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Tetrahedron Letters
Tetrahedron Letters 47 (2006) 3767–3771

Highly regioselective Friedel–Crafts alkylation of indoles with α,β-unsaturated *N*-acylbenzotriazoles

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Received 26 December 2005; revised 16 March 2006; accepted 17 March 2006
Available online 12 April 2006

Abstract—The Friedel–Crafts alkylation rather than acylation of indoles was realized with α,β-unsaturated acylbenzotriazoles catalyzed by samarium(III) iodide under reflux in anhydrous THF. The reaction was highly regioselective, and a series of new 3-substituted indole derivatives were obtained in moderate to good yields with the potential to be further transformed into various indole derivatives due to the presence of active acylbenzotriazole moiety.

α,β-Unsaturated *N*-acylbenzotriazoles, essentially a special type of α,β-unsaturated amides with the –C=C–CON– structure present therein, can be treated as a new class of α,β-unsaturated carbonyl compounds (or electron-deficient alkenes). They were found to be good Michael acceptors as well as acylating agents depending on the attacking electrophiles. For example, anhydrous hydrazine were readily acylated by *N*-cinnamoylbenzotriazoles affording good to excellent yields of cinnamoyl hydrazides;[1a] the lithium enolates of ketones were acylated with α,β-unsaturated acylbenzotriazoles to prepare γ,δ-unsaturated β-diketones.[1b] We found that *N*-cinnamoylbenzotriazoles were also good acylating agents for thiolates thus providing an efficient synthesis of α,β-unsaturated thioesters;[2] besides being convenient and mild N-, C- and S-acylating reagents as mentioned above. Our recent investigation revealed[3] that when aliphatic amines were the electrophiles, acylation reaction took place exclusively to give cinnamoylamides, while aromatic amines attacked the 4-position of *N*-cinnamoylbenzotriazoles with high regioselectivity to produce moderate to good yields of Michael adducts.

N-acylbenzotriazoles derived from saturated carboxylic acids have been well documented as highly efficient acylating agents[4] and in the presence of titanium chloride they undergo Friedel–Crafts acylation of indoles to afford 3-acylindoles.[5] The unique features of α,β-unsaturated acylbenzotriazoles prompted us to further investigate its reaction with indoles.

In continuation with our previous study of the aza-Michael conjugate addition of aromatic amines to *N*-cinnamoylbenzotriazoles,[3] the reaction between indole (**1a**) and α,β-unsaturated acylbenzotriazoles (**2a**) was examined first with a base such as triethylamine as a promoter to test the possibility of the N-alkylation of indole (the Michael addition of indole with its 1-position, the N atom to α,β-unsaturated acylbenzotriazoles), but the reaction ended up with no expected product formed. However, subsequent investigation found that Lewis acid such as SmI_3 could catalyze the Michael addition of indole with its 3-position to **2a** smoothly. That was, in contrast to the fact that saturated *N*-acylbenzotriazoles were effective Friedel–Crafts acylating agents for indoles, α,β-unsaturated acylbenzotriazoles worked as good Friedel–Crafts alkylating agents for indoles, showing excellent regioselectivity.

The Friedel–Crafts alkylation of indole with activated alkenes (also known as conjugate addition of indole to electro-deficient olefins) has drawn much attention in recent years due to the carbon–carbon bond formation where useful 3-substituted indole derivatives as important building blocks for natural product synthesis can be produced.[6] However, though the conjugate addition of indole to enones and nitro alkenes[7] promoted by various catalysts or under a variety of conditions including

Keywords: Indoles; Friedel–Crafts alkylation; *N*-Cinnamoylbenzotriazoles; Samarium(III) iodide.
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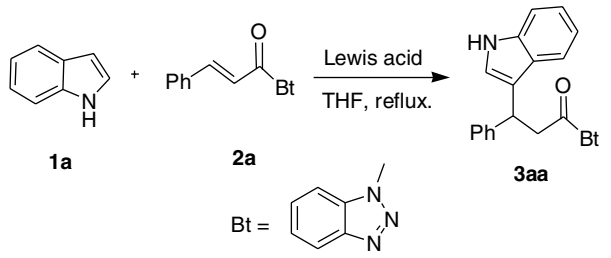
doi:10.1016/j.tetlet.2006.03.110

ultrasonic irradiation[7p] and photoinduction[7v] tends to be a subject of current interest and reports concerning the enatioselective addition of indole to alkylidene malonates can frequently be found,[8] studies concerning other electron-deficient olefins as the Michael acceptor to realize the Friedel–Crafts alkylation of indole are less known. Yadav et al. reported[7o] that $InCl_3$ could effectively catalyze the conjugate addition of indoles to enones, nitro alkenes and benzylidene malononitriles, but not to methyl acrylate and acrylonitrile. Catalyzed by $Bi(OTf)_3$, methyl acrylate and acrylonitrile were reported[7n] to undergo the Friedel–Crafts alkylation of indole with moderate yields, but a systematic study concerning α,β-unsaturated esters and nitriles was unknown to the best of our knowledge. Herein, α,β-unsaturated acylbenzotriazoles as a new kind of Michael acceptors (Friedel–Crafts alkylating agents) for indoles were reported and the investigation resulted in a new class of 3-substituted indole derivatives.

A series of experiments were carried out to search for an appropriate Lewis acid as the catalyst for the reaction shown in Scheme 1 and the results are listed in Table 1. All runs were carried out for 8 h and among the 6 Lewis acids tested, SmI_3 gave the best results (Table 1, entries 1–6). Apart from the desired adducts **3aa**, cinnamic acid (the hydrolyzed product of **2a**) as well as the recovered **2a** were also obtained after usual work-up. The presence of Lewis acid facilitated the hydrolysis of **2a** greatly and therefore anhydrous reagent and solvent were required for the success of the reaction. Although $TiCl_4$ was proved to be an effective promoter for the acylation of indoles with *N*-acylbenzotriazoles,[5] it was not so successful for promoting the Friedel–Crafts alkylation of indoles with *N*-cinnamoylbenzotriazole (Table 1, entry 4). Under reflux in anhydrous THF, the presence of 50 mol % SmI_3 afforded the Friedel–Crafts alkylation products in 87% yield (Table 1, entry 6). When the reaction was further carried out with catalytic amount (20 mol %) of SmI_3, comparable yields (Table 1, entry 7) could be obtained within reasonably prolonged period of time. When the reaction catalyzed by SmI_3 was carried out in solvents other than THF, such as dry CH_2Cl_2, toluene and CH_3CN, no significant improvement was observed both in reaction time and product yields (Table 1, entries 8–10). Thus for the Friedel–Crafts alkylation here, reflux in dry THF in the presence of 20 mol % of SmI_3 was developed for the standard reaction conditions.



Scheme 1.

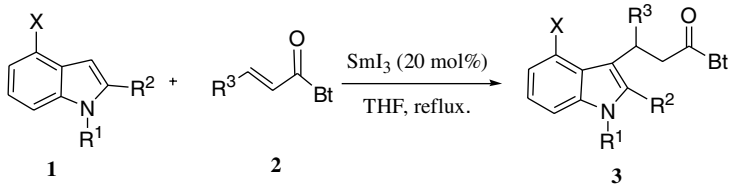
The general applicability of this reaction was illustrated by the fact that a variety of *N*-cinnamoylbenzotriazoles (**2a**–**f**) reacted well with both unsubstituted and substituted indoles affording the corresponding 3-alkylated indole derivatives **3** in moderate to good yields (Scheme 2 and Table 2). Unsubstituted indole **1a** undergoing smooth 3-alkylation with **2a**–**g** usually in 10 h afforded **3aa**–**ag** in 59–92% yields (Table 2, entries 1–7, 17). An introduction of a substituent such as methyl or phenyl at the 2-position led to a prolonged period of time for the completed alkylation. 2-Methylindole **1b** required 13–16 h (Table 2, entries 8–10) while 2-phenylindole **1c** required even longer time as much as 20–26 h so as to afford satisfactory yields (Table 2, entries 11, 12). N-substitution such as *N*-benzylindole (**1d**) was also investigated and generally still longer times were necessary (Table 2, entries 13–15). 4-Nitro-2-methyl indole **1e** with a strong electron-withdrawing group even located heteroannularly at the 4-position failed to produce the expected alkylation product and in fact no reaction occurred (Table 2, entry 16). The α,β-unsaturated acylbenzotriazoles derived from crotonic acid (**2h**) was also used as the alkylating agent, which was reacted with **1a** smoothly to give the corresponding alkylated indoles (Table 2, entry 17).

The SmI_3 catalyst was prepared in situ by reacting 1 equiv of samarium power with 1.5 equiv of iodine in dry THF at room temperature with stirring for 0.5 h.

Table 1. Screening of Lewis acids and reaction conditions for the Friedel–Crafts alkylation of indole with α,β-unsaturated acylbenzotriazoles **2a**

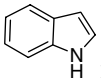
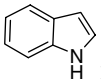
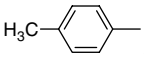
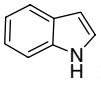
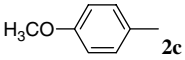
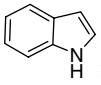
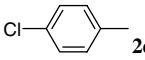
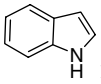
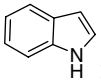
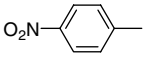
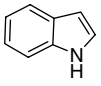
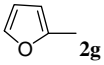
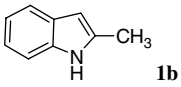
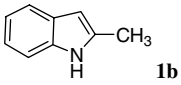
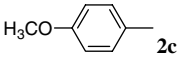
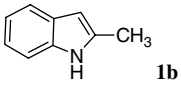
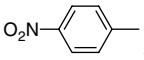
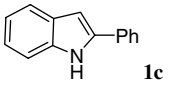
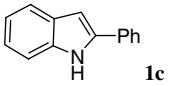
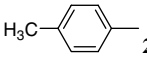
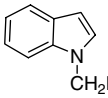
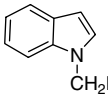
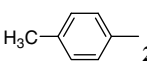
Entry[a]	Lewis acid	Catalyst (mol %)	Solvent	Time (h)	Yield[b] (%) of **3aa**
1	$AlCl_3$	50	THF	8	53
2	$CuCl_2$	50	THF	8	0
3	$ZnCl_2$	50	THF	8	0
4	$TiCl_4$	50	THF	8	25
5	$BF_3{\cdot}Et_2O$	50	THF	8	0
6	SmI_3	50	THF	8	87
7	SmI_3	20	THF	10	89
8	SmI_3	20	CH_2Cl_2	18	76
9	SmI_3	20	Toluene[c]	10	70
10	SmI_3	20	CH_3CN	10	81

[a] All the runs were carried out under reflux conditions unless otherwise specified.
[b] Isolated yields.
[c] Reaction performed at 80 °C.



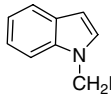
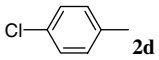
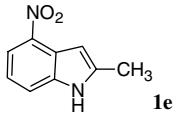
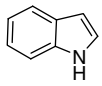
Scheme 2.

Table 2. Samarium(III) iodide-catalyzed Friedel–Crafts alkylation of indoles with α,β-unsaturated acylbenzotriazoles[a,9]

Entry	Indoles **1**	R^3 of **2**	Products[b]	Time (h)	Yield (%)[c]
1	 **1a**	 **2a**	**3aa**	10	89
2	 **1a**	 **2b**	**3ab**	10	92
3	 **1a**	 **2c**	**3ac**	10	86
4	 **1a**	 **2d**	**3ad**	10	92
5	 **1a**	 **2e**	**3ae**	15	87
6	 **1a**	 **2f**	**3af**	9	90
7	 **1a**	 **2g**	**3ag**	18	59
8	 **1b**	 **2a**	**3ba**	13	82
9	 **1b**	 **2c**	**3bc**	15	82
10	 **1b**	 **2f**	**3bf**	16	67
11	 **1c**	 **2a**	**3ca**	25	63
12	 **1c**	 **2b**	**3cb**	20	88
13	 **1d**	 **2a**	**3da**	25	61
14	 **1d**	 **2b**	**3db**	26	83

(*continued on next page*)

Table 2 (*continued*)

Entry	Indoles **1**	R^3 of **2**	Products[b]	Time (h)	Yield (%)[c]
15	 **1d**	 **2d**	**3dd**	22	88
16	 **1e**	 **2a**	—	20	—[d]
17	 **1a**	Me– **2h**	**3ah**	14	82

[a] All reactions were carried out in dry THF under reflux with 20 mol % of samarium(III) iodide.
[b] Alkylated products[10] were characterized by ^{1}H NMR, ^{13}C NMR, IR and elemental analysis.
[c] Isolated yields.
[d] No reaction.

Nitrogen protection was unnecessary and the simple procedure made it promising for large-scale manipulation.

In conclusion, we presented a first catalytic regioselective alkylation of indoles with α,β-unsaturated acylbenzotriazoles. The synthesized new type of 3-alkylated indoles possess *N*-acylbenzotriazole moiety and would be promising acylating agents capable of realizing various N-, C-, S-, and O-acylation[4] and could be further transformed into versatile indole derivatives.

Acknowledgement

We are grateful to Zhejiang Provincial Natural Science Foundation of China (Project No. Y405035) for financial support.

References and notes

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9. General experimental procedure. To 10 mL of dry THF were added Sm powder (0.03 g, 0.2 mmol) and I_2 (0.077 g, 0.3 mmol), the mixture was stirred at rt for 0.5 h to obtain the SmI_3–THF solution. To the solution were added indole (1 mmol) and *N*-cinnamoylbenzotriazole (1 mmol), the resulting mixture was refluxed for indicated time (Table 2) until the disappearance of *N*-cinnamoylbenzotriazole (monitored by TLC). Then it was quenched with dilute hydrochloric acid (0.3 M) and extracted with diethyl ether (3×20 mL). The combined organic layer was washed with saturated $Na_2S_2O_3$ and brine, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by preparative TLC on silica gel with ethyl acetate and cyclohexane (1:2) as eluent to afford pure products **3**.
10. Compound **3aa**, **1-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-(1*H*-indol-3-yl)-3-phenylpropan-1-one,** mp 168–169 °C. ν_{max}: 3416 (NH), 3063, 3027, 2924, 2883, 1721 (C═O), 1601 (Ar) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 8.22 (d, 1H, $J = 8.0$ Hz, ArH), 8.10 (d, 1H, $J = 8.0$ Hz, ArH), 7.99 (s, 1H, NH), 7.62–7.60 (m, 1H, ArH), 7.48–7.43 (m, 4H, ArH), 7.31–7.27 (m, 3H, ArH), 7.17–7.15 (m, 3H, ArH), 7.05–7.03 (m, 1H, ArH), 5.20 (dd, 1H, $J = 8.0$, 8.0 Hz, CH), 4.31 (dd, 1H, $J = 8.0$, 8.0 Hz, CH), 4.17 (dd, 1H, $J = 8.0$, 8.0 Hz, CH). ^{13}C NMR (100 MHz, $CDCl_3$): 170.8, 146.2, 143.1, 136.6, 131.1, 130.3, 128.6, 127.8, 126.7, 126.6, 126.2, 122.4, 121.4, 120.1, 119.7, 119.4, 118.5, 114.6, 111.1, 42.0 38.8. Anal. $C_{23}H_{18}N_4O$. Calcd. C, 75.39; H, 4.95; N, 15.29. Found C, 75.20; H, 5.01; N, 15.23.

Compound **3bc**, **1-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-(4-methoxyphenyl)-3-(1-methyl-1*H*-indol-3-yl)propan-1-one**, decomposed beyond 76 °C. ν_{max}: 3411 (NH), 3099, 3058, 2925, 2848, 1736 (C═O), 1611 (Ar) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 8.19 (d, 1H, $J = 8.0$ Hz, ArH), 8.08 (d, 1H, $J = 8.0$ Hz, ArH), 7.76, (s, 1H, NH), 7.58–7.56 (m, 2H, ArH), 7.47–7.45 (m, 1H, ArH), 7.36 (d, 2H, $J = 8.0$ Hz, ArH), 7.20 (d, 1H, $J = 8.0$ Hz, ArH), 6.97–7.12 (m, 2H, ArH), 6.81 (d, 2H, $J = 8.0$ Hz, ArH), 5.16 (dd, 1H, $J = 8.0$, 8.0 Hz, CH), 4.38 (dd, 2H, $J = 8.0$, 8.0 Hz, CH), 3.75 (s, 3H, CH_3), 2.43 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): 171.1, 158.0, 146.1, 135.3, 131.7, 131.1, 130.2, 128.4, 127.3, 126.0, 121.0, 120.1, 119.5, 119.1, 114.5, 113.8, 113.0, 110.3, 55.2, 40.7, 36.5, 26.9, 12.3. Anal. $C_{25}H_{22}N_4O_2$. Calcd. C, 73.15; H, 5.40; N, 13.65. Found C, 73.39; H, 5.48; N, 13.59.

Compound **3cb, 1-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-(2-phenyl-1*H*-indol-3-yl)-3-*p*-tolylpropan-1-one**, decomposed beyond 95 °C. ν_{max}: 3293 (NH), 3058, 3022, 2924, 2850, 1742 (C═O), 1603 (Ar) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 8.10 (d, 1H, $J = 8.0$ Hz, ArH), 8.02 (m, 2H, ArH, NH), 7.66 (d, 1H, $J = 8.0$ Hz, ArH), 7.57–7.55 (m, 1H, ArH), 7.44–7.26 (m, 9H, ArH), 7.18–7.16 (m, 1H, ArH), 7.10–7.08 (m, 3H, ArH), 5.36 (dd, 1H, $J = 8.0$, 8.0 Hz, CH), 4.45 (dd, 1H, $J = 8.0$, 8.0 Hz, CH), 4.22 (dd, 1H, $J = 8.0$, 8.0 Hz, CH), 2.30 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): 170.8, 146.0, 140.2, 136.2, 135.9, 135.8, 132.6, 131.0, 130.0, 129.2, 128.7, 128.6, 128.0, 127.5, 127.4, 125.9, 122.2, 120.8, 120.0, 119.9, 114.5, 113.4, 111.0, 41.3, 37.4, 21.0. Anal. $C_{30}H_{24}N_4O$. Calcd. C, 78.92; H, 5.30; N, 12.27. Found C, 79.17; H, 5.42; N, 12.15.

Compound **3dd**, **1-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-(1-benzyl-1*H*-indol-3-yl)-3-(4-chlorophenyl)propan-1-one**, mp 138–140 °C. ν_{max}: 3062, 3027, 2923, 2853, 1730 (C═O), 1614 (Ar) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 8.21 (d, 1H, $J = 8.0$ Hz, ArH), 8.10 (d, 1H, $J = 8.0$ Hz, ArH), 7.63–7.61 (m, 1H, ArH), 7.49–7.47 (m, 2H, ArH), 7.39–7.36 (m, 2H, ArH), 7.25–7.20 (m, 5H, ArH), 7.14–7.01 (m, 6H, ArH), 5.30 (s, 2H, CH_2), 5.18 (dd, 1H, $J = 8.0$, 8.0 Hz, CH), 4.26 (dd, 1H, $J = 8.0$, 8.0 Hz, CH), 4.13 (dd, 1H, $J = 8.0$, 8.0 Hz, CH). ^{13}C NMR (100 MHz, $CDCl_3$): 170.5, 146.2, 141.7, 137.3, 137.0, 132.4, 131.0, 130.5, 129.2, 128.8, 128.7, 127.6, 127.0, 126.7, 126.6, 126.2, 125.6, 122.3, 120.2, 119.5, 117.0, 114.5, 109.8, 50.0, 41.9, 38.3. Anal. $C_{30}H_{23}ClN_4O$. Calcd. C, 73.39; H, 4.72; N, 11.41. Found C, 73.16 H, 4.79; N, 11.35.