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Efficient Ruthenium-Catalyzed Dehydrogenative Synthesis of 2,4,6-triaryl-1,3,5-triazines from Aryl Methanols and Amidines

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By using $[RuCl_2(p\text{-Cymene})]_2/Cs_2CO_3$ as an efficient catalyst system, the readily available, inexpensive aryl methanols were firstly employed for dehydrogenative synthesis of aryl substituted 1,3,5-triazine derivatives. Due to the inherent stability of alcohols in contrast with aldehydes, our synthetic protocol is adaptable to a broad substrate scope, there is no need for stringent protection during the whole operation process, and it has the potential to prepare valuable products that are currently inaccessible or challenging to prepare using conventional methods. It is a significant important complement to the conventional synthetic methodologies.

Introduction

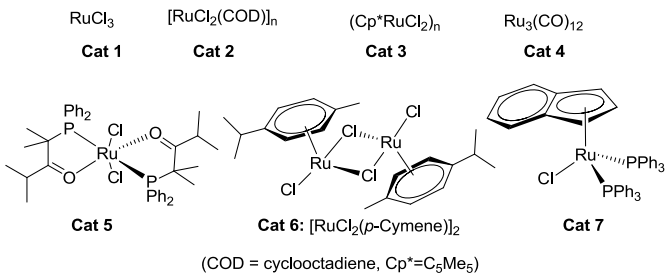
Aryl substituted 1,3,5-triazine derivatives constitute a significant important class of nitrogen-containing heterocycles that exhibit diverse biological activities.[1] And they are also powerful chelating ligands for the preparation of liquid crystal,[2] organometallic materials[3] and efficient hydrogenation catalysts.[4] Despite of these extensive functions, there are only a few methods reported for the preparation of this type of compounds. Generally, this goal can be realized by the following three conventional protocols: (1) Suzuki-coupling reactions using halogenated 1,3,5-triazines with aryl boronic acids;[5] (2) The cyclotrimerization of nitriles;[6] (3) The cyclization of aromatic aldehydes with amidines.[7] However, the Suzuki-coupling reactions require less-environmentally benign halogenated substrates and produce stoichiometric amount of undesirable waste. And the cyclotrimerization of nitriles generally needs excess of amines as the co-catalysts, which could increase the complexity of the work-up procedure. Interestingly, the condensation of aromatic aldehydes with amidines has provided a direct pathway for the synthesis of aryl substituted 1,3,5-triazine derivatives. However, the use of aldehydes as the coupling partners could frequently meet some problems as follows: (1) The active aldehyde groups may easily suffer from a oxidation reaction, leading to formation of undesirable by-products unless the synthetic operation follows stringent protection under inert gas;[8] (2) Aldehydes could undergo a decarbonylation reaction at harsh reaction conditions such as high temperature, which results in low product yields;[9] (3) Some aldehydes including heteroaryl ones are of high cost or not readily available, the method for variation of products is hence restricted. On the basis of these facts, the search for readily available, inexpensive and stable alternatives of aldehydes would provide new avenue for the synthesis of aryl substituted 1,3,5-triazines and is of high importance.

In recent years, the use of abundant and sustainable alcohols for carbon-carbon (C-C) and carbon-nitrogen (C-N) bond formations has received considerable attention.[10,11] By employing suitable catalyst systems, the dehydrogenation of the alcohols leading to *in-situ* formation of aldehydes (or ketones) is recognized as the key point for the formation of desired products. Inspired by these elegant contributions, we believed that alcohols could also be applied as *latent* aldehydes for the synthesis of aryl substituted 1,3,5-triazines. Comparing to aldehydes, alcohols exhibit a variety of advantages such as cost-effectiveness, thermodynamic stability, abundance and sustainability. Replacing aldehydes with alcohols to react with amidines would have the potential to prepare valuable products that are currently inaccessible or challenging to prepare using conventional methods.

Herein, we wish to develop a new method for the synthesis of aryl substituted 1,3,5-triazines directly from primary alcohols and amidines. To the best of our knowledge, such a synthetic protocol has not been reported yet.

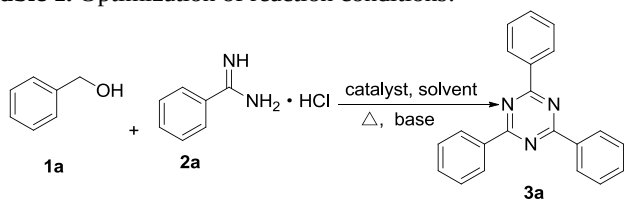
Results and discussion

With the above-described idea in mind, we then tried to examine the possibility of direct synthesis of 2,4,6-triphenyl-1,3,5-triazine **3a** from benzylic alcohol **1a** and benzamidine hydrochloride **2a**. The reaction was initially conducted at 110 ℃ for 16 h by using 1 equivalent of K_2CO_3 in DMSO. However, we failed to obtain even trace amount of expected product (Table 1, entry 1). Gratifyingly, a 21% product yield was detected by means of GC analysis while 1 mol% of $RuCl_3$ was introduced into the reaction mixture under the same conditions (Table 1, entry 2). The exclusive formation of product **2a** indicates that intermediate 2, 4, 6-triphenyl-1, 2-dihydro-1, 3, 5-triazine undergoes a thermodynamic favourable dehydrogenation step, forming the stable aromatic compound. Encouraged by this result, we then performed a thorough ruthenium catalyst screen using the same reaction as the model (Table 1, entries 2-8). $[RuCl_2(p\text{-Cymene})]_2$ (**cat 6**) was found to be the best catalyst, giving product **3a** in a 46% yield. Using $[RuCl_2(p\text{-Cymene})]_2$ as a catalyst, screening various organic and inorganic bases in DMSO indicated that organic base is ineffective for the formation of product (Table 1, entry 9), while Cs_2CO_3 gave a significant higher product yield (Table 1, entry 10).Thus we selected $[RuCl_2(p\text{-Cymene})]_2$ as our preferred catalyst, Cs_2CO_3 as our preferred base, other polar and less-polar solvent were subsequently evaluated, the results showed that these solvents are less effective in comparison with DMSO (Table 1, entries 13-15). By using the preferred catalyst, base and solvent, it was found that the decrease of reaction time or increase of reaction temperature would lead to decreased product yields (Table 1, entries 16 and 17). However, increasing the catalyst loading from 1 mol% to 1.5 mol% resulted in an increased yield (Table 1, entry 18), and further increase of catalyst loading did not improve the yield any more (Table 1, entry 19). Hence, the best reaction conditions are summarized as follows: 1.5 mol% of $[RuCl_2(p\text{-Cymene})]_2$ catalyst, 1 equivalent of Cs_2CO_3, DMSO as the reaction solvent, and at 110 ^oC（Table 1, entry 18).



Scheme 1. Catalysts employed for optimization of reaction conditions.

Table 1. Optimization of reaction conditions.[a]



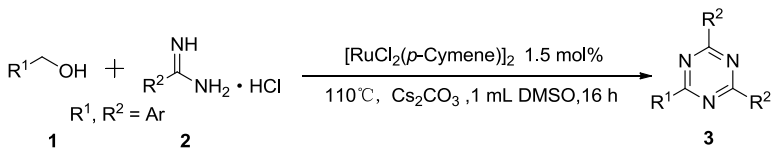
Entry	Catalyst	Base	Solvent	Yield[b] % of 3a
1	-	K_2CO_3	DMSO	-
2	Cat 1	K_2CO_3	DMSO	21
3	Cat 2	K_2CO_3	DMSO	28
4	Cat 3	K_2CO_3	DMSO	34
5	Cat 4	K_2CO_3	DMSO	30
6	Cat 5	K_2CO_3	DMSO	41
7	Cat 6	K_2CO_3	DMSO	46
8	Cat 7	K_2CO_3	DMSO	41
9	Cat 6	NEt_3	DMSO	<10
10	Cat 6	Cs_2CO_3	DMSO	72
11	Cat 6	*t*-BuOK	DMSO	32
12	Cat 6	CH_3ONa	DMSO	28
13	Cat 6	Cs_2CO_3	DMF	61
14	Cat 6	Cs_2CO_3	toluene	42
15	Cat 6	Cs_2CO_3	2-Methyl-2-butanol	21
16[c]	Cat 6	Cs_2CO_3	DMSO	64
17[d]	Cat 6	Cs_2CO_3	DMSO	70
18[e]	Cat 6	Cs_2CO_3	DMSO	85
19[f]	Cat 6	Cs_2CO_3	DMSO	85

[a] Reaction conditions: Unless otherwise specified, all reactions were carried out without inert gas protection by using **1a** (1.5 mmol), **2a** (1 mmol), catalyst (1 mol%), solvent (1 mL), temperature (110 ℃), base (1 mmol), reaction time (16 h). [b] GC Yield. [c] Reaction time (12 h). [d] Reaction temperature (130 ℃). [e] Catalyst loading (1.5 mol%). [f] Catalyst loading (2 mol%).

With the optimized reaction conditions in hand, we then tested the generality and the limitations of this ruthenium/Cs_2CO_3-catalyzed synthetic protocol. Firstly, the reactions of aryl and alkyl amidines in combination with different substituted benzylic alcohols were examined. As shown in table 2, all the reactions using aryl amidines proceeded smoothly and furnished desired products in good to excellent isolated yields (Table 2, entries 1-11). Interestingly, halogen (-Cl) as well as electron-donating groups (-Me, -OMe) are apparently well-tolerated (Table 2, entries 2-3 and 7-11). Even benzylic alcohols having a strong electron-withdrawing group (-NO_2) with different substitution patterns could also be transformed into the corresponding products in an efficient manner (Table 2, entries 4-6), and the *meta*-substituted one gave the product in a higher yield, it is conceivable that the *meta*-substituted substrate is relatively stable than those of *para*- and *ortho*-substituted ones under the standard conditions. While using the same amidine, the substituents possessing different electron properties on the aryl ring of benzylic alcohols slightly influence the product yields. In general, the electron-rich substrate such as 4-methoxy benzylic alcohol gave the products in relatively higher yields (Table 2, entries 2, 8 and 10), which could also be assigned to its inherent stability in comparison with other benzylic alcohols. However, the reaction of *n-amyl* alcohol **1g** with **2a** failed to yield even trace amount of expected product (Table 2, entry 12). This phenomenon

might be attributable to the dehydrogenation of simple alcohols is relatively challenging than that of benzylic alcohols, and the amidines suffer a decomposition prior to the dehydrogenation of alcohols. Similarly, less stable alkyl amidine such as acetamidine hydrochloride **2d** even with benzylic alcohol **1a** could not yield the expected product (Table 2, entry 13).

Table 2. Synthesis of aryl substituted 1,3,5-triazine using simple benzylic alcohols.[a]



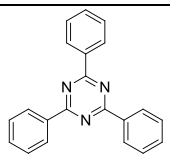
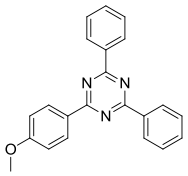
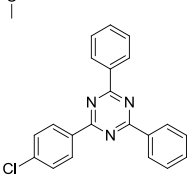
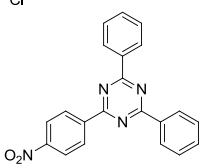
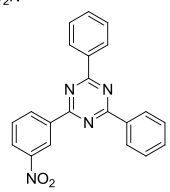
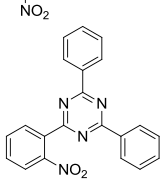
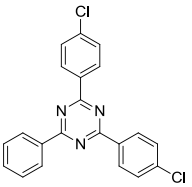
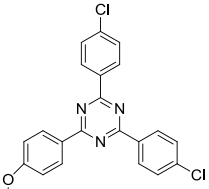
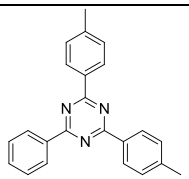
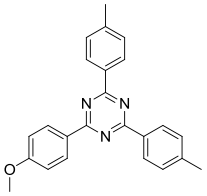
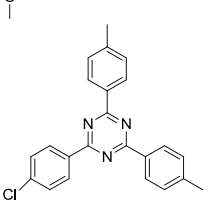
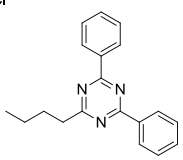
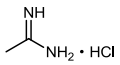
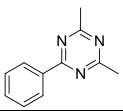
Entry	Alcohol 1	Amidine 2	Product	Yield (%)[b]
1	**1a**: R^1 = Ph	**2a**: R^2 = Ph		**3a**, 85
2	**1b**: R^1 = 4-OMe-C_6H_4	**2a**		**3b**, 87
3	**1c**: R^1 = 4-Cl-C_6H_4	**2a**		**3c**, 78
4	**1d**: R^1 = 4-NO_2- C_6H_4	**2a**		**3d**, 65
5	**1e**: R^1 = 3-NO_2- C_6H_4	**2a**		**3e**, 80
6	**1f**: R^1 = 2-NO_2- C_6H_4	**2a**		**3f**, 72
7	**1a**	**2b**: R^2 = 4-Cl-C_6H_4		**3g**, 67
8	**1b**	**2b**		**3h**, 74

Table 2. (continued)

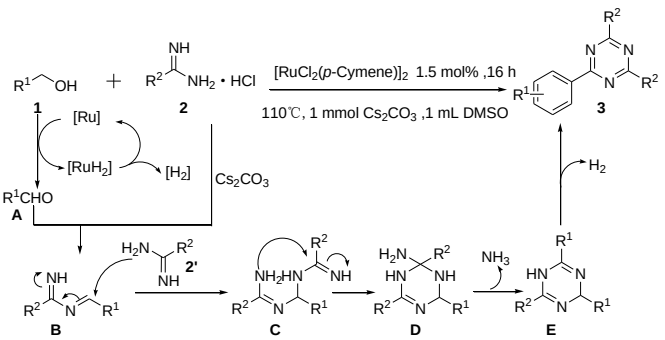
Entry	Alcohol 1	Amidine 2	Product	Yield (%)[b]
9	**1a**	**2c**: R^2 = 4-Me-C_6H_4		**3i**, 64
10	**1b**	**2c**		**3j**, 68
11	**1c**	**2c**		**3k**, 61
12	**1g:** 	**2a**		**3l**, -
13	**1a**	**2d:** 		**3m**, -

[a] Reaction conditions: Unless otherwise specified, all reactions were carried out without inert gas protection by using 1 (1.5 mmol), 2 (1 mmol), catalyst (1.5 %mol), solvent (1 mL), temperature (110 ℃), base (1 mmol), reaction time (16 h). [b] Yields of isolated pure product.

Hence, the dehydrogenation rate of alcohols is considered to be key factor for the formation of products. Notably, owing to the aryl groups are *ortho* to the nitrogen atoms, the obtained 2,4,6-triaryl-1,3,5-triazines have the potentials to be applied as C^N ligands for the preparation of cyclometalted organometallic materials[12] or C^N^C ligands for the elaboration of pincer complexes.[13]

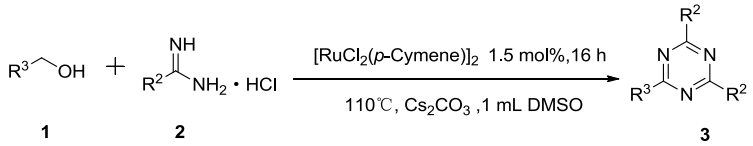
Upon a thorough literature investigation, it was found that the synthesis of heteroaryl substituted 1,3,5-triazines has been scarcely explored with the conventional methods. Herein, we wish to prepare this type of compounds by employing our synthetic protocol. Representative heteroaryl substituted methanols such as pyridyl methanols (Table 3, see **1h**-**1k)**, furyl methanol **1l** and thiazol-2-ol **1m** were selected as the coupling partners for the cyclization reactions with different amidines. Gratifyingly, all the reactions underwent efficiently and furnished the products in moderate to excellent isolated yields. Similar to the compounds described in table 2, the obtained heteroaryl substituted 1,3,5-triazines could also be potentially valuable C^N or C^N^C ligands. Additionally, the products arising from pyridin-2-ylmethanol derivatives (see **1j**, **1k**) and thiazol-2-ylmethanol **1m** provide the potentials to be used as N^N^C ligands for the preparation of novel pincer complexes.[14]

On the basis of transition metal-induced dehydrogenation as substrate activation strategy[10,11] as well as the conventional 1,3,5-triazine syntheses, a plausible pathway for the generation of 2,4,6-triaryl-1,3,5-triazines from alcohols and amidines is depicted in scheme 2. The reaction initiates with the dehydrogenation of aryl methanol **1** induced by cooperative actions of ruthenium catalyst and Cs_2CO_3, amidine **2'** neutralized by Cs_2CO_3 from its hydrochloride salt **2** then condenses with the *in-situ* formed aldehyde **A** to give azadiene **B**. The subsequent inter- and intra-molecular nucleophilic addition of amino group to electrophilic carbon center would afford intermediate **C** and racemic aminals **D**. Then, the thermodynamic favourable deamination would release dihydrotriazine **E** and ammonia. Finally, desired product **3** is formed via dehydrogenative aromatization of **E** promoted by ruthenium catalyst or air oxidation.



Scheme 2. Proposed mechanism for the formation of 2,4,6-triaryl-1,3,5-triazines from alcohols and amidines

Table 3. Synthesis of aryl substituted 1,3,5-triazine using heteroaryl methanols.[a]



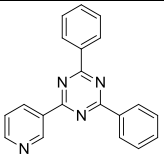
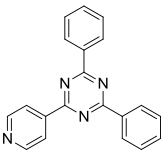
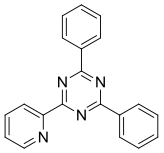
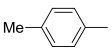
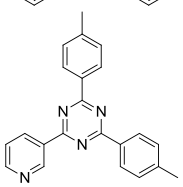
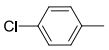
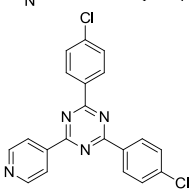
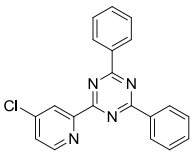
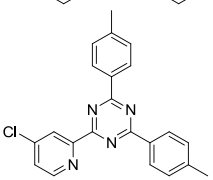
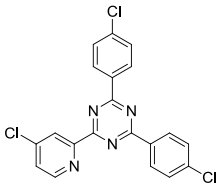
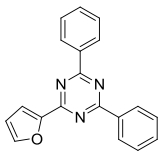
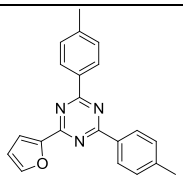
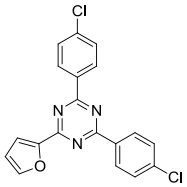
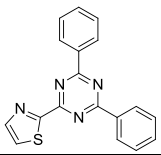
Entry	Alochol 1	Amidine 2	Product	Yield (%)[b]
1	**1h**: R^3 = 	**2a**: R^2 = Ph		**3n**, 78
2	**1i**: R^3 = 	**2a**		**3o**, 74
3	**1j**: R^3 = 	**2a**		**3p**, 66
4	**1h**	**2b**: R^2 = 		**3q**, 54
5	**1i**	**2c**: R^3 = 		**3r**, 63
6	**1k**: R^3 = 	**2a**		**3s**, 71
7	**1k**	**2b**		**3t**, 58
8	**1k**	**2c**		**3u**, 65
9	**1l**: R^3 = 	**2a**		**3v**, 67

Table 3. (continued)

Entry	Alochol 1	Amidine 2	Product	Yield (%)[b]
10	**1l**	**2b**		**3w**, 52
11	**1l**	**2c**		**3x**, 57
12	**1m**: R^3 = 	**2a**		**3y**, 73

[a] Reaction conditions: Unless otherwise specified, all reactions were carried out without inert gas protection by using 1 (1.5 mmol), 2 (1 mmol), catalyst (1.5 %mol), solvent (1 mL), temperature (110 ℃), base (1 mmol), reaction time (16 h). [b] Yields of isolated pure product.

Conclusions

In summary, we have presented a new and straightforward method for the synthesis of 2,4,6-triaryl-1,3,5-triazines by using commercially available $[RuCl_2(p\text{-Cymene})]_2/Cs_2CO_3$ as a catalyst system. Abundant and easily available alcohols were firstly employed as the coupling partners to react with amidines, and the dehydrogenative cyclization process underwent efficiently and furnished the products in good to excellent isolated yields. In addition to utilization of simple benzylic alcohols, heteroaryl methanols could also be converted into heteroaryl substituted 1,3,5-triazines. Due to the inherent stability of alcohols in contrast with aldehydes, our synthetic protocol is adaptable to a broad substrate scope, providing the potential to prepare valuable products that are currently inaccessible or challenging to prepare using the conventional methods, and there is no need for stringent protection during the whole operation process. Hence, it is a significant important complement to the conventional synthetic methodologies. Based on the importance of 2,4,6-triaryl-1,3,5-triazines in biology, organic and material chemistry, this practical synthetic strategy has the potential to be frequently used.

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Experimental

General information

All the obtained products were characterized by melting points (m.p), ^{1}H-NMR, infrared spectra (IR), and high resolution mass spectra (HRMS). The ^{1}H-NMR spectra of known compounds were found to be identical with ones reported in the literatures. Additionally, all the new compounds were further characterized by ^{13}C-NMR. Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; IR spectra were recorded on a FTLA2000 spectrometer; 1H-NMR spectra were obtained on Bruker-400; High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-600 spectrometer. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; All the reagents were purchased from commercial sources (J&KChemic, TCI, Fluka, Acros, SCRC), and used without further purification.

Typical procedure for synthesis of 2,4,6-triphenyl-1,3,5-triazine (3a).

To a solution of benzyl alcohol (0.162 g, 1.5 mmol) and benzamidine hydrochloride (0.156 g,1 mmol) in DMSO (1mL) were added $[RuCl_2\text{-}(p\text{-Cymene})]_2$ (0.015 mmol, 4.5 mg) and Cs_2CO_3 (0.325 g, 1 mmol). The reaction mixture was heated at 110 ℃ for the 16 h in a sealed tube without insert any gas protection. Afterwards, water (10 mL) and dichloromethane (20 mL) were added, the layers were separated, then the aqueous layer was extracted with dichloromethane (2×10 mL).The combined organic layers were dried with anhydrous Na_2SO_4, and concentrated under vacuum. The residue was directly purified by flash chromatography on silica gel eluting with petroleum ether (60-90 ℃): ethyl acetate (15:1) to give 2,4,6-triphenyl-1,3,5-triazine 3a as a white solid (0.123 g, 85%).

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Electronic Supplementary Information (ESI) available: images of ^{1}H and ^{13}C NMR of all products. See DOI: 10.1039/b000000x/

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