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β-DIKETONE SYNTHESIS BY REACTION OF α-HALOKETONES WITH ACID CHLORIDES OR ACID ANHYDRIDES PROMOTED BY SAMARIUM TRIIODIDE

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ABSTRACT: Promoted by SmI_3, α-haloketones were reacted with acid chlorides or acid anhydrides and β-diketones were synthesized via intermediate samarium enolates.

Recently the application of lanthanoid compounds in organic synthesis has been of great interest[1]. Very recently carbon-carbon bond formation reactions mediated by trivalent lanthanoid compounds have rapidly increased. α-Haloketones react with aldehydes in the presence of CeI_3 to give α,β-unsaturated ketones[2]. We reported similar reactions promoted by SmI_3[3]. We assumed therein that samarium enolate formation from α-haloketones is the key step of the reaction. Some months ago, Mori reported that in the presence of SmI_2 or SmI_3 α-haloketones can react with α-ketocarboxylates and α-diketones to form α-hydroxy-γ-ketocarboxyhelates and 2-hydroxy-1,4-diketones[4]. Here we wish

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to report a facile synthesis of α-diketones from α-haloketones and acid chlorides or acid anhydrides mediated by SmI_3.

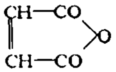
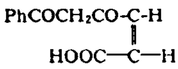
$$C_6H_5COCH_2Br + RCOCl \xrightarrow[r.t.]{SmI_3} C_6H_5COCH_2COR$$

$$C_6H_5COCH_2Br + (RCO)_2O \xrightarrow[r.t]{SmI_3} C_6H_5COCH_2COR$$

TABLE 1. Reaction Conditions and Yields with Acid Chlorides

No	Acid Chlorides	β-Diketones	Reaction Time(h)	Yields(%)
1	CH_3COCl	$PhCOCH_2COCH_3$	0.5	65
2	CH_3CH_2COCl	$PhCOCH_2COCH_2CH_3$	0.5	82
3	$CH_3CH_2CH_2COCl$	$PhCOCH_2COCH_2CH_2CH_3$	1	67
4	$(CH_3)_2CHCH_2COCl$	$PhCOCH_2COCH_2CH(CH_3)_2$	1	72
5	$CH_3(CH_2)_4COCl$	$PhCOCH_2CO(CH_2)_4CH_3$	1	79
6	$PhCOCl$	$PhCOCH_2COPh$	0.5	71
7	$CH_3(CH_2)_7COCl$	$PhCOCH_2CO(CH_2)_7CH_3$	1	64
8	$CH_3(CH_2)_{10}COCl$	$PhCOCH_2CO(CH_2)_{10}CH_3$	1	60

TABLE 2. Reaction Conditions and Yields with Acid Chlorides

No	Acid Anhydrides	β-Diketones	Reaction Time(h)	Yields(%)
1	$(CH_3CO)_2O$	$PhCOCH_2COCH_3$	1	80
2		 $\begin{array}{c}PhCOCH_2CO\text{-}C\text{-}H\\ \|\\ HOOC\text{—}C\text{—}H\end{array}$	1.5	91
3	$(CH_3CH_2CO)_2O$	$PhCOCH_2COCH_2CH_3$	1	86
4	$(CH_3CH_2CH_2CO)_2O$	$PhCOCH_2COCH_2CH_2CH_3$	1	90
5	$[(CH_3)_2CHCH_2CO]_2O$	$PhCOCH_2COCH_2CH(CH_3)_2$	1.5	85
6	$[CH_3(CH_2)_4CO]_2O$	$PhCOCH_2CO(CH_2)_4CH_3$	1.5	81
7	$(PhCO)_2O$	$PhCOCH_2COPh$	1.5	75

Similar to the reactions mentioned above, this reaction proceeds quickly and smoothly at room temperature and gives good yields. The acid anhydrides give better yields than acid chlorides. The solvent (CH_3CN) and the acid chlorides and acid anhydrides must be dried thoroughly and freshly redistilled, otherwise the amounts of byproducts due to reduction of α-haloketones will be increased. This suggests that the reaction intermediates may be the samarium (Ⅲ) enolates formed in situ from α-haloketones. THF can not be used as solvent as in the presence of SmI_3 acid chlorides and acid anhydrides lead to THF ring opening[5].

Experimental

^1H NMR spectra were recorded in CCl_4 on JEOL PM 60si spectrometer using TMS as internal standard. IR spectra were obtained on a PE 683 spectrometer. Melting points are reported uncorrected.

The solvents used were pre-dried according to standard procedures. The acid chlorides and acid anhydrides used were freshly redistilled before use. The reactions were performed in a Schlenk type glass apparatus under a nitrogen atmosphere.

General procedure for the preparation of β-diketones: α-haloketone (1mmol) in CH_3CN (2ml) and acid chloride (1mmol) in CH_3CN (2ml) were added sequentially to the SmI_3 (1mmol) in CH_3CN (10ml) at room temperature. After being stirred for 1hr, dilute hydrochloric acid (0.1M, 1ml) was dropped into the solution and the resulting mixture was stirred for a few minutes. Before the reaction mixture was extracted with ether some of the CH_3CN was evaporated in vacuum. After usual work-up, the product was separated by preparative TLC (silica gel) with cyclohexane and ethyl acetate as eluent.

1-Phenyl-1, 3-butadione: m. p. 61°C; ^{1}H-NMR: 1. 98 (s, 3H), 5. 93 (s, 1H), 7. 20-7. 28 (m, 3H), 7. 60-7. 76 (m, 2H), OH unfound. IR: 1700, 1670cm^{-1}.

1-Phenyl-1, 3-pentadione: oil; ^{1}H-NMR: 1. 01-1. 25(t, 3H), 2. 16-2. 51(q, 2H), 6. 10 (s, 1H), 7. 33-7. 42 (m, 3H), 7. 73-7. 90 (m, 2H) 15. 97 (s, 1H), ; IR: 1610cm^{-1}.

1-Phenyl-1, 3-hexadione: m. p. 30-31°C; ^{1}H-NMR: 0. 90-1. 12 (t, 3H), 1. 43-2. 00 (m, 2H), 2. 26-2. 50 (t, 2H), 6. 30 (s, 1H), 7. 38-7. 46 (m, 3H), 7. 80-7. 95(m, 2H) 16. 27(s, 1H); IR: 1610cm^{-1}.

1-Phenyl-5-methyl-1, 3-hexadione: oil; ^{1}H-NMR: 0. 90, 0. 98 (d, 6H), 1. 96-2. 25 (m, 3H), 6. 03 (s, 1H), 7. 40-7. 47 (m, 3H), 7. 80-7. 95 (m, 2H), 16. 26(s, 1H); IR: 1610cm^{-1}.

1-Phenyl-1, 3-octadione: oil; ^{1}H-NMR: 0. 85-1. 76 (m, 9H), 2. 25-2. 47 (t, 2H), 6. 03 (s, 1H), 7. 36-7. 45 (m, 3H), 7. 77-7. 93 (m, 2H), 16. 20(s, 1H); IR: 1610cm^{-1}.

1, 3-Diphenyl-1, 3-propadione: m. p. 74-75°C; ^{1}H-NMR: 6. 73 (s, 1H), 7. 42-7. 50 (m, 6H), 7. 90-8. 05 (m, 4H), 17. 00 (s, 1H); IR: 1605cm^{-1}.

1-Phenyl-1, 3-undecadione: oil, ^{1}H-NMR: 0. 85-1. 80 (m, 15H), 2. 22-2. 45 (t, 2H), 6. 03 (s, 1H), 7. 32-7. 43 (m, 3H), 7. 74-7. 90 (m, 2H), 16. 15 (s, 1H); IR: 1605cm^{-1}.

1-Phenyl-1, 3-tetradecadione: oil, ^{1}H-NMR: 0. 85-1. 80 (m, 21H), 2. 22-2. 45 (t, 2H), 6. 03 (s, 1H), 7. 32-7. 43 (m, 3H), 7. 74-7. 90 (m, 2H) 16. 15(s, 1H); IR: 1605cm^{-1}.

6-Phenyl-4, 6-dione-2-hexenic acid: m. p. 169-170°C; ^{1}H-NMR: (dimethyl-d_6 sulfoxide/TMS): 6. 57, 6. 83, 7. 10, 7. 36(q, 2H), 7. 07 (s, 1H), 7. 56-7. 70 (m, 3H), 8. 02-8. 20 (m, 2H); IR: 1605cm^{-1}.

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