Synthesis of 2*H*-Indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione Derivatives Using Wet Cyanuric Chloride under Solvent-Free Condition

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A simple and facile synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione derivatives has been accomplished by a three-component condensation reaction of dimedone, aromatic aldehydes and phthalhydrazide under solvent-free conditions in the presence of wet cyanuric chloride as a catalyst.

Keywords: 2*H*-Indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione; Dimedone; Phthalhydrazide; Cyanuric chloride; Solvent-free; Multicomponent reation.

INTRODUCTION

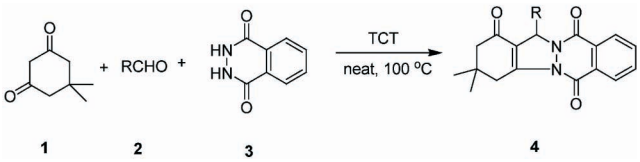
Phthalazine are important heterocycles that are known to possess multiple biological activities such as antimicrobial,[1] anticonvulsant,[2] antifungal,[3] anticancer,[4] and anti-inflammatory activities.[5] Therefore, a number of methods have been reported for the synthesis of phthalazine derivatives.[6] Nevertheless the development of new synthetic methods for the efficient preparation of heterocycles containing phthalazine ring fragment is an interesting challenge. Recently, synthesis of 2*H*-indazolo[2,1-*b*]-phthalazine-1,6,11(13*H*)-trione derivatives have been reported using *p*-TSA,[7] Me_3SiCl,[8] silica sulfuric acid,[9] H_2SO_4,[10] $Mg(HSO_4)_2$,[11] and silica supported poly phosphoric acid[12] as catalysts. However, many of these methodologies are associated with one or more disadvantages such as use of expensive catalyst or toxic organic solvents (8, 11), strong acidic conditions (7, 10), and harsh reaction conditions (7-12).

Recently, 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride, TCT) has emerged as an inexpensive and easily available reagent in organic synthesis.[13] In this paper, we wish to report, a simple and facile synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione derivatives by a three-component condensation reaction of dimedone, aromatic aldehydes and phthalhydrazide under solvent-free conditions in the presence of wet cyanuric chloride as a catalyst.

RESULTS AND DISCUSSION

In order to optimize the reaction conditions, we first examined the amount of catalyst and the reaction temperature, the reaction of dimedone, benzaldehyde and phthalhydrazide to the corresponding 3,4-dihydro-3,3-dimethyl-13-phenyl-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione was studied under solvent-free conditions in the presence of wet-cyanuric chloride at different temperatures. The results are summarized in Table 1. As shown in Table 1, the reaction using 3 mol % cyanuric chloride at 100 °C proceeded in highest yield.

Scheme I



Based on the optimized reaction conditions, a range of 2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione derivatives was synthesized by the reaction of dimedone, aldehyde and phthalhydrazide. The reaction proceeded at 100 °C within 25 min in excellent yields after the addition of 3 mol % cyanuric chloride (Table 2). The structures of the products were established from their spectral properties (^{1}H NMR, ^{13}C NMR and elemental analysis) and also by comparison with available literature data.

HCl generated *in situ*, from cyanuric chloride, efficiently catalyzes these reactions, a plausible mechanism is shown in Scheme II. Accordingly, cyanuric chloride reacts with 'incipient' moisture and releases 3 equvient of HCl

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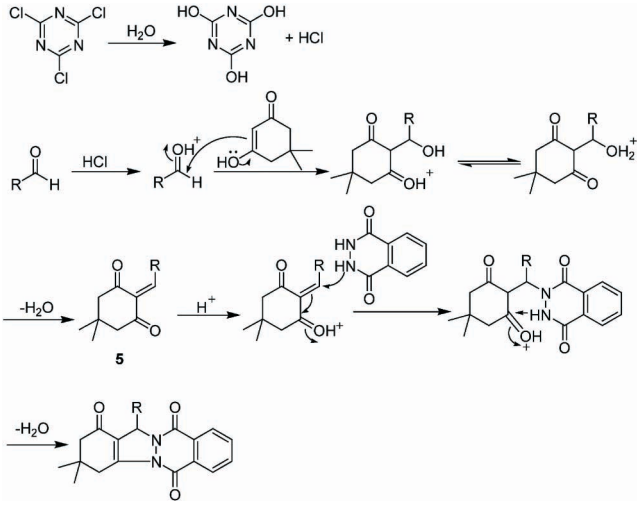
Table 1. The amounts of catalyst and temperature optimization for the synthesis of 3,4-dihydro-3,3-dimethyl-13-phenyl-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione[a]

Entry	TCT/mol%	Temperature/°C	Time/min	Yield/%[b]
1	0	100	60	0
2	1	100	45	68
3	2	100	45	80
4	3	25	120	0
5	3	50	60	46
6	3	80	45	57
7	3	90	30	78
8	3	100	15	96
9	3	110	15	95
10	3	120	15	96
11	4	90	20	88
12	4	100	20	94
13	5	100	20	89
14	6	100	20	90
15	7	100	15	92
16	8	100	15	94

[a] Reaction conditions: dimedone (1 mmol); benzaldehyde (1.2 mmol); phthalhydrazide (1 mmol); H_2O (3 drops); neat.
[b] Isolated yield.

and cyanuric acid (removable by washing with water) as by-product. The formation of products **4a-4i** can be rationalized by initial formation of heterodiene **5** by standard Knoevenagel condensation of dimedone and aromatic aldehyde in the presence of a catalytic amount of HCl. Subsequent Michael-type addition of phthalhydrazide to the heterodienes followed by cyclization and dehydration afford the corresponding products **4a-4i**.

Scheme II



To recognize the capability of the present method in comparison with reported methods for the preparation of 2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione derivatives from dimedone, aromatic aldehydes and phthalhydrazide, the model reaction of dimedone, benzaldehyde and phthalhydrazide was described. While in most of these cases comparative yields of the desired product were obtained following the TCT-catalyzed procedure, the reported procedures required expensive catalyst or toxic organic solvents (entry 3, 4, 6), strong acidic conditions (entry 1, 4), high catalyst loading (entry 1-6), and long reaction time (4, 5). These results clearly demonstrate that TCT is an equally or more efficient catalyst for this three-component reaction.

Table 2. Synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione derivatives[a]

Entry	R	Time/min	Yield/%[b]	m.p./°C (Lit. m.p.)
a	C_6H_5	15	96	205-207 (204-206) [10]
b	4-Cl-C_6H_4	15	97	262-264 (258-260) [10]
c	4-MeO-C_6H_4	10	95	220-221 (218-220) [9]
d	4-Me-C_6H_4	10	96	228-230 (226-231) [10]
e	4-NO_2-C_6H_4	15	91	220-222 (216-218) [10]
f	3-NO_2-C_6H_4	20	91	270-270 (269-271) [10]
g	4-F-C_6H_4	15	94	220-220-2 (221-223) [10]
h	2-Cl-C_6H_4	15	91	262-264 (266-269) [10]
i	2,4-Cl_2-C_6H_3	10	95	222-224 (218-220) [10]
j	3,4-Cl_2-C_6H_3	10	90	262-264
k	3,4,5-MeO-C_6H_2	25	89	233-235 (232-234) [10]

[a] Reaction conditions: dimedone (1 mmol); aldehyde (1.2 mmol); phthalhydrazide (1 mmol); TCT (0.03 mmol); H_2O (3 drops); neat; 100 °C.
[b] Isolated yield.

Table 3. Effect of catalyst on the reaction of dimedone, benzaldehyde and phthalhydrazide

Entry	Reagent and Conditions	Time/min	Yield/%	Ref.
1	*p*-Toluenesulfonic acid, solvent-free, 80 °C, 30 mol%	10	93	7
2	Poly phosphoric acid-SiO_2, solvent-free, 100 °C, 5 mol%	6	93	12
3	$Mg(HSO_4)_2$, solvent-free, 100 °C, 10 mol%	4	88	11
4	H_2SO_4, [bmim][BF_4], 80 °C, 15 mol%	30	94	10
5	Silica sulfuric acid, solvent-free, 100 °C, 6.5 mol%	7	91	9
6	TMSCl, CH_3CN/DMF (8:2), 80 °C,	30	90	8
7	TCT, solvent-free, 100 °C, 3 mol%	15	96	This work

In summary, a novel and highly efficient methodology for the synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione by a three-component condensation reaction of dimedone, aromatic aldehydes and phthalhydrazide under solvent-free conditions in the presence of wet-cyanuric chloride as a catalyst is reported. In addition, this protocol describes a very fast, user friendly, 'green' and low cost procedure for the synthesis of these products. Furthermore, cyanuric chloride is a catalyst with cyanuric acid as byproduct that is removable by washing with water. This easy removal of the catalyst makes this method a better choice for chemical industries.

EXPERIMENTAL

NMR spectra were determined on Bruker AV-400 spectrometer at room temperature using TMS as internal standard, coupling constants (*J*) were measured in Hz; Elemental analysis were performed by a Vario-III elemental analyzer; Melting points were determined on a XT-4 binocular microscope and were uncorrected; Commercially available reagents were used throughout without further purification unless otherwise stated.

General Procedure for synthesis of 4

A mixture of dimeone (1 mmol), aldehydes (1.2 mmol), phthalhydrazide (1 mmol), cyanuric chloride (0.03 mmol) and H_2O (3 drops) was heated at 100 °C for the appropriate time (Table 2). The reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature and washed with water. The solid products were purified by recrystallization from aqueous EtOH (25%).

3,4-Dihydro-3,3-dimethyl-13-phenyl-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione (4a)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.37-8.27 (m, 2H), 7.86 (dd, 2H, *J* = 3.2, 7.6 Hz), 7.42 (d, 2H, *J* = 7.2 Hz), 7.37-7.29 (m, 3H), 6.46 (s, 1H), 3.43 (d, 1H, *J* = 18.8 Hz), 3.25 (dd, 1H, *J* = 2.4, 18.8 Hz), 2.35 (s, 2H), 1.22 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 192.1, 156.0, 154.3, 150.8, 136.4, 134.5, 133.5, 129.1, 129.0, 128.7, 128.0, 127.7, 127.1, 118.6, 65.0, 50.9, 38.0, 34.6. 28.7, 28.5; Anal. calcd for $C_{23}H_{20}N_2O_3$: C 74.18, H 5.41, N 7.52; found: C 74.25, H 5.36, N 7.48.

3,4-Dihydro-3,3-dimethyl-13-(4-chlorophenyl)-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione (4b)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.38-8.26 (m, 2H), 7.88-7.85 (m, 2H), 7.37 (d, 2H, *J* = 8.4 Hz), 7.31 (d, 2H, *J* = 8.4 Hz), 6.42 (s, 1H), 3.41 (d, 1H, *J* = 18.8 Hz), 3.25 (dd, 1H, *J* = 2.0, 18.8 Hz), 2.35 (s, 2H), 1.27-1.21 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 192.1, 156.0, 154.4, 151.1, 134.9, 134.6, 134.5, 133.7, 129.0, 128.9, 128.5, 128.0, 127.7, 118.0, 64.3, 50.9, 38.0, 34.7, 28.7, 28.4; Anal. calcd for $C_{23}H_{19}ClN_2O_3$: C 67.90, H 4.71, N 6.89; found: C 67.95, H 4.82, N 6.79.

3,4-Dihydro-3,3-dimethyl-13-(4-methoxylphenyl)-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione (4c)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.36-8.26 (m, 2H), 7.86-7.83 (m, 2H), 7.35 (d, 2H, *J* = 8.8 Hz), 6.86 (d, 2H, *J* = 8.4 Hz), 6.43 (s, 1H), 3.77 (s, 3H), 3.43 (d, 1H, *J* = 18.8 Hz), 3.24 (dd, 1H, *J* = 2.0, 18.8 Hz), 2.35 (s, 2H), 1.29-1.22 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 192.2, 159.7, 156.0, 154.2, 150.7, 134.4, 133.4, 129.1, 128.9, 128.5, 128.3, 127.9, 127.7, 118.5, 114.1, 64.6, 55.2, 51.0, 38.0, 34.6, 28.7, 28.5; Anal. calcd for $C_{24}H_{22}N_2O_4$: C 71.63, H 5.51, N 6.96; found: C 71.59, H 5.62, N 7.02.

3,4-Dihydro-3,3-dimethyl-13-(4-methylphenyl)-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione (4d)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.37-8.27 (m, 2H), 7.87-7.83 (m, 2H), 7.31 (d, 2H, *J* = 8.0 Hz), 7.15 (d, 2H, *J* = 7.6 Hz), 6.43 (s, 1H), 3.43 (d, 1H, *J* = 18.8 Hz), 3.25 (dd, 1H, *J* = 2.0, 18.8 Hz), 2.34 (s, 2H), 2.31 (s, 3H), 1.22 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 192.2, 156.0, 154.2, 150.7, 138.5, 134.4, 133.4, 133.3, 129.4, 129.1, 127.9,

127.7, 118.7, 64.8, 51.0, 38.0, 34.6, 28.7, 28.4, 21.2; Anal. calcd for $C_{24}H_{22}N_2O_3$: C 74.59, H 5.74, N 7.25; found: C 74.62, H 5.69, N 7.37.

3,4-Dihydro-3,3-dimethyl-13-(4-nitrophenyl)-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione (4e)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.40-8.24 (m, 2H), 8.21 (d, 2H, *J* = 8.8 Hz), 7.90 (dd, 2H, *J* = 1.6, 5.6 Hz), 7.62 (d, 2H, *J* = 8.8 Hz), 6.52 (s, 1H), 3.42 (d, 1H, *J* = 19.2 Hz), 3.27 (dd, 1H, *J* = 2.0, 19.2 Hz), 2.34 (s, 2H), 1.29-1.20 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 192.0, 155.9, 154.5, 151.6, 147.9, 143.4, 134.8, 133.9, 128.9, 128.6, 128.2, 128.0, 127.8, 124.0, 117.3, 64.1, 50.8, 38.0, 34.7, 28.7, 28.4; Anal. calcd for $C_{23}H_{19}N_3O_5$: C 66.18, H 4.59, N 10.07; found: C 66.21, H 4.50, N 10.01.

3,4-Dihydro-3,3-dimethyl-13-(3-nitrophenyl)-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione (4f)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.41-8.25 (m, 2H), 8.18 (d, 2H, *J* = 7.2 Hz), 7.92-7.89 (m, 3H), 7.57 (t, 1H, *J* = 7.2 Hz), 6.54 (s, 1H), 3.45 (d, 1H, *J* = 19.6 Hz), 3.29 (dd, 1H, *J* = 2.0, 19.6 Hz), 2.36 (s, 2H), 1.27-1.19 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 192.1, 156.0, 154.6, 151.8, 148.5, 138.6, 134.8, 134.2, 133.9, 129.7, 129.0, 128.6, 128.2, 127.7, 123.7, 121.5, 117.1, 64.1, 50.8, 38.0, 34.7, 28.7, 28.4; Anal. calcd for $C_{23}H_{19}N_3O_5$: C 66.18, H 4.59, N 10.07; found: C 66.18, H 4.65, N 10.05.

3,4-Dihydro-3,3-dimethyl-13-(4-fluorophenyl)-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione (4g)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.37-8.26 (m, 2H), 7.88-7.85 (m, 2H), 7.43-7.39 (m, 2H), 7.03 (t, 2H, *J* = 8.8 Hz), 6.44 (s, 1H), 3.42 (d, 1H, *J* = 18.8 Hz), 3.25 (dd, 1H, *J* = 2.4, 18.8 Hz), 2.35 (s, 2H), 1.27-1.22 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 192.1, 163.9, 161.5, 156.0, 154.4, 151.0, 134.6, 133.6, 132.2, 129.0, 128.9, 128.0, 127.7, 118.2, 115.8, 115.6, 64.3, 50.9, 38.0, 34.6, 28.7, 28.4; Anal. calcd for $C_{23}H_{19}FN_2O_3$: C 70.76, H 4.91, N 7.18; found: C 70.82, H 4.88, N 7.26.

3,4-Dihydro-3,3-dimethyl-13-(2-chlorophenyl)-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione (4h)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.39-8.25 (m, 2H), 7.89-7.84 (m, 2H), 7.49 (d, 1H, *J* = 6.8Hz), 7.34-7.22 (m, 3H), 6.69 (s, 1H), 3.42 (d, 1H, *J* = 18.8 Hz), 3.25 (dd, 1H, *J* = 2.0, 18.8 Hz), 2.33 (s, 2H), 1.27-1.22 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 192.1, 156.2, 154.2, 151.8, 134.5, 133.6, 133.0, 132.5, 130.5, 129.9, 129.0, 128.7, 128.0, 127.7, 127.2, 64.1, 50.8, 38.0, 34.6, 28.8, 28.4; Anal. calcd for $C_{23}H_{19}ClN_2O_3$: C 67.90, H 4.71, N 6.89; found: C 70.02, H 4.69, N 6.95.

3,4-Dihydro-3,3-dimethyl-13-(2,4-dichlorophenyl)-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione (4i)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.38-8.24 (m, 2H), 7.90-7.86 (m, 2H), 7.43 (d, 1H, *J* = 8.0Hz), 7.35-7.27 (m, 2H), 6.64 (s, 1H), 3.40 (d, 1H, *J* = 18.8 Hz), 3.25 (dd, 1H, *J* = 2.4, 18.8 Hz), 2.38-2.29 (m 2H), 1.23-1.21 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 192.1, 156.1, 154.3, 152.1, 135.1, 134.6, 133.7, 131.7, 130.4, 129.0, 128.5, 128.1, 127.7, 127.6, 116.1, 64.2, 50.8, 38.0, 34.6, 28.8, 28.4; Anal. calcd for $C_{23}H_{18}Cl_2N_2O_3$: C 62.60, H 4.11, N 6.35; found: C 62.76, H 4.02, N 6.48.

3,4-Dihydro-3,3-dimethyl-13-(3,4-dichlorophenyl)-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione (4j)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.39-8.27 (m, 2H), 7.90-7.87 (m, 2H), 7.46-7.42 (m, 2H), 7.32 (dd, 1H, *J* = 2.0, 7.6 Hz), 6.39 (s, 1H), 3.41 (d, 1H, *J* = 19.2 Hz), 3.25 (dd, 1H, *J* = 1.6, 19.2 Hz), 2.35 (s, 2H), 1.27-1.22 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 192.0, 155.9, 154.5, 151.4, 136.6, 134.7, 133.8, 133.0, 132.8, 130.7, 128.9, 128.8, 128.7, 128.1, 127.7, 126.8, 117.5, 63.8, 50.8, 38.0, 34.7, 28.6, 28.5; Anal. calcd for $C_{23}H_{18}Cl_2N_2O_3$: C 62.60, H 4.11, N 6.35; found: C 62.65, H 4.23, N 6.30.

3,4-Dihydro-3,3-dimethyl-13-(3,4,5-trimethoxyl)-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione (4k)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.38-8.30 (m, 2H), 7.89-7.87 (m, 2H), 6.64 (s, 2H), 6.40 (s, 1H), 3.83-3.81 (m, 9H), 3.46 (d, 1H, *J* = 18.8 Hz), 3.24 (dd, 1H, *J* = 2.0, 18.8 Hz), 2.37 (s, 2H), 1.26-1.24 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 192.2, 156.1, 154.5, 153.3, 150.8, 138.2, 134.6, 133.6, 131.8, 129.0, 128.9, 128.0, 127.7, 118.3, 104.6, 65.0, 60.7, 56.2, 50.9, 38.1, 34.6, 29.7, 28.9, 28.1; Anal. calcd for $C_{26}H_{26}N_2O_6$: C 67.52, H 5.67, N 6.06; found: C 67.62, H 5.74, N 6.01.

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