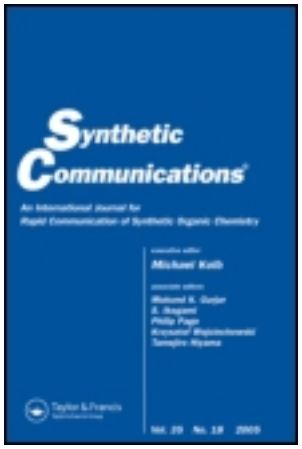

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Cerium(III)-Catalyzed Synthesis of Schiff Bases: A Green Approach

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CERIUM(III)-CATALYZED SYNTHESIS OF SCHIFF BASES: A GREEN APPROACH

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The reaction of primary aromatic amines with aryl aldehydes is found to be catalyzed by cerium chloride heptahydrate under solvent-free conditions to give the corresponding Schiff bases in good yields.

Keywords: $CeCl_3 \cdot 7H_2O$; green chemistry; Schiff bases; solvent free

INTRODUCTION

Aromatic imines or Schiff bases are nitrogen-containing organic compounds that are reported to exhibit analgesic, antimicrobial, antibacterial, and anti-inflammatory activity.[1] They are conventionally prepared by condensation of an aldehyde/ketone with a primary aromatic amine and with the simultaneous removal of water using molecular sieves or a Dean–Stark apparatus.[2] Several modified methods for synthesis of Schiff bases have been reported in the literature, including use of catalysts such as $ZnCl_2$,[3] $TiCl_4$,[4] alumina,[5] P_2O_5,[6] and $Mg(ClO_4)_2$,[7] besides activation of the reaction mixture by infrared (IR) irradiation.[8] Environmentally friendly methods for the synthesis of imines have been reported in the literature. Touchelte[9] has reported the solventless synthesis of imines by grinding o-vanillin and p-toluidine, resulting in quantitative yields of the product. Varma et al.[10] reported the solvent-free synthesis of imines under microwave conditions using montmorillonite K10 as a solid support. Recently, Gopalakrishnan et al.[11] reported the synthesis of imines catalyzed by CaO under microwave conditions. Ethyl lactate as a tunable solvent recently has been found to be useful in the synthesis of aryl aldimines.[12]

RESULTS AND DISCUSSION

Several Schiff bases were synthesized both in the presence and absence of $CeCl_3 \cdot 7H_2O$, and the results are summarized in Scheme 1 and Table 1. In a typical

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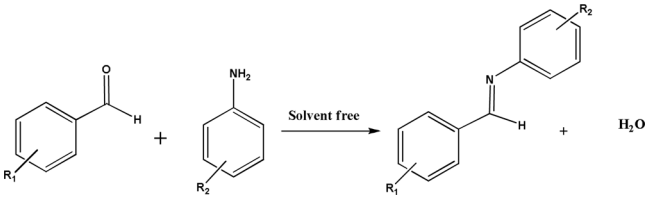


Scheme 1. Synthesis of Schiff bases **1–6**.

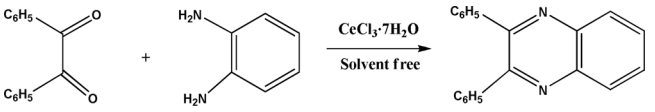
procedure, an equimolar mixture of aldehyde (10 mmol) and amine (10 mmol) were taken in a porcelain dish and mixed thoroughly. $CeCl_3 \cdot 7H_2O$ (1 mmol) was added and the entire reaction mixture was mixed vigorously. The progress of the reaction was monitored by thin-layer chromatography (TLC). The mixture melted initially and then solidified, indicating formation of the imine. The product was recrystallized using absolute alcohol. The procedure for the reaction in the absence of $CeCl_3 \cdot 7H_2O$ was the same as before. The products were characterized by IR (C=N stretching between 1610 and 1630 cm^{-1}) and comparison of their melting points with the reported data.

In case of deactivated amines (entries 1 and 2), the reaction does not proceed in the absence of $CeCl_3 \cdot 7H_2O$. However, addition of catalytic amounts of $CeCl_3 \cdot 7H_2O$ results in the formation of the Schiff base in a very short time. Similarly, deactivated aldehydes having electron-releasing substituents (entry 3) underwent the reaction faster in the presence of the catalyst, probably because of coordination of the carbonyl oxygen with cerium, which enhanced the electrophilicity of the carbon. In the case of reactions using anisaldehyde, it was observed that addition of catalytic amounts of the catalyst reduced the reaction time considerably from 2 h to a few minutes (entries 4–6). Todd[13] had reported the synthesis of various Schiff bases derived from anisaldehyde by refluxing amines with aldehydes in ethanol. The melting points of the products obtained in the present work compare well with those reported in the literature. The $CeCl_3 \cdot 7H_2O$-catalyzed reaction was found

Table 1. Synthesis of Schiff bases in the presence and absence of $CeCl_3 \cdot 7H_2O$

No.	R_1	R_2	$CeCl_3$	Time (min)	Melting point (°C)[a]	Yield[b] (%)
1	H	4-NO_2	—	120	—	No reaction
			1:1:0.1	30	144 (138–140)[6]	41
2	H	3-NO_2	—	120	—	No reaction
			1:1:0.1	10	66 (66–68)[6]	88
3	2-OH	H	—	120	47 (47–49)[15]	68
			1:1:0.1	30	47	91
4	4-OCH_3	H	—	120	59 (57–62)[13]	50
			1:1:0.1	5	59	85
5	4-OCH_3	4-Cl	—	60	92 (93)[13]	82
			1:1:0.1	5	92	89
6	4-OCH_3	3-NO_2	—	120	—	No reaction
			1:1:0.1	50	109 (109–110)[13]	80

[a]Figures in parentheses correspond to reported melting points.
[b]Yields of recrystallized product.



Scheme 2. Synthesis of 2,3-diphenylquinoxaline.

to be effective in the synthesis of 2,3-diphenylquinoxaline, by condensation of o-phenylenediamine and benzil (Scheme 2). In the absence of the catalyst, the reaction requires refluxing in ethanol for more than 30 min.[14] However, addition of catalytic amounts of the catalyst avoided the use of solvent and refluxing conditions and gave good yields of the product, albeit in 2 h.

CONCLUSION

In conclusion, we have developed a simple, solvent-free procedure for the synthesis of Schiff bases, catalyzed by $CeCl_3 \cdot 7H_2O$. The method works well with deactivated amines and aldehydes to give the desired product in good yields. The present method is advantageous over the conventional procedure, in that it does not require azeotropic removal of water by using excess of aromatic solvents.

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