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Efficient one-pot three-component synthesis of 2*H*-indazole [2,1-*b*]phthalazine-1,6,11(13*H*)-triones at room temperature

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Abstract: Tetrabutylammonium bromide (TBAB) and cesium carbonate (Cs_2O_3) catalyzed, one-pot three-component synthesis of 2*H*-indazole[2,1b]phthalazine-1,6,11(*13H*)-triones was developed at room temperature in ethanol. Both electron donating and withdrawing groups are compatible under the optimized reaction parameters.

Keywords: TBAB; Cs_2CO_3; indazole[2,1-b]phthalazine-1,6,11(*13H*)-triones; catalysis.

1. Introduction

Synthesis of novel heterocyclic scaffolds is a continued area for the organic chemists since few decades due to their wide applicability.[1] Nitrogen heterocycles consisting of phthalazine functionality are essential owing to possessing various biological activities such as anticonvulsant, cardiotonic, vasorelaxant, antifungal, anticancer, anti-inflammatory activities.[2] Fused phthalazines have been found effective for the inhibition of p38 MAP kinase[3], selective binding of GABA receptor,[4] as anti-anxiety drug,[5] antitumor agent,[6] and high affinity ligand to the a 2dl subunit of calcium channel.[7]

2. Background

Synthetic procedures available for these compounds include PEG-6000,[8] phospho molybdic acid (PMA)-SiO_2,[9] silica sulfuric acid,[10] TMSCl,[11] *N*-halosulfonamides,[12] $Ce(SO_4)_24H_2O$,[13] CAN,[14] montmorillonite k-10,[15] heteropoly acids,[16] ultrasound,[17] dodecylphosphonic acid (DPA),[18] ionic liquds,[19] *p*-TSA,[20] Ni-NPs,[21] Fe_3O_4 at silica sulfuric acid,[22] $Mg(HSO_4)_2$,[23] starch sulfate,[24] mesoporous SBA-15 silica,[25] Fe_3O_4 at SiO_2-imid-PMAn magnetic nanoparticles,[26] $[Et_3N\text{-}SO_3H]HSO_4$,[27] inorganic-organic hybrid material Al-SBA-15-TPI/$H_6P_2W_{18}O_{62}$,[28] $MoO_3/\alpha\text{-}Al_2O_3$,[29] β-Cyclodextrin,[30] silica-supported $LA_{0.5}CA_{0.5}CrO_3$ nanoparticles,[31] $Y(OTf)_3$,[32] $NiFe_2O_4$ particles,[33] nano $\gamma\text{-}Al_2O_3/BF_3/Fe_3O_4$,[34-35] etc.

Among the existing methodologies developed so far, utilization of harsh organic solvents, elevated temperatures, easily unavailable and expensive reagents, was a major drawback. Surprisingly,

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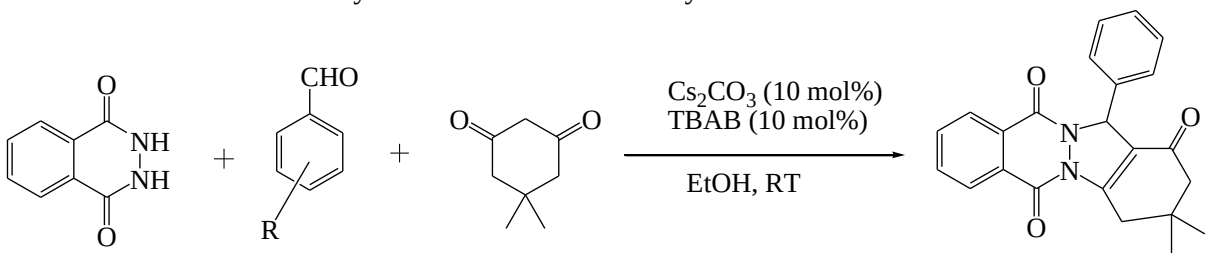
literature data proved that there are only few reports found on the synthesis of target compounds at *room temperature* conditions.[16,20] In this regard, there is a need of hour to develop cost-effective, environmentally benign synthetic methodology using less hazardous solvents.

3. Experimental

Mixture of aldehyde (1.2 mmol), phthalhydrazide (1 mmol), dimedone (1 mmol), catalyst TBAB (10 mol%) and Cs_2CO_3 (10 mol%) was stirred for the specified time as mentioned in Table 2, at room temperature in ethanol (EtOH, 5 mL). After completion TLC, the reaction mixture was washed with diethyl ether (3x15 mL) and the organic layer was evaporated on rotary evaporator to obtained crude product which was purified by recrystallization in 25% aq. ethanol. The spectral data is provided in supporting information.

4. Present Study

In continuation of our efforts to synthesize various heterocyclic moieties using green catalysis,[36-38] herein, we wish to report the synthesis of target compounds using easily accessible cesium carbonate and tetrabutyl ammonium bromide catalyst.



Scheme 1. Synthesis of 2*H*-indazolo [2,1-*b*] phthalazine-1,6,11(13*H*)-triones
R = Cl, F, Br, NO_2, OH, Me, OMe etc

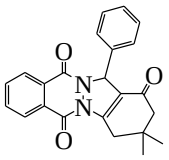
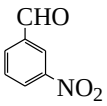
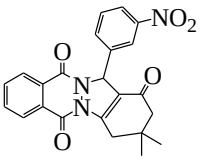
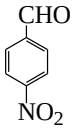
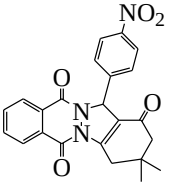
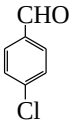
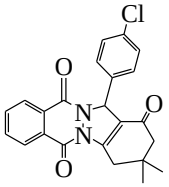
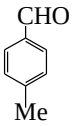
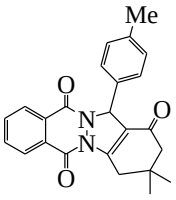
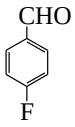
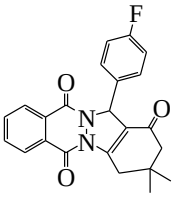
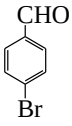
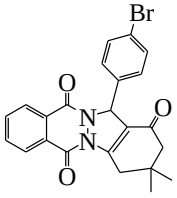
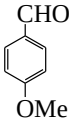
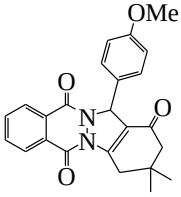
We initiated our studies by subjecting the mixture of 4-chlorobenzaldehyde, phthalhydrazide and dimedone in the presence of TBAB and Cs_2CO_3 at room temperature and the results were presented in (Table 1**)**. It is evident that in absence of base catalyst, the yield of the product was poor (Table 1, entry 1). On the other hand, the addition of Cs_2CO_3 (5 mol%) with TBAB (5 mol%) (Table 1, entry 3) dramatically enhanced the reactivity to give desired product in 70% yield. Using Cs_2CO_3 alone (5 mol %) also resulted in poor yield (Table 1, entry 2). Further optimization revealed that TBAB (10 mol %) and Cs_2CO_3 (10 mol%) at room temperature in ethanol was enough to complete the reaction within 1 h and gave desired product is 95% yield (Table 1, entry 5). A reduced yield was observed when the amount of TBAB and Cs_2CO_3 was increased respectively (Table 1, entries 6 and 7). In order to evaluate the effect of reaction medium on the yield of the desired product, we investigated various solvents such as ethanol, CH_3CN, THF and methanol (MeOH). The results indicated that (Table 1, entries 8, 9, 10) use of ethanol is better as compared to CH_3CN, THF and methanol.

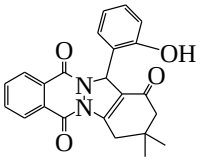
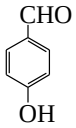
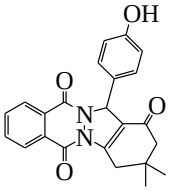
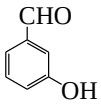
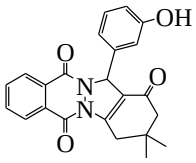
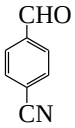
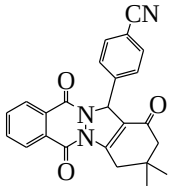
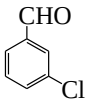
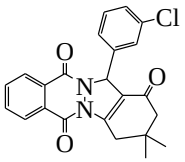
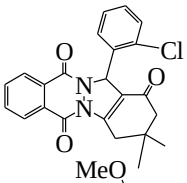
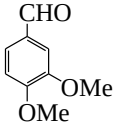
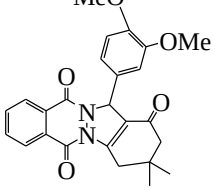
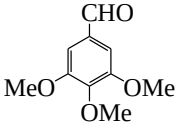
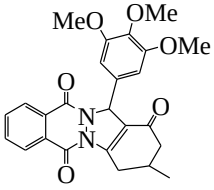
Table 1. Synthesis of **4d** under various conditions

Entry	TBAB (mol%)	Cs_2CO_3 (mol%)	Reaction Conditions	Yield (%)[a]
1	5	--	EtOH, rt, 5 h	30
2	--	5	EtOH, rt, 5 h	25
3	5	5	EtOH, rt, 4 h	70
4	7	7	EtOH, rt, 4 h	80
5	10	10	EtOH, rt, 1h	95
6	12	12	MeOH, rt, 1 h	92
7	15	15	EtOH, rt, 4 h	90
8	10	10	CH_3CN, rt, 4 h	85
9	10	10	THF, rt, 1 h	80
10	10	10	MeOH, rt, 1 h	90

[a]Isolated yields

Table 2. Synthesis of 2*H*-indazole[2,1-b]phthalazine-trione derivatives, by combining TBAB and Cs_2CO_3 as catalyst at room temperature (**4a-p**)

Entry	Substrate	Product		Time (min)	Yield (%)
1			**4a**	40	92
2			**4b**	47	91
3			**4c**	45	93
4			**4d**	49	95
5			**4e**	35	87
6			**4f**	50	86
7			**4g**	42	91
8			**4h**	37	85

Entry	Substrate	Product		Time (min)	Yield (%)
9			**4i**	42	84
10			**4j**	43	91
11			**4k**	41	90
12			**4l**	55	80
13			**4m**	52	85
14			**4n**	45	83
15			**4o**	37	87
16			**4p**	40	82

[a]Isolated yields

The present methodology was extended to different aldehydes to see the tolerability of various functional groups incroporated and the results were summarized in Table 2. Both electron-withdrawing groups such as nitro and halide groups or electron-donating groups reacted well to offer

the corresponding product (**4a-p**) in short experimental times with high yields. The structure of the compound was determined by spectral methods. The presence of a singlet at 6.40 in ^{1}H NMR and peaks at 2375 and 1669 cm^{-1} in IR spectra clearly indicate the formation of **4a**.

A comparison of the current method with those reported in the literature for the synthesis of 2*H*-indazolo [2,1-*b*] phthalazine-1,6,11(13*H*)-trione as the example has been provided in Table 3.

Table 3. Literature survey of the synthesis of 2*H*-indazolo[2,1-*b*] phthalazine-1,6,11(13*H*)-trione

Entry	Catalyst	Quantity	Condition	Time h/min	Solvent	Ref.
1	PPA-SiO_2	0.5mmol	100 °C	/5-10	Neat	[3b]
2	MNPs-PSA	30 mg	100 °C	/35	Neat	[3c]
3	TBBDA or PBBS	0.05mg/0.1g	100 °C	/10	Neat	[12]
4	CAN	5 mol%	50 °C	2/	PEG-400	[14]
5	Silica SO_3H	0.25g	100 °C	/10	Neat	[10]
6	Pressler catal. $H_{11}[NaP_5W_{30}O_{110}]/SiO_2$	50%	reflux	/10	Neat	[23b]
7	Ni-NP_5	10 mol%	80 °C	/10	Neat	[21]
8	K-10	5 mol%	MW, 80 °C	/10	Neat	[15]
9	Fe_3O_4@Silica Sulfuric acid	0.075g	100 °C	/35	Neat	[22]
10	PEG-OSO_3H	8 mol%	80 °C	/10-15	Neat	[8]
11	$Cu(OAc)_2$ Sodium ascorbate *p*-TSOH	10 mol% 20 mol% 20 mol%	reflux	2-3/	Ethanol	-
12	$Ce(SO_4)_2.4H_2O$	2.5 mol%	125 °C	/5-10	Neat	[13]
13	$Mg(HSO_4)_2$	0.25 g	100 °C	/5-10	Neat	[23]
14	TMSCl	0.5 equiv	80 °C	/5-10	Neat	[11]
15	$Mg(HSO_4)_2$	0.25 g	100 °C	/30-60	CH_3CN DMF	-
16	DPA	10 mol%	80 °C	/5-10	Neat	[18]
17	H_2SO_4 [bmim]BF_4	0.15 mmol 0.5 mL	Reflux 80 °C	/30 /30	H_2O/Ethanol Neat	[19]
18	Starch Sulfate	0.08 g	80 °C	/5-10	Neat	[24]
19	*p*-TSA	0.3 mmol	80 °C	/10	Neat	[20]
20	TBAB Cs_2CO_3	10 mol% 10 mol%	RT	/30	Ethanol	Present work

The reported methods in Table 3, not only required longer reaction times but also suffered from use of drastic conditions and poor yields. Compared to the reported methods (Table 3), present procedure offers the high yield in short reaction time and noteworthy feature is the reactions are performed at ambient temperature.

5. Conclusion

In conclusion, we have developed an easy, efficient and green protocol for the synthesis of 2*H*-indazole [2,1-*b*] phthalazine-1,6-11(13*H*)-triones in ethanol. The method offers marked improvement with its operational simplicity, low reaction time, high yield of pure products and at room temperature. We do hope that this improved methodology will be a value addition in the synthesis of the target scaffolds.

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Supporting Information

Supporting information accompanies this paper on http://www.acgpubs.org/journal/organic-communications

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