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FULL-LENGTH PAPER

The Michael addition of indoles and pyrrole to α-, β-unsaturated ketones and double-conjugate 1,4-addition of indoles to symmetric enones promoted by pulverization-activation method and Thia-Michael addition catalyzed by wet cyanuric chloride

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Abstract A new, facile, and efficient procedure for conjugate addition of indole and pyrrole with Michael acceptors have been developed for pulverization–activation reaction catalyzed by wet cyanuric chloride (2,4,6-trichloro-[1,3,5]-triazine or TCT) through grinding under solvent-free conditions at room temperature. Also, double-conjugate 1,4-addition of indoles to dibenzylidenacetones and conjugate addition of thiols with Michael acceptors using wet-TCT as catalyst is reported.

Keywords TCT · Conjugate 1,4-addition · α-, β-unsaturated compounds · Solvent-free

Introduction

In recent years, considerable attention has been focused on the development of efficient and operationally simple protocols for carbon–carbon and carbon–heteroatom bonds formation for the construction of valuable molecules. Addition reactions of indoles, amines, and thiols to α-, β-unsaturated compounds have received much interest because a number of their derivatives occur in nature and possess a variety of biological activities [1,2]. Thus, the development of facile and environmentally friendly synthetic methods for the preparation of these compounds constitutes an active area of investigation in pharmaceutical and organic synthesis. The Michael addition is one of the most useful carbon–carbon bond-forming reactions and has wide synthetic applications in organic synthesis [3]. This reaction is traditionally catalyzed by strong bases that often lead to undesirable side reactions [4]. A variety of Lewis acids are found to catalyze this reaction, and these procedures are also not free from disadvantages [5]. Thus, a number of milder reagents and Lewis acids catalysts such as Al_2O_3 [6], K_2CO_3 [7], rhodium complex [8], ruthenium complex [9], clay-supported nickel bromide [10], quaternary ammonium salt [11], $InBr_3$ [12], $InCl_3$ [13], $Bi(NO_3)_3$ [14], I_2 [15], $Bi(OTf)_3$ [16], $HClO_4/SiO_2$ [17], GaI_3 [18], PTSA [19], sulfamic acid [20], Ru(III) [21], NH_4Cl [22], and N-phenyltris(dimethylamino)iminophosphorane immobilized on polystyrene resin [23] have been developed over the past few years. Unfortunately, a number of these procedures have one or the other disadvantages such as longer reaction time, use of excessive expensive catalyst, harsh reaction conditions, failure to provide addition product and tedious experimental procedure. Consequently, there is a need for a catalytically efficient method for these transformations, which might work under mild and more economical conditions. As a part of our ongoing research program to develop new synthetic methodologies [24–26], we found that cyanuric chloride (2,4,6-trichloro-[1,3,5]-triazine or TCT) as a stable, non-volatile, inexpensive, and safe reagent, which has been used synthetically for the preparation of various types of compounds such as alkyl chloride [27], Beckmann rearrangement products [28], isonitriles [29], bis(indolyl)methanes [30], etc.

Results and discussion

In this article, we are reporting a simple and facile method for conjugate addition of indoles and pyrrole to Michael

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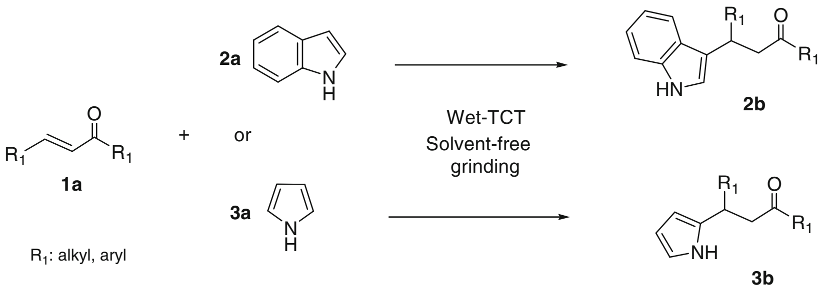


Scheme 1 Conjugate addition of indoles and pyrrole to Michael acceptors

Table 1 Screening for optimum reaction conditions[a]

Entry	Conditions	Time (h)	yield (%)[b]
1	EtOH/20 mol% TCT	2	90
2	$CHCl_3$/20 mol% TCT	3.5	80
3	CCl_4/20 mol% TCT	5	40
4	CH_3CN/20 mol% TCT	3.5	90
5	THF/20 mol% TCT	3	85
6	CH_2Cl_2/20 mol% TCT	4	85
7	MeOH/20 mol% TCT	3.5	85
8	H_2O/20 mol% TCT	2.5	0
9	Solvent-free/20 mol% TCT/grinding	1.5	92
10	Solvent-free/10 mol% TCT/grinding	6	80
11	Solvent-free/10 mol% wet-TCT/grinding	0.083	98
12	Without TCT in solvent or solvent-free	10 or 0.3	0

[a] Reaction condition: 1a (1 mmol) and solvent (3 mL), r.t.
[b] Isolated yield

acceptors under solvent-free conditions in the presence of wet-TCT as catalyst (Scheme 1).

In a preliminary experiment, treatment of indole (**2a**) with 1, 3-diphenylpropenone (**1a**) in CH_3CN using 20 mol% cyanuric chloride (2,4,6-trichloro-[1,3,5]-triazine or TCT) as catalyst at room temperature for 3 h afforded the 3-substituted indole adduct **2b** in 75% yield after recrystallization from ethanol–water. Product **2b** was characterized by spectroscopic analysis. Encouraged by this result, we proceeded to study the effect of solvent and reaction conditions on the Michael addition for the synthesis of 3-substituted indoles (**2b**) (Table 1). As shown in Table 1, the best conversion was observed when the reaction was performed in the presence of 10 mol% of wet-TCT for 5 min under pulverization–activation method at room temperature (Table 1, entry 11).

Under the optimized reaction conditions, a variety of α-, β-unsaturated ketones and electron-deficient olefins were tested via a pulverization–activation method catalyzed by 10 mol% wet-TCT (PAMC-wet TCT) through the grinding of indole with these Michael acceptors under solvent-free conditions. The reactions proceeded easily and the products were isolated with comparable yields in short reaction times (Table 2, entries 1–15).

Apparently the pyrrole Michael addition was also done in the same fashion as indole Michael addition (solvent-free pulverization–activation). On the basis of the results obtained, the reaction was extended to pyrrole, and it was found that wet-TCT can also efficiently catalyzed the reaction of pyrrole with different α-, β-unsaturated ketones, affording 2-substituted pyrrole derivatives with comparable yields (Table 2, entries 16–20).

Thia-Michael addition products of α-, β-unsaturated carbonyl compounds are very important building blocks for the synthesis of bioactive compounds [31], and heterocycles [32], and are also used as chiral auxiliary for the synthesis of optically active α-hydroxy aldehydes [33]. Therefore, the development of an efficient and selective catalyst for the construction of carbon–sulfur bond is of interest in organic synthesis. In continuation of our ongoing research program to develop better and newer synthetic methodologies [24–26], we perceived that wet-TCT (cyanuric chloride) might be a very useful catalyst for Thia-Michael reaction (Scheme 2).

In a set of initial experiments, 1, 3-diphenylpropenone was allowed to react with thiophenol in an equimolar ratio in the presence of a varied quantity of wet-TCT and various conditions. After a series of experimentations, it was observed that excellent yield of the Michael adduct can be achieved by reacting a mixture of 1, 3-diphenylpropenone (1 equiv.), thiophenol (1.1 equiv.), and wet-TCT (10 mol %) in acetonitrile (3 mL) at room temperature. Aliphatic and aromatic thiols can be used in the optimized procedure with numerous cyclic and acyclic α-, β-unsaturated carbonyl compounds. Products were isolated with comparable yields and the results were summarized in Table 2 (entries 21–26).

In continuation of our research work to explore new reactions promoted by TCT, we found that wet-TCT (cyanuric chloride) smoothly catalyzes the reaction of indoles and dibenzylidenacetones leading to two C–C bonds in one-pot under solvent-free conditions, resulting in desired adducts (Scheme 3).

The generality of the procedure was evaluated by the reaction of a number of dibenzylidenacetones with indole under pulverization–activation method at room temperature. The

Table 2 Michael addition of indole, pyrrole and thioles to Michael acceptors catalyzed by wet-TCT

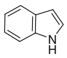
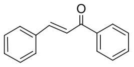
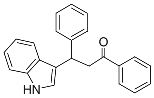
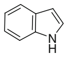
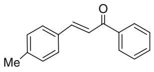
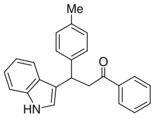
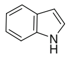
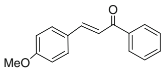
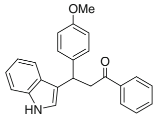
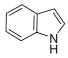
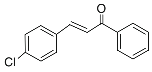
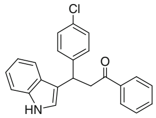
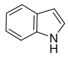
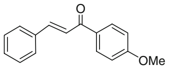
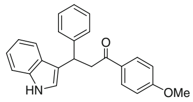
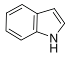
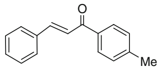
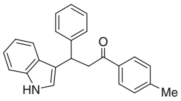
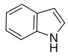
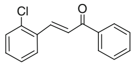
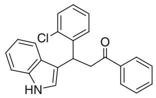
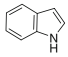
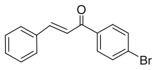
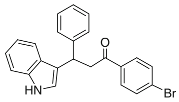
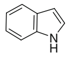
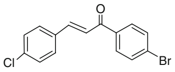
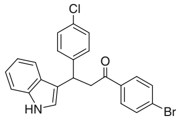
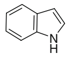
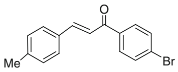
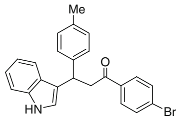
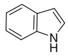
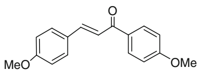
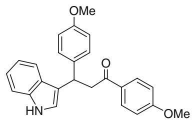
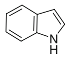
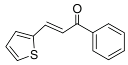
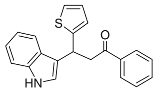
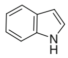
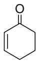
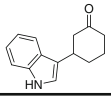
Entry	Nucleophile	Electrophile	Products[a]	Time (min.)	Yield (%)[b]	Ref.
1				3	96	[19]
2				5	95	[19]
3				5	90	[19]
4				2.5	98	[19]
5				4	98	[36]
6				5.5	90	[19]
7				3.5	96	[34]
8				7	85	[34]
9				5	98	-
10				6	95	-
11				3.5	96	[36]
12				6	90	[19]
13				7.5	92	[16]

Table 2 continued

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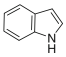
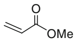
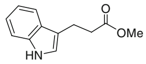
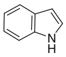
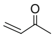
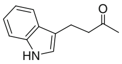
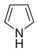
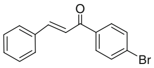
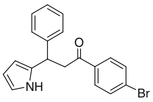
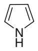
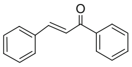
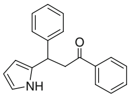
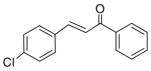
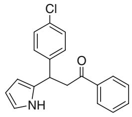
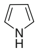
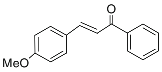
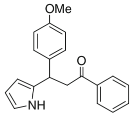
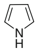
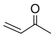
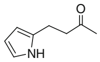
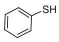
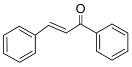
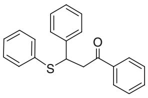
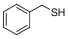
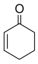
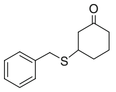
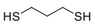
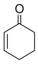
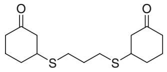
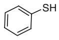
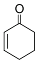
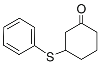
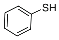
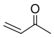
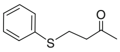
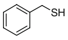
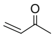
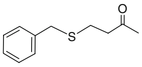
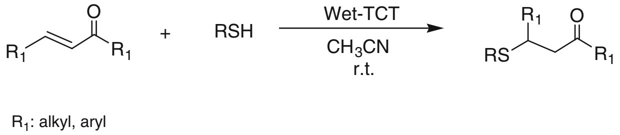
14				5	80	[16]
15				6	92	[16]
16				5	98	-
17				5	90	[35]
18				6	96	-
19				5.5	92	[35]
20				5	80	[35]
21[c]				15	85	[17]
22				5	95	[16]
23				30	90	[17]
24				15	75	[16]
25				10	92	[16]
26				5	95	[17]

[a] Products were characterized by ^{1}H-NMR, ^{13}C-NMR, IR, and comparison with reported data;
[b] Isolated yields
[c] Entry 21–26, conditions: Wet-TCT, CH_3CN, r.t.



Scheme 2 Thia-Michael addition

reactions proceeded smoothly, and the adducts were isolated in comparable yields in short reaction times (Table 3, entries 1–7). Dibenzylidenacetone has two conjugated double bonds; interestingly, both mono-addition products (Table 3, entry 1) and double-addition products (Table 3, entry 2) were obtained in good yields by controlling the ration of indole.

The plausible mechanism of the reaction is as shown below (Fig. 1). The adventitious moisture reacts with TCT to release 3 mol of HCl [37] and cyanuric acid (removable by water washing) as by product. The HCl generated in situ acts as a protic acid to activate the carbonyl oxygen of α-, β-unsaturated compounds.

Scheme 3 Reaction of indoles and dibenzylidenacetones

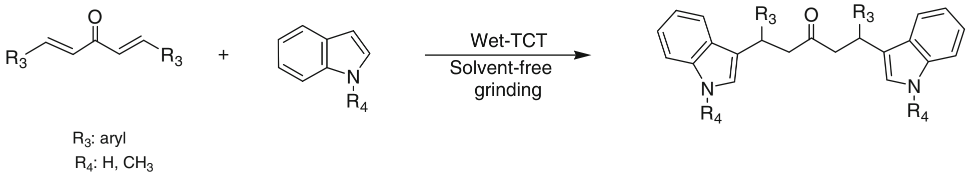
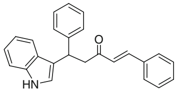
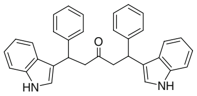
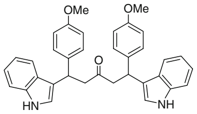
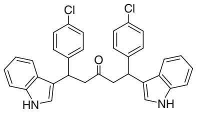
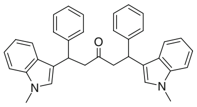
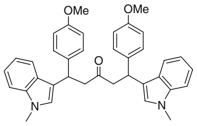
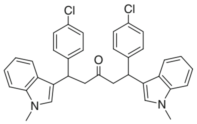
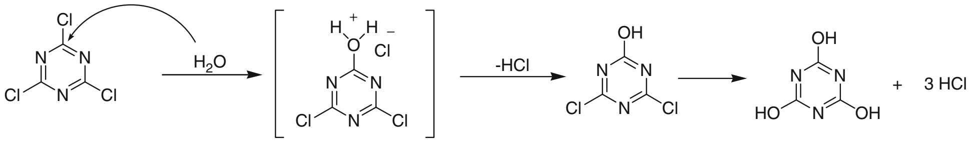


Table 3 Wet-TCT-catalyzed double Michael addition of indoles to symmetric enones

Entry	Products[a]	Time (min.)	Yield (%)	Ref.
1		8	90	[18]
2		10	95	[21]
3		12	80	[21]
4		10	85	[21]
5		15	70	[21]
6		15	75	[21]
7		15	75	[21]

[a] Products were characterized by ^{1}H-NMR, ^{13}C-NMR, IR, and comparison with reported data

Fig. 1 Plausible mechanism



A proposed mechanistic pathway for the reaction of indole with dibenzylidenacetone conducted in the presence of wet-TCT is presented in Scheme 4 [21].

Conclusions

In conclusion, we have developed an efficient and cost-effective method for Michael addition of indole and pyrrole to Michael acceptors and double conjugate 1,4-addition of indoles to symmetric enones, with pulverization–activation method catalyzed by wet cyanuric chloride (2,4,6-trichloro-[1,3,5]-triazine or TCT) through grinding under solvent-free conditions at room temperature. This method has advantages such as ease of process, mild condition, high yields, short reaction times, and is a novel method for the synthesis of important 3-substituted indole derivatives and 2-substituted pyrrole derivatives. In addition, we have developed an efficient procedure for the C–S bond formation catalyzed with wet-TCT under mild conditions.

Experimental section

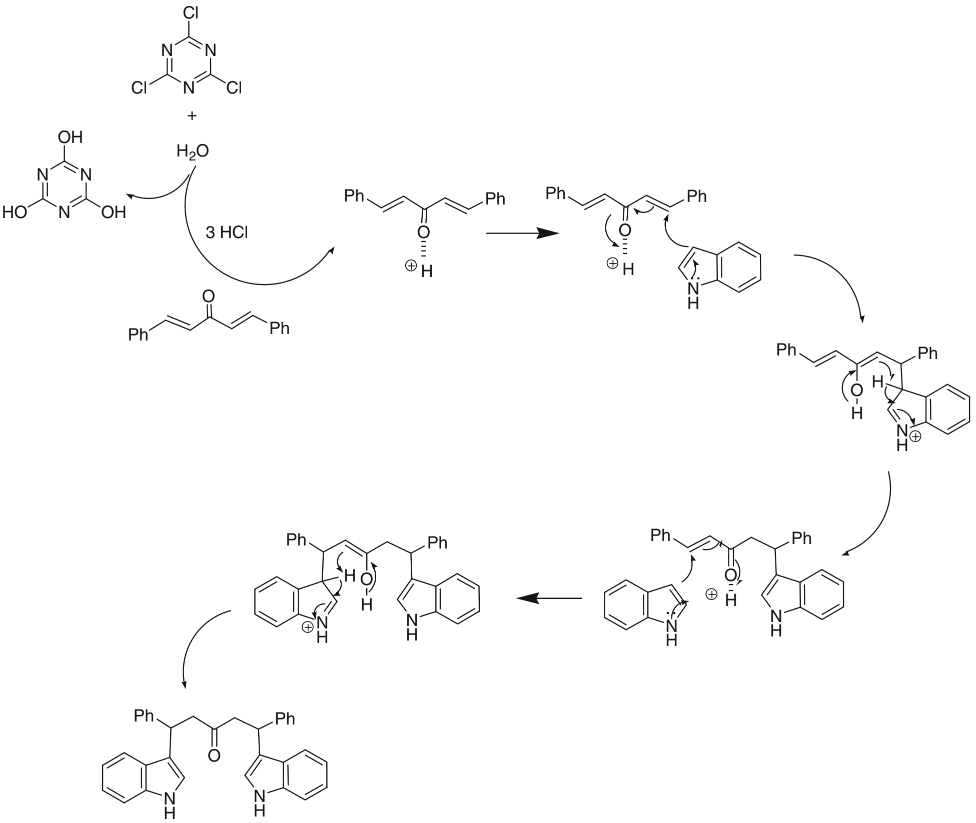
All commercially available chemicals were obtained from Merck and Fluka companies, and used without further purifications unless otherwise stated. ^{1}H-NMR spectra were recorded on a Jeol 90 MHz FT NMR spectrometer using TMS as internal standard, and chemical shifts are in δ (ppm). Infrared (IR) was conducted on a Perkin Elmer GX FT-IR spectrometer. All yields refer to isolated products.

The Michael addition of indole and pyrrole to α-, β-unsaturated carbonyl compounds: General Procedure

A mixture of indole or pyrrole (1 mmol), α-, β-unsaturated carbonyl compound (1 mmol), TCT (10 mol%) and double-distilled H_2O (2 drops) were mixed and ground with pestle in a mortar for an appropriate time at room temperature. After completion of the reaction (monitored by TLC, hexane/acetone 3:1), the reaction mixture was diluted with water (20 mL) and stirred for 5 min at room temperature. The resulting solid products were collected by filtration and recrystallized from ethanol–water (70:30).

General procedure for the Michael addition of thiols to α-, β-unsaturated carbonyl compounds:

Scheme 4 Proposed mechanistic pathway for the reaction of indole with dibenzylidenacetone



To a mixture of thiol (1.1 mmol), α-, β-unsaturated carbonyl compound (1 mmol) in CH_3CN (3 mL), TCT (10 mol %), and double-distilled H_2O (2 drops) were added. The mixture was allowed to be stirred at room temperature for a specified period as indicated in Table 2. The reaction was monitored by TLC (3:1 n-hexane/acetone). After completion of the reaction, the solvent was evaporated. Then, water (20 mL) was added and stirred for 5 min at room temperature. The resulting solid products were collected by filtration and were recrystallized from ethanol.

Wet cyanuric chloride catalyzed double Michael addition of indole to dibenzylidenacetones:

A mixture of indole (2 mmol), dibenzylidenacetone (1 mmol), TCT (10 mol%), and double-distilled H_2O (2 drops) were mixed and ground with pestle in a mortar for an appropriate time at room temperature. After completion of the reaction (monitored by TLC, hexane/acetone 3:1), the reaction mixture was diluted with water (20 mL) and stirred for 5 min at room temperature. The resulting solid products were collected by filtration and were recrystallized from ethanol–water (70:30).

Spectra data of **9(2a)**: Solid; mp 130–132°C. IR (KBr): 3398, 3084, 3056, 3026, 1681, 1596, 1579, 1489, 820, 768, 746, 689 cm^{-1}.^{1}H-NMR (FT-90 MHz, $CDCl_3$) : $\delta_=$ 8.04 (s, NH, 1H), 7.19–7.87 (m, ArH, 12H), 7.01 (s, indole ring, 1H), 4.97 (t, $J = 7.2$ Hz, CH, 1H), 3.71–3.85 (m, CH_2, 2H). Anal. calcd for $C_{23}H_{17}BrClNO$: C, 62.96; H, 3.91; N, 3.19. Found: C, 62.52; H, 3.75; N, 3.06. MS (EI): m/z = 437 (M^+, 75%), 438 (M + 1, 19%), 439 (M + 2, 100%).

Spectra data of **10(2a)**: Solid; mp 160–161°C. IR (KBr): 3422, 1670, 1250, 1032 cm^{-1}. ^{1}H-NMR (FT-90 MHz, $CDCl_3$) : $\delta_=$ 8.05 (s, NH, 1H), 7.10–7.98 (m, ArH, 12H), 7.05 (s, iodole ring, 1H), 5.00 (t, $J = 7.2$ Hz, CH, 1H), 2.25–3.73 (m, CH_2, 2H). Anal. calcd for $C_{24}H_{20}BrNO$: C, 68.91; H, 4.82; N, 3.35. Found: C, 68.47; H, 4.54; N, 3.26. MS (EI): m/z = 417 (M^+, 99%), 418 (M + 1, 19%), 419 (M + 2, 100%).

Spectra data of **16(3b)**: Solid, mp 125–127°C. IR (KBr): 3395, 1690, 1420, 1275, 1041 cm^{-1}.^{1}H-NMR (FT-90 MHz, $CDCl_3$) : $\delta_=$ 8.25 (brs, NH, 1H), 6.50–8.12 (m, ArH, 12H), 5.10 (t, $J = 8.0$ Hz, CH, 1H), 3.52–3.61 (m, CH_2, 2H). Anal. calcd for $C_{19}H_{16}BrNO$: C, 64.42; H, 4.55; N, 3.95. Found: C, 64.35; H, 4.34; N, 3.64. MS (EI): m/z = 353 (M^+, 100%), 338 (M + 1, 21%), 339 (M + 2, 99%).

Spectra data of **18(3b)**: Solid, mp 120-122°C. IR (KBr): 3410, 1685, 1420, 1262, 1020 cm^{-1}.^{1}H-NMR (FT-90 MHz, $CDCl_3$) : $\delta_=$ 8.35 (brs, NH, 1H), 6.50–7.95 (m, ArH, 12H), 5.00 (t, $J = 8.1$ Hz, CH, 1H), 3.50–3.65 (m, CH_2, 2H). Anal. calcd for $C_{19}H_{16}ClNO$: C, 73.66; H, 5.21; N, 4.52. Found: C, 73.45; H, 4.98; N, 4.46. MS (EI): m/z = 309(M^+, 100%), 310(M + 1, 21%), 311 (M + 2, 34%).

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