36(t, 2H),5. 27,15. 26(s,2H)

IR(KBr,cm^{-1},υ):1728,1746

m—Chlorobenzoylacetone(5a):mp 44—45℃

^{1}H—NMR(CCl_4,TMS):2. 06(s,3H),7. 23—7. 73(m,8H),5. 97, 15. 80(s,2H)

IR(KBr,cm^{-1},υ):1680,1724

Di(m—Chlorobenzoyl)methane(5b):mp 135—136℃

^{1}H—NMR($CDCl_3$,TMS):6. 76(s,2H),7. 30—7. 93(m,8H)

IR(KBr,cm^{-1},υ):1683,1725

p—Toluoylacetone(6a):oil

^{1}H—NMR(CCl_4,TMS):2. 03(s,3H),2. 30(s,3H),7. 03—7. 15(d, 2H),7. 57—7. 70(d,2H),5. 97,16. 06(s,2H)

IR(cm^{-1},υ):1694,1738

Di(p—Toluoyl) methane(6b):mp 117—118℃

^{1}H—NMR(CCl_4,TMS):2. 36(s,6H),6. 73(s,2H),7. 13—7. 27(d, 4H),7.80—7.93(d,4H)

IR(KBr,cm^{-1},υ):1690,1745

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