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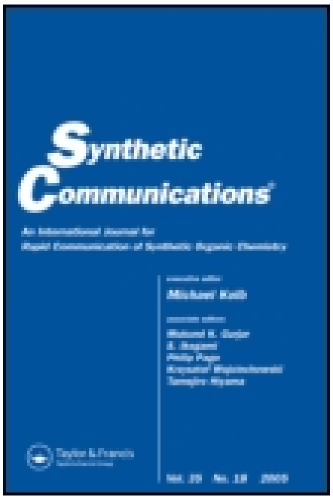

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UREA NITRATE CATALYZED IMINO DIELS-ALDER REACTIONS: SYNTHESIS OF CYCLOPENTAQUINOLINES, PYRANOQUINOLINES, AND FUROQUINOLINE DERIVATIVES

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UREA NITRATE CATALYZED IMINO DIELS-ALDER REACTIONS: SYNTHESIS OF CYCLOPENTAQUINOLINES, PYRANOQUINOLINES, AND FUROQUINOLINE DERIVATIVES

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ABSTRACT

Urea nitrate is found to be an efficient catalyst for the imino Diels-Alder reaction of aldimines with cyclopentadiene, 3,4-dihydropyran and dihydrofuran is reported for the first time. One pot synthesis of cyclopentaquinolines from benzaldehyde, aromatic amines with cyclopentadiene catalyzed by urea nitrate is also reported.

Pyranoquinoline moiety is present in many alkaloids such as flindersine, oricine and veprisine[1] and their derivatives possess wide range of biological activities such as psychotropic,[2] antiallergenic,[3] antiinflammatory[4] and estronegic[5] activities. Furoquinoline skeleton is present in many alkaloids like skimmianine and balfouridine.[6] Lewis acids like $BF_3{\cdot}Et_2O$,[7]

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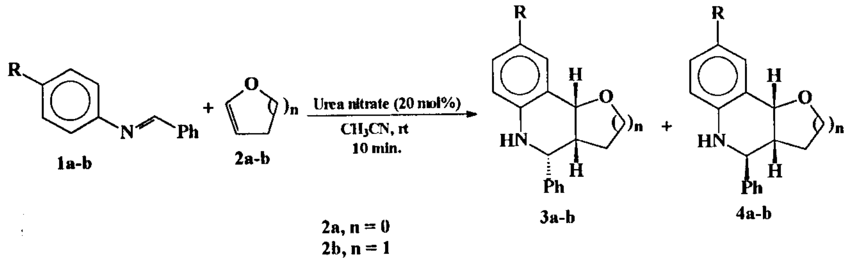
$InCl_3$,[8] lanthanide triflates[9] and $GdCl_3$[10] has been found to catalyze the reaction of aldimines with electron rich dienophiles. However, to the best of our knowledge there is no report available for urea nitrate as a catalyst for the reaction of imines with electron rich alkenes. Since urea nitrate is an inexpensive, easy to prepare, explored its ability to catalyze the imino Diels-Alder reactions effectively in shorter reaction times. Recently urea nitrate was used for the regioselective nitration of 4-halonitrobenzenes to 4-halo-orthodinitro benzene derivatives.[11]

In the presence of 20 mol% urea nitrate, *N*-benzylidene aniline (**1a**) was treated with 3,4-dihydropyran in acetonitrile at room temperature. After 10 min the pyranoquinolines **3a** and **4a** obtained in a ratio of 33:67 in an overall yield of 74% (Scheme 1). The results obtained with other substituents and with dihydrofuran are given in Table 1.



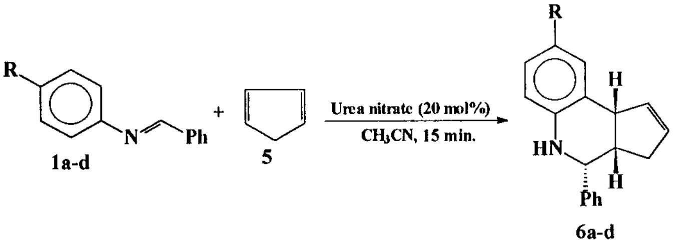
Scheme 1.

Urea nitrate also catalyzes the reaction of cyclopentadiene with *N*-benzylidene aniline **1a** and resulted in the formation of cyclopentaquinoline **6b** in 78% yield (Scheme 2). The results obtained with other substituents are given in Table 2.

Table 1. Synthesis of Pyrano and Furanoquinolines* Catalyzed by 20 mol% Urea Nitrate

Entry	Schiff Base	R	*n*	Time (min)	Product Ratio 3:4	Overall Yield (%)
1	**1a**	H	0	10	33:67	77
2	**1a**	H	1	10	33:67	74
3	**1b**	Cl	1	10	32:68	78

*Products were characterized by IR, NMR and Mass Spectra.

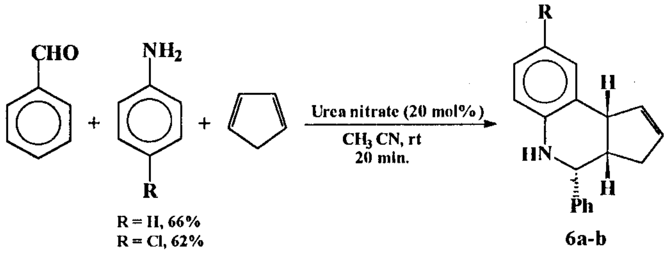


Scheme 2.

Table 2. Synthesis of Cyclopentaquinolines Catalyzed by 20 mol% Urea Nitrate

Schiff Base	Substituent R	Time (min)	Yield (%)
1a	H	15	78
1b	Cl	15	71
1c	COOH	15	61
1d	NO_2	15	59

The one pot synthesis of cyclopentaquinolines is also achieved by the reaction of benzaldehyde, substituted aniline with cyclopentadiene catalyzed by urea nitrate (Scheme 3).



Scheme 3.

In conclusion, this paper describes a simple method for obtaining the quinoline derivatives using cheaper urea nitrate as a catalyst in shorter reaction time and also has an advantage that only 20 mol% required for the cycloadditions.

EXPERIMENTAL

To a stirred solution of Schiff base **1b** (2.5 mmol) and cyclopentadiene (0.330 g, 5 mmol) in acetonitrile (10 mL) was added urea nitrate (0.093, 20 mol%) and stirred at room temperature for 15 min. The reaction mixture poured over ice water and extracted with chloroform (3 × 10 mL). The combined organic layer was washed with saturated $NaHCO_3$ (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, then concentrated under reduced pressure. The residue was purified by column chromatography using silica-gel (60–120 mesh) and eluted with petroleum ether:ethyl acetate (95:5) to afford **3b** as pale yellow crystalline solid in 71% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 (m, 5H), 7.04 (d, 1H, $J = 2.1$ Hz), 6.93 (dd, 1H, $J = 2.2$ Hz, $J = 8.6$ Hz), 6.55 (d, 1H, $J = 8.5$ Hz), 5.82 (m, 1H), 5.69 (m, 1H), 4.61 (d, 2H, $J = 2.9$ Hz), 4.09 (d, 1H, $J = 8.6$ Hz), 3.76 (br s, 1H), 3.05 (m, 1H), 2.67 (m, 1H), 1.86 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.1, 142.3, 133.4, 130.8, 128.6, 128.4, 127.6, 127.3, 126.4, 123.4, 116.9, 57.9, 46.2, 45.7, 31.4; MS (*m/z*); 281 (M^+), 283 (M + 2); IR (KBr): 3363, 1470 cm^{-1}.

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