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Formation of α,α'-Bis(substituted benzylidene)cycloalkanones from Masked Aldehydes Promoted by Samarium(III) Triiodide

Xiao Xia WANG[1], Yong Min ZHANG[1,2]*

[1]Department of Chemistry, Zhejiang University (Xixi Campus) , Hangzhou 310028
[2] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032.

Abstract: 1,1-Diacetates **1** and N-[(1-benzotriazol-1-yl)alkyl]amides **2**, both masked forms of aldehydes, could undergo deprotection and condensation with cycloalkanones in a one-pot procedure promoted by samarium(III) iodide (SmI_3) to afford α,α'-bis(substituted benzylidene) cycloalkanones in good yields.

Keywords: Samarium(III) triiodide, α,α'-bis(substituted benzylidene)cycloalkanone,1,1-diacetate, N-[(1-benzotriazol-1-yl)alkyl]amide.

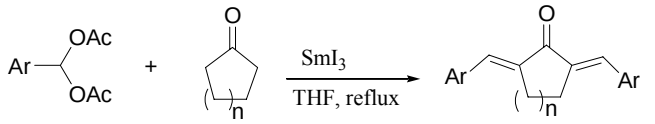
Recently, lanthanide compounds have gained increasing popularity as versatile reagents in organic synthesis[1]. Whilst our investigation on the application of samarium reagents, we have found samarium triiodide could promote the synthesis of *β*-diketones[2], α,β-unsaturated ketones[3] and samarium triiodide were also found to be an efficient catalyst for the thio acetal formation[4] and tetrahydrofuran ring opening reactions[5]. Recently, we found SmI_3 could promote the deprotection of 1,1-diacetates, and bearing in mind that SmI_3 could promote the formation of α,α'-bis(substituted benzylidene)cycloalkanones[6] from the condensation reaction of trimethyl silyl enol ethers of cycloalkanone with aldehydes, therefore we are interested in elucidating, if the deprotection and the condensation reaction could be realized by SmI_3 in one pot. Our studies showed that both 1,1-diacetates and N-[(1-benzotriazol-1-yl)alkyl]amides could undergo deprotection and condensation reaction with cycloalkanones by SmI_3 in one pot to afford α,α'-bis(substituted benzylidene)cycloalkanones in good yields.

Scheme 1 shows α,α'-bis(substituted benzylidene)cycloalkanones **3** or **4** can be obtained from 1,1-diacetates and cycloalkanones. The reaction could not proceed at room temperature. However, in 2-3 hours under reflux conditions, α,α'-bis(substituted benzylidene)cycloalkanones could be isolated with good yields promoted by an appropriate amount of SmI_3. When catalytic amount (0.1-0.2 eq.) of SmI_3 was used, the reaction was incomplete even after refluxing for one day. One equivalent of SmI_3 can ensure the disappearance of the starting materials in reasonable time (**Table 1**). More

*E-mail: yongminzhang@css.zju.edu.cn

amount of SmI_3 has no obvious effect in improving the yields or shortening the reaction time.

Scheme 1



1 **2** **3** (n = 1) **4** (n = 2)

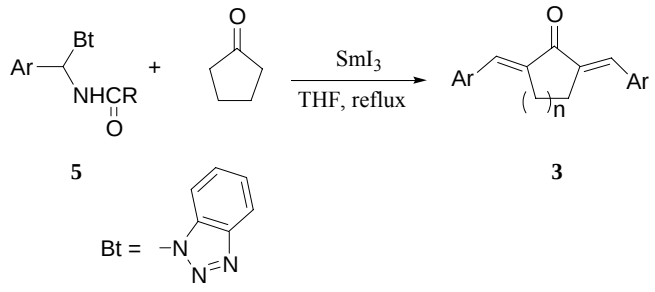
Table 1 Reaction of 1,1-diacetates with cycloalkanones **2** promoted by SmI_3

n	Ar	Reaction time (h)	Product	Yield (%)[a]
1	C_6H_5	2	**3a**	82
1	4-ClC_6H_4	3	**3b**	79
1	4-$CH_3C_6H_4$	2	**3c**	87
1	4-$CH_3OC_6H_4$	2	**3d**	83
1	2,6-$Cl_2C_6H_3$	2	**3e**	71
1	3,4-$(CH_2OCH_2)C_6H_3$	2	**3f**	85
1	C_6H_5CH=CH	10	**3g**	68
1	2-ClC_6H_4	3	**3h**	87
1	3-BrC_6H_4	3	**3i**	83
2	C_6H_5	10	**4a**	78[b]
2	4-ClC_6H_4	10	**4b**	73[b]
2	4-$CH_3C_6H_4$	10	**4c**	76[b]

[a] Isolated yields based on compound **1.** [b]Two equivalents of TMSCl was added.

Further investigation found that N-[(1-benzotriazol-1-yl)alkyl]amides, when treated with one equivalent of SmI_3 under reflux conditions, could also react with cyclopentanones to give α,α'-bis(substituted benzylidene)cyclopentanones in satisfactory yields (**Scheme 2**).

Scheme 2



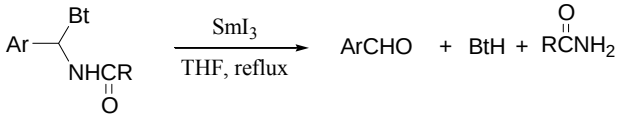
5 **3**

Table 2 Reaction of N-[(1-benzotriazol-1-yl)alkyl]amides with cyclopentanone promoted by SmI_3

Ar	R	Product	Reaction time(h)	Yield(%)
C_6H_5	C_6H_5	**3a**	5	80
C_6H_5	CH_3	**3a**	3	73
$CH_3C_6H_4$	CH_3	**3c**	3	68
$CH_3OC_6H_4$	C_6H_5	**3d**	3	76

To clarify the formation of products **3**, N-(1-benzotriazol-1-ylalkyl)amides alone were treated with SmI_3 in THF to make it clear, if there was any reaction occur. It was found that at room temperature, no obvious decomposition could be observed. However, under reflux conditions, the corresponding aldehydes, benzotriazole and amides could be isolated. Thus N-[(1-benzotriazol-1-yl)alkyl]amides served as a masked form of aldehydes here (**Scheme 3**).

Scheme 3



In conclusion, the deprotection and condensation reaction of deprotection and condensation 1,1-diacetates or N-[(1-benzotriazol-1-yl)alkyl]amides with cycloalkanones was discovered in a one-pot procedure promoted by SmI_3.

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7. *General procedure for the synthesis of α,α'-bis(substituted benzylidene)cycloalkanones (**4**):* Under nitrogen atmosphere, samarium powder (0.15 g, 1.0 mmoL) and iodide (0.39 g, 1.55 mmol) in dry THF (10 mL) were stirred for 1 hour at room temperature to obtain a yellow suspension, to which was added a solution of 1 mmol of 1,1-diacetates or N-[(1-benzotriazol-1-yl)alkyl]amides and 1 mmol of cycloalkanone in 2 mL of THF, the resulting mixture was then refluxed till the starting materials disappeared (monitored by TLC). After evaporating most of the THF, 3 mL of hydrochloric acid (0.2 mol/L) was added. Usually the products were precipitated, subsequent filtration and recrystallization from methanol afforded the pure products. If no precipitate was produced after the adding of hydrochloric acid, the mixture was extracted with diethyl ether (3 × 15 mL). The combined extracts were washed with saturated solution of $Na_2S_2O_3$, then a saturated solution of NaCl and dried over anhydrous Na_2SO_4. After evaporating the solvent under reduced pressure, the crude solid products were obtained. Recrystallization from 95% EtOH or MeOH afforded the products in pure form.
8. Physical data: **3a**. m.p. 184~186°C, (lit.[9] 188~189°C); **3b**. m.p. 227~229°C, (lit.[10] 231°C); **3c**. m.p. 242~244°C, (lit.[10] 245~246°C); **3d**. m.p. 213~215°C, (lit.[10] 219~220°C); **3e**. m.p. 182-188°C (accompanied by decomposition); ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 7.52 (s, 2H), 7.36~7.38 (m, 4H), 7.21~7.25 (m, 2H), 2.62 (s, 4H); IR (KBr) ν(cm^{-1}): 3060, 2933, 1704, 1633, 1578, 1554; MS (70eV) *m/z* (%): 361 (M^+-35, 100), 363 (95.86), 325 (12.72), 291 (6.49), 255 (5.49), 226 (8.46), 202 (18.47), 161 (13.98), 149 (38.26), 113 (47.65); Anal. Calcd for $C_{19}H_{12}Cl_4O$: C 57.32, H 3.04; Found C 57.21, H 3.14; **3f**. m.p.247-249°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 7.36 (s, 2H), 7.23~7.25 (d, 4H, *J* = 8.8 Hz), 7.03~7.05 (d, 2H, *J* = 7.6 Hz), 6.11 (s, 4H), 3.04 (s, 4H); IR (KBr) ν(cm^{-1}):2909, 1682, 1632, 1612, 1597; MS (70eV) *m/z* (%):349 (M^++1, 22.58), 348 (M^+, 100), 347 (91.49), 102 (97.96); Anal. Calcd for $C_{21}H_{16}O_5$: C 72.41, H 4.63; Found C 72.36, H 4.65; **3g**. m.p.216-218°C (lit.[6] 215-216°C); **3h**. m.p. 150-152°C (lit.[11] 152.3~152.6°C); **3i**. m.p. 208-210°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 7.74 (s, 2H), 7.52~7.53 (m, 6 H), 7.33 (t, 2 H, *J* = 8.0 Hz), 3.13 (s, 4 H); IR (KBr) ν(cm^{-1}): 3059, 2920, 1687, 1623, 1603, 1554, 1180; MS (70 eV) *m/z* (%): 420 (M^+, 19.30), 419 (25.69), 418 (41.02), 417 (42.56), 416 (M^+, 20.91), 339 (71.48), 337 (72.44), 129 (42.56), 115 (100); Anal. Calcd for $C_{19}H_{14}Br_2O$**:** C 54.58, H 3.38; Found C 54.52, H 3.43; **4a**. m.p. 115-116°C (lit.[12] 116~117°C); **4b**. m.p. 144-147°C (lit.[13] 146~148 °C); **4c**. m.p. 171-173°C (lit.[13] 171~173°C).

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