Pergamon

Tetrahedron Letters 43 (2002) 5431–5433

TETRAHEDRON
LETTERS

Formation of 1,2-diketones by samarium diiodide promoted reaction of *N*-acylbenzotriazoles

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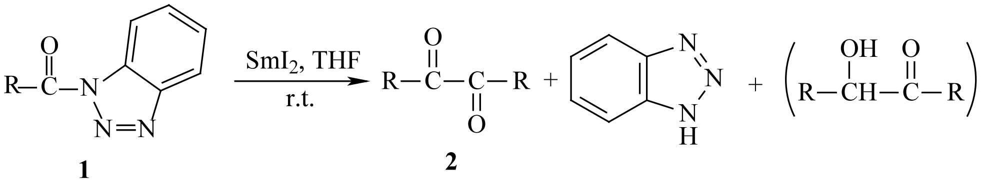
Received 19 March 2002; accepted 7 June 2002

Abstract—Transformation of *N*-acylbenzotriazoles **1** into 1,2-diketones **2** in good to excellent yields has been realized by the use of samarium diiodide at room temperature. © 2002 Elsevier Science Ltd. All rights reserved.

Benzotriazole is a very useful synthetic auxiliary[1] and its application in organic chemistry has been extensively investigated. There have been reports that benzotriazole acts as a good leaving group when treated with samarium reagents. Aurrecoechea showed that α-dialkylaminoalkylbenzotriazole derivatives, when treated with samarium diiodide, could afford 2-azaalkyl radicals, which could undergo dimerization to form vicinal diamines.[2] Our group have found that allylsamarium bromide could substitute the benzotriazole group in *N*-aminoalkylbenzotriazoles to give homoallyl amines.[3] We now wish to report our recent research on the reactivity of *N*-acylbenzotriazoles towards samarium diiodide. As shown in Scheme 1 and Table 1, aromatic *N*-acylbenzotriazoles when treated with samarium diiodide in THF at room temperature afford the 1,2-diketones in reasonable to excellent yields.

It was reported that acid chlorides could be coupled by samarium diiodide into 1,2-diketones.[4] Similarly, keto cyanides were reported to give 1,2-diketones by a reductive coupling reaction promoted by SmI_2 or ZnI_2.[5] In both cases, acyl anion species and $RCO^•$ radicals were deduced or even verified[6] to be the intermediates with Cl^- or CN^- as the leaving group. In this investigation, acyl anion species and $RCO^•$ radicals may also be involved with benzotriazole anion acting as a leaving group. Despite the similarity in the reaction mechanism, the present study is a very useful method for the synthesis of 1,2-diketones. Unlike acyl chlorides and keto cyanides, the preparation of which[7] is tedious, requires high temperature or the use of toxic cyanides, *N*-acylbenzotriazoles are stable crystalline solids and readily available from carboxylic acids and *N*-(1-methanesulfonyl)benzotriazole.[8] Furthermore, benzotriazole as an auxiliary group can be recovered almost quantitatively after the reaction and therefore the method has the potential of recycling the starting material. These characteristics coupled with short reaction times and mild reaction conditions may make the method an attractive one for the preparation of aromatic 1,2-diketones.

A typical procedure is as follows: under a nitrogen atmosphere, 1*H*-1,2,3-benzotriazol-1-yl-(4-chlorophenyl)methanone (0.258 g, 1 mmol) dissolved in



Scheme 1.

Keywords: samarium diiodide; reductive coupling; acylbenzotriazoles; 1,2-diketones; *vic*-dibenzotriazoylalkene.

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PII: S0040-4039(02)01080-8

Table 1. SmI_2 promoted coupling of *N*-acylbenzotriazoles giving 1,2-diketones[a]

Entry	R	SmI_2 (equiv.)	Product	Reaction time (min)	Yield (%)[c]
1	C_6H_5	2.2	**2a**	10	68 (26)
2	C_6H_5	3.3	**2a**	180[b]	60 (29)
3	*m*-ClC_6H_4	2.2	**2b**	5	95 (0)
4	*m*-ClC_6H_4	3.3	**2b**	180[b]	92[d] (0)
5	*m*-ClC_6H_4	2.2[e]	**2b**	5	96[d] (0)
6	*m*-ClC_6H_4	2.2[f]	**2b**	180	83 (12)
7	*p*-ClC_6H_4	2.2	**2c**	5	93 (0)
6	*p*-BrC_6H	2.2	**2d**	5	95 (0)
8	*p*-IC_6H_4	2.2	**2e**	5	92 (0)
9	*p*-$CH_3C_6H_4$	2.2	**2f**	5	68 (trace)
10	*o*-$CH_3OC_6H_4$	2.2	**2g**	5	52 (trace)
11	*p*-$Et_2NC_6H_4$	2.2	**2h**	5	65 (trace)
12	2-Furyl	2.2	**2i**	5	53 (trace)
13	*p*-$NO_2C_6H_4$	2.2	**2j**	5	0 (0)
14	3-Pyridyl	2.2	**2k**	5	0 (0)
15	4-Pyridyl	2.2	**2l**	5	0 (0)
16	*n*-C_4H_9	2.2	**2m**	10	11 (35)
17	*n*-C_6H_{12}	2.2	**2n**	10	16 (30)

[a] The reaction was conducted at room temperature unless otherwise specified.

[b] The characteristic blue color of SmI_2 still persisted.

[c] The yield of α-hydroxy ketones obtained is shown in parentheses.

[d] No obvious decrease in the yield of 1,2-diketone.

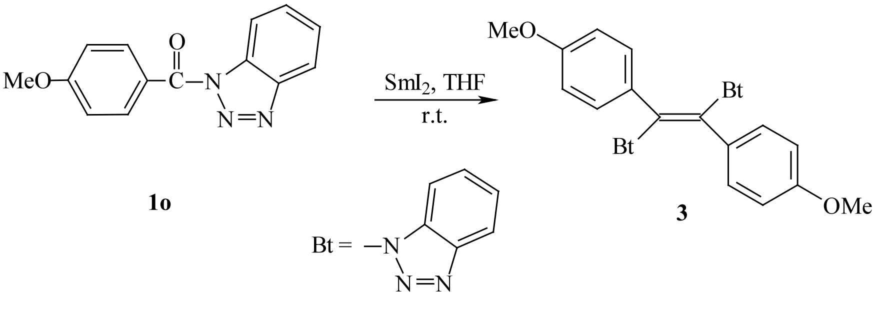
[e] The run was carried out with 2.2 equiv. of SmI_2 and 1.1 equiv. of samarium powder at room temperature.

[f] This run was carried out with 2.2 equiv. of SmI_2 and 1.1 equiv. of samarium powder under reflux conditions.

dry tetrahydrofuran (3 mL) was added at room temperature to 2.2 mmol of a 0.1 M SmI_2–THF solution. The resulting solution turned yellow in 5 min. Dilute hydrochloric acid (2 M, 5 mL) was added and the resulting mixture was extracted with diethyl ether (3×20 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulphate, and concentrated under reduced pressure. The residue was separated by preparative TLC on silica gel with ethyl acetate and cyclohexane (1:3) as eluent to afford 1,2-bis(4-chlorophenyl)ethanedione (0.259 g, 93%).

As for aromatic *N*-acylbenzotriazoles, the reaction was strongly influenced by the substituent on the aromatic ring. With an electron-withdrawing group present, the reaction was very clean and afforded 1,2-diketones exclusively, in high yields, whereas *N*-acylbenzotriazoles possessing an electron-donating group attached to the aromatic ring gave relatively lower yields. Although an iodo group on the aromatic ring is potentially reactive towards SmI_2,[9] we were surprised to find that the reaction can tolerate the iodo group (entry 8) and afford the 1,2-bis(4-iodophenyl)ethanedione in excellent yield. However, substrates **1j** (entry 13), **1k** (entry 14) and **1l** (entry 15) failed to give any detectable products besides benzotriazole. It is probable that the corresponding radicals produced undergo decarbonylation[10] before their dimerization or electron transfer from SmI_2 to form an acyl anion species. Aliphatic *N*-acylbenzotriazoles mainly afford α-ketol compounds in low yields instead of the corresponding 1,2-diketones (entries 16 and 17). Finally, when R is a *p*-methoxyphenyl group (substrate **lo**), *vic*-di(1*H*-1,2,3-benzotriazol-1-yl)alkene **3** was obtained in 68% yield under the same SmI_2–THF conditions (Scheme 2).

N-Acylbenzotriazoles may be seen as a special type of amide and *vic*-di(1*H*-1,2,3-benzotriazol-1-yl)alkene **3** may be looked on as a product formed from the deoxygenative coupling reaction of amides. Bearing in mind that the deoxygenative coupling reaction of amides could be effectively realized using the SmI_2/Sm system,[11] we treated substrate **1b** with the SmI_2/Sm



Scheme 2.

system (entries 5 and 6). However, the expected deoxygenative coupling product was not obtained with the 1,2-diketone as the major product and the α-ketol compound as by-product.

In conclusion, with good yields, mild reaction conditions as well as easily accessible starting materials, the present work may provide a useful method for the preparation of 1,2-diketones.[12]

Acknowledgements

We are grateful to the National Natural Science Foundation of China (Project No. 29872010) and the NSF of Zhejiang province for financial support.

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12. Typical physical data of compounds **2e**, **2h** and **3** are listed. Compound **2e**, **bis(4-iodophenyl)ethanedione**, mp 243–245°C. ν_{max}: 3066, 1664 (C=O), 1579 (Ar) cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): 8.03 (4H, d, $J=8.43$ Hz, ArH), 7.67 (4H, d, $J=8.44$ Hz, ArH). Compound **2h**, **bis(4-diethylaminophenyl)ethanedione**, mp 85–87°C. ν_{max}: 2972, 2933, 2902, 2871, 1645 (C=O), 1585, 1546, 1527 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 7.85 (4H, d, $J=8.72$ Hz, ArH), 6.70 (4H, d, $J=7.30$ Hz, ArH), 3.43 (8H, q, $J=7.00$ Hz, CH_2), 1.20 (12H, t, $J=7.00$ Hz, CH_3). Compound **3**, ***vic*-di(1*H*-1,2,3-benzotriazol-1-yl)alkene**, mp 138–140°C. ν_{max}: 1605 (C=C), 1504 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 8.72–8.74 (4H, m, ArH), 8.50 (2H, d, $J=8.4$ Hz, ArH). 8.05 (2H, d, $J=8.0$ Hz, ArH), 7.93–7.95 (2H, m, ArH), 7.78–7.80 (2H, m, ArH), 7.10 (4H, d, $J=9.0$ Hz, ArH), 3.93 (6H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): 162.54, 159.74, 146.15, 141.21, 135.40, 130.55, 129.32, 128.98, 128.25, 114.40, 55.48. m/z (%): 237 ($M^+/2$, 1.88), 209 (100), 166 (38.38). Anal. $C_{28}H_{22}N_6O_2$. Calcd C, 70.89; H, 4.64; N, 17.72. Found C, 70.80; H, 4.59; N, 17.65%.