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Synthesis of functionalized isoxazole–oxindole hybrids *via* on water, catalyst free vinylogous Henry and 1,6-Michael addition reactions†

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Various 3-substituted-3-hydroxy isoxazole–oxindole hybrids were synthesized *via* the vinylogous Henry reaction of 3,5-dimethyl-4-nitroisoxazole and isatin using water as a reaction medium under catalyst free conditions at 50 °C. Systematic studies were carried out to understand the role of the water on the reaction by using D_2O, brine, ethylene glycol and PEG-400 as a reaction medium along with organic solvents. Among all of these, water (0.170 mol concentration) was found be more efficient giving desired products in 82–99% yields in 45–120 min. Further the quaternary centre (3° alcohol) generated was used for the creation of a double bond which was again used for a 1,6-Michael reaction to produce highly functionalized isoxazole–oxindole derivatives.

Introduction

The isoxazole unit is present in many drug molecules such as AMPA, ibotanic acid, leflunomide, β-lactamase-resistant antibiotics, aleglitazar, darglitazone, isoxicam *etc.*[1] and a useful precursor for many organic compounds.[2] Oxindoles, particularly 3-hydroxy-2-oxindole with a quaternary hydroxyl moiety is present in many natural and biologically active molecules and considered as a privileged structure in medicinal chemistry[3] (Fig. 1). Also, this scaffold was used as an intermediate for the synthesis of natural products like (+)-folicanthine, convolutamydine series *etc.*[4] The natural abundance, environmentally friendly nature, biological relevance and donor–acceptor properties of water make it as a special reagent/catalyst or reaction medium for organic synthesis.[5] After the reports from Breslow[6] and Sharpless[7] on the role of water in accelerating the rate of the reaction, chemists started exploring the polarity, hydrophobic, hydrophilic, hydrogen bonding properties of water with organic molecules.[8] As a result, the utility of water in organic synthesis has increased considerably.[5,9] Recently, the "in water" and "on water" concepts are gaining attention for the synthesis of simple and complex molecules.[10] Development of environmentally free, green chemical processes for the synthesis of medicinally important molecules are still demanding in academic and industrial research.[11]

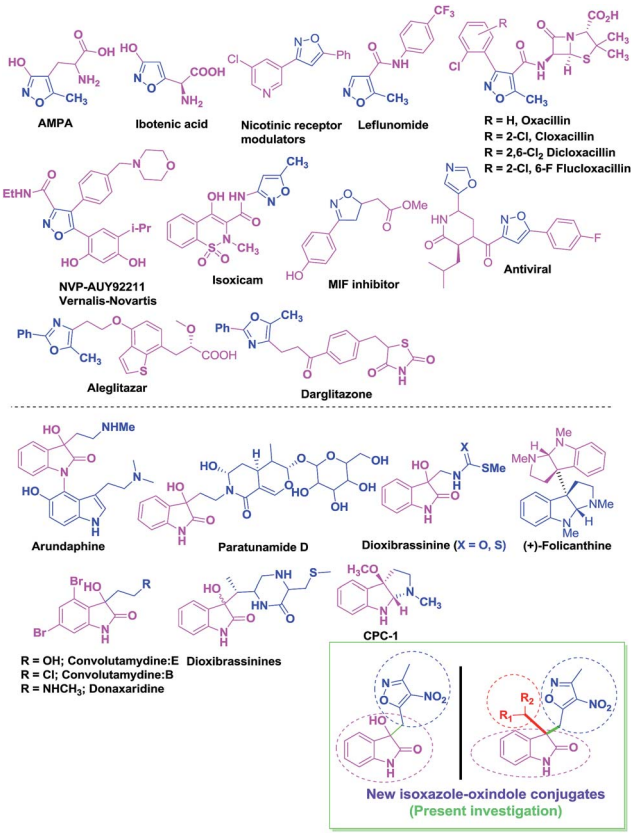

Fig. 1 Different natural and biologically active molecules containing isoxazoles and 3-hydroxy-3-substituted 2-oxindole moieties.

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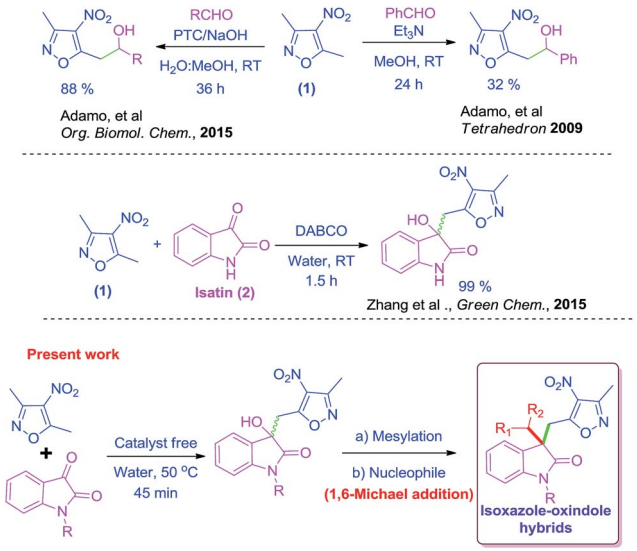
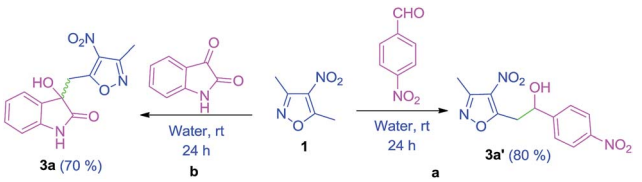


Fig. 2 Reported methods and present work for the construction of 3°-hydroxy containing oxindoles and construction of isoxazole–oxindole hybrids.

3,5-Dialkylated-4-nitroisoxazole (**1**) is an interesting substrate which is used as nucleophile and synthon (as masked ester).[12] In this regard, Adamo and co-workers demonstrated vinylogous Henry reaction using inorganic and organic bases (Fig. 2).[13] The use of isatin (**2**) for nucleophilic addition reactions with compounds containing active methylene groups such as thiazolidinedione, pyrazolones, 3-thiazolidinedione and nitro alkanes is gaining attention in the literature using "on water" concept.[14] In the similar lines, Zhang *et al.*, reported the vinylogous Henry reaction of 3,5-dialkylated-4-nitroisoxazole and isatin using DABCO as catalyst[15] (Fig. 2). Considering the importance of isoxazole, oxindole moieties and in continuation of our interest in green synthesis,[16] here in we report the construction of tertiary hydroxyl containing quaternary centred isoxazole–oxindole hybrids using vinylogous Henry reaction of isatin (electrophile partner) and 3,5-dimethyl-4-nitroisoxazole (nucleophile partner) in aqueous medium ("on water") under catalyst free conditions. The 3°-hydroxy group of resulting isatin–isoxazole was further utilised for the generation of unsaturated system which was again used for the 1,6-Michael addition with different nucleophiles. The products generated here will have both oxindole and isoxazole moieties (3,3-disubstitution) can be used for further functionalization and may show enhanced biological properties than the individual molecules alone (Fig. 2; present work).

Results and discussion

As mentioned above, the direct vinylogous reaction was performed using 3,5-dimethyl-4-nitroisoxazole (**1**) and 4-nitrobenzaldehyde under catalyst free, on water conditions at room temperature[13] to give the desired Henry adduct **3a′** with 80% yield in 24 h. Similarly, the reaction of **1** with isatin gave the Henry adduct **3a** in 70% yield (Scheme 1). Towards optimization



Scheme 1 Catalyst free on water Henry reaction at room temperature (before optimization).

of the reaction, parallel experiments were conducted using different reaction media (protic polar solvents (water, methanol, ethanol, brine, ethylene glycol and PEG-400), aprotic solvents (polar and non-polar; D_2O, DMF, DMSO, chloroform and acetonitrile)) and temperature (0 °C to 50 °C) as shown in Table 1 (entries 1–15). It is interesting to note that the reaction is working well at 50 °C in water compare to non-aqueous and other protic solvents giving the yields up to 99% of the desired product. Later, systematic studies were performed to examine the role of water in different concentrations and it was found that 2 mL (0.170 molar concentrations) is best suitable conditions for the success of the reaction (entries 16–22; Table 1).

Fig. 3, indicate the homogeneity of the reaction mixture when the organic solvents (DMF, DMSO, chloroform and acetonitrile, ethylene glycol and PEG 400) and brine are used as reaction medium (Fig. 3ii). This is because of the solubility of

Table 1 Optimization of reaction conditions: all the reactions were performed at 50 °C (0.339 mmol scale)

S. no.	Solvent	Reaction concentration[d] (in mol)	Reaction time (h)	Isolated yield[a] (%)
1	Neat		48	ND
2	Water	0.170	24	70[b]
3	**Water**	**0.170**	**24**	**99**
4	Water	—	48	20[c]
5	MeOH	—	48	20
6	EtOH	—	48	25
7	DMF	—	48	15
8	DMSO	—	48	25
9	CH_3CN	—	48	ND
10	Toluene	—	48	ND
11	$CHCl_3$	—	48	ND
12	Brine	—	48	30
13	D_2O	—	48	ND
14	Ethyleneglycol	—	48	ND
15	PEG-400	—	48	ND
16	Water (5 mL)	0.068	2	60
17	Water (4 mL)	0.085	2	70
18	Water (3 mL)	0.113	2	60
19	**Tap water (2 mL)**	**0.170**	**45 min**	**99**
20	Water (1 mL)	0.340	2	85
21	Water (0.5 mL)	0.680	2	60
22	**Distilled water (2 mL)**	**0.170**	**45 min**	**99**
23	**HPLC water (2 mL)**	**0.170**	**45 min**	**99**

[a] Isolated yields. [b] Room temperature. [c] Reaction performed at 0 °C. [d] The concentration effect was studied only for water mediated reactions; ND = not detected.

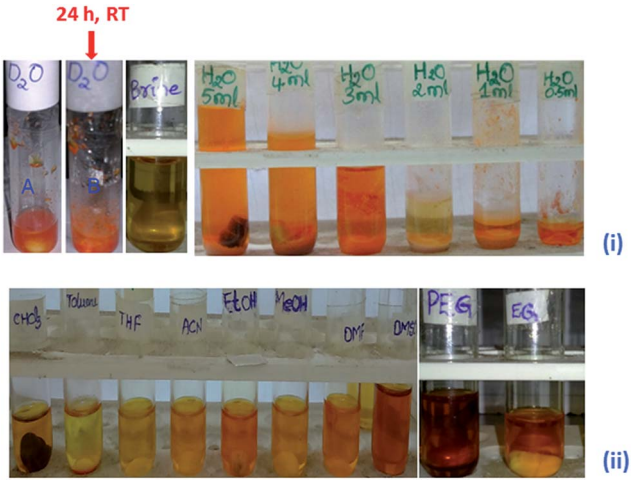


Fig. 3 Monitoring the progress of the reactions using different reaction media.

starting materials in the respective medium. Whereas, when water is used for the reaction, the mixture is heterogeneous in nature due to insoluble nature of the starting materials which may be leading the formation of aggregates and hydrogen bonds which in turn are helping for the success of the reaction by "on water" concept. This is further supported from brine (which can form partial hydrogen bonding) and D_2O (which cannot participate in hydrogen bonding) experiments in which 30% and 0% yields were obtained respectively.

As mentioned above the insoluble nature of organic molecules "on water" and hydrogen bonding of water with organic molecules (nitro group of isoxazole and keto group of isatin) is helping to increase the nucleophilic character of γ-carbon of isoxazole and electrophilic character of isatin may be bringing both the coupling partners together and increasing the rate of the reaction even in the absence of base. Based on this, we propose mechanism of the reaction as shown in Fig. 4. Further studies to understand detailed mechanism on complex example are under progress in our laboratory.

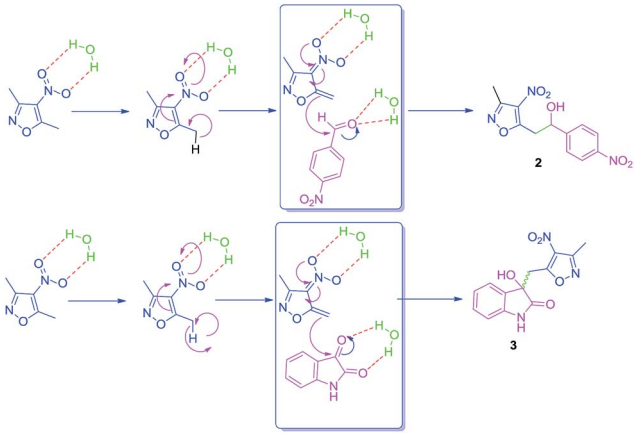


Fig. 4 Plausible reaction mechanism for the formation of Henry adducts (**2** and **3**).

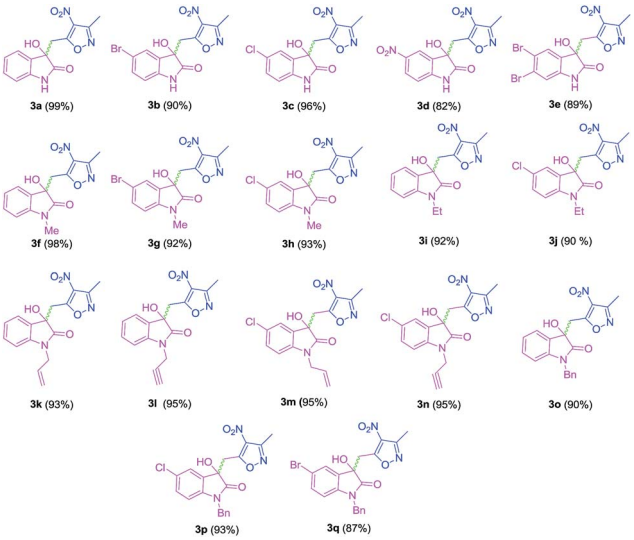
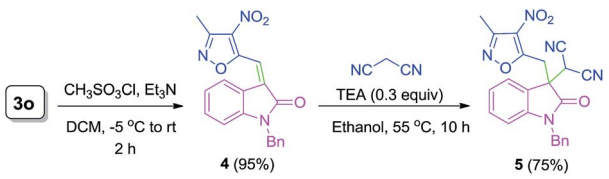


Fig. 5 Various isoxazole–oxindole hybrids (**3a–3q**).

After optimizing the reaction conditions, different isatins with electron donating and withdrawing groups on aromatic ring and with N-substitutions were reacted with 3,5-dimethyl-4-nitroisoxazole (**1**) to give functionally diverse isoxazole–oxindole hybrids (**3a–3q**) as shown in Fig. 5. In all the cases the reaction went for completion within 45–120 min. The substrates with electron withdrawing groups (nitro, bromo, dibromo) require more time compare with the substrates containing electron donating groups on aromatic ring (Scheme 2).

After successful synthesis of isoxazole–oxindole hybrids under catalyst free conditions, we intended to explore the Henry adducts for 1,6-Michael addition further. Thus, the olefinic system **4** was prepared *via* mesylation followed by elimination reaction using **3o**. The resulting styrene derivative (**4**) was reacted with malononitrile in presence of triethylamine (30 mol%) in ethanol at 55 °C to give the 1,6-Michael adduct (**5**) in

Scheme 2 Catalyst free "on water" Henry reaction at 50 °C (optimized conditions).



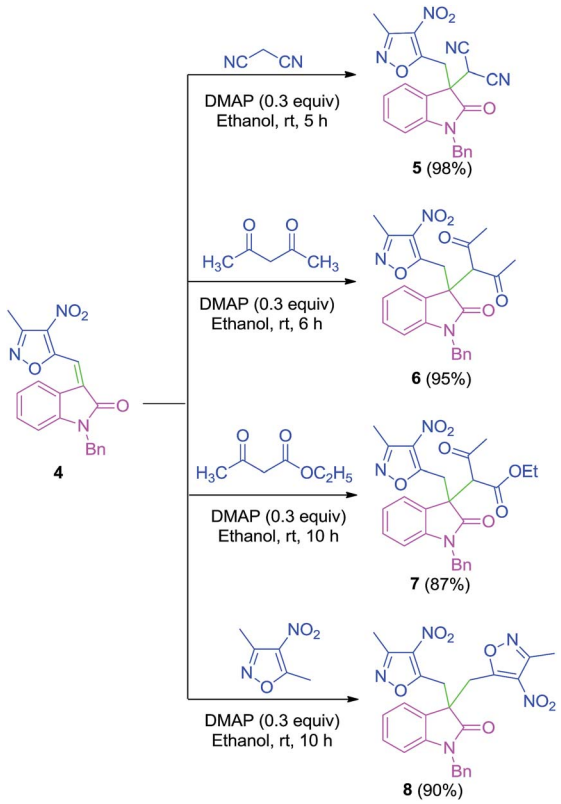
Scheme 3 Generation of olefin **4** and 1,6-Michael addition reaction with malononitrile.

Table 2 Reaction conditions: room temperature. All the reactions were performed 0.055 mmol scale at room temperature

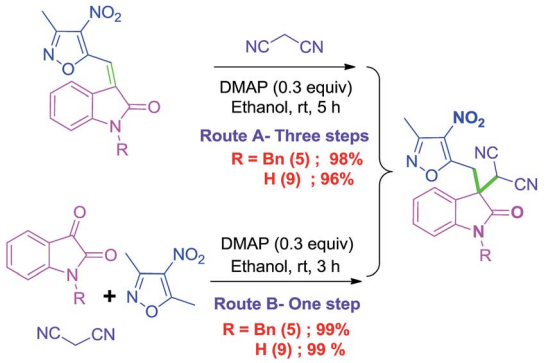
S. No.	Base	Solvent	Reaction time (h)	Isolated yield[a] (%)
1	TEA	EtOH	5	75[b]
2	TEA	Water	24	25[b]
3	TEA	EtOH	24	50
4	Et_2NH	EtOH	24	20
5	$(Pr^i)_2NEt$	EtOH	24	60
6	Piperidine	EtOH	24	50
7	Pyrrolidine	EtOH	24	40
8	Morpholine	EtOH	24	38
9	Pyridine	EtOH	24	ND
10	DBU	EtOH	24	65
11	**DMAP**	**EtOH**	**5**	**98**
12	DMAP	Water	24	60
13	Imidazole	EtOH	24	ND
14	Cs_2CO_3	EtOH	40	40
15	K_2CO_3	EtOH	24	25
16	Na_2CO_3	EtOH	24	20
17	$NaHCO_3$	EtOH	24	ND

[a] Isolated yield. [b] Reflux condition (50 °C).

75% yield (Scheme 3). After confirmation of the product by ^{1}H-, ^{13}C-NMR and mass spectra, the reaction was optimized using different bases (organic and inorganic) and solvent systems (EtOH, water) as shown in Table 2. After optimizing the conditions for 1,6-Michael addition, different carbon-nucleophiles were reacted with the olefin intermediate to highly functionalized (quaternary centred) isoxazole–oxindole hybrids (Scheme 4). Though substrate dependent reactivity was observed, the derivatives generated here can be used for further functionalization.



Scheme 4 1,6-Michael addition reaction of olefin 4 with different carbon-nucleophiles (optimized conditions).



Scheme 5 One-pot synthesis of quaternary centred isoxazole–oxindole hybrids using DMAP as catalyst.

Since the generation of quaternary centred isoxazole–oxindole derivatives (Scheme 4) require multiple steps for the preparation and the yields of 1,6-Micheal addition step are substrate dependent, the one-pot reaction of isatin and 3,5-dimethyl-4-nitroisoxazole was attempted. Thus, isatin, 3,5-dimethyl-4-nitroisoxazole and malononitrile were reacted together in presence of DMAP (30 mol%) at room temperature to give the quaternary centred isoxazole–oxindole hybrids (**5** and **9**) in quantitative (up to 99%) yield with N-substituted and unsubstituted isatins (Scheme 5). Further expansion of this methodology on complex systems is under progress in our laboratory.

Conclusion

In conclusion, we have demonstrated an efficient synthesis of functionalized isoxazole–oxindole hybrids with quaternary centre under green and catalyst free conditions using water as solvent. The solvent screening studies support "on water" and hydrogen bonding concepts and the role of water for the success of the reaction without base/catalyst. The shorter reaction times, simple purification (>99% purity) methods make this methodology efficient for the generation of library of compounds for medicinal chemistry. Also, the 1,6-Michael adducts can be further used for transforming in to useful drug like molecules.

Experimental

Materials and methods

All the starting materials and solvents were purchased from, SD-Fine and Sigma-Aldrich Spectrochem and used without further purification. Melting points were determined in open capillaries using Stuart SMP30 melting point apparatus and uncorrected. NMR spectra were recorded on Bruker 400, 500, MHz

spectrometer using $CDCl_3$, CD_3OD and DMSO-*d*6 as solvents (and reported in δ ppm). The mass spectra were recorded on Bruker-micro-TOF MS analyser. FT-IR was recorded on PerkinElmer instrument and KBr was used for making pellet.

General procedure for the synthesis of 3-hydroxy-3-((3-methyl-4-nitroisoxazol-5-yl)methyl)indolin-2-one (3a–3q)

To a solution of isatin (0.339 mmol, 1 equiv.), in water (2 mL), was added 3,5-dimethyl-4-nitroisoxazole (0.59 mmol, 1.5 equiv.) and stirred at 50 °C for 45–120 min. After completion of the reaction (monitored by TLC), the contents were cooled to room temperature. The crude compound obtained was filtered and washed with water to give desired compound (see ESI† for the ^{1}H- ^{13}C-NMR and mass spectra).

Preparation of (*E*)-1-benzyl-3-((3-methyl-4-nitroisoxazol-5-yl) methylene)indolin-2-one (4)

To a solution of 3-hydroxyl isoxazole–indolinone (**3o**) (0.5 g, 1.38 mmol) in DCM (10 mL) was added drop wise methanesulfonyl chloride (0.47 g, 4.15 mmol) 0 °C. The mixture was stirred for 10 min and trietylamine (0.42 g, 4.15 mmol) was added drop wise. Stirring continued for 30 min at 0 °C. Then the reaction mixture was allowed to warm to room temperature and stirred for 1.5 h. After completion of the reaction (monitored by TLC), DCM was evaporated under reduced pressure to give the crude product. To this, cold methanol (2 × 2 mL) was added, stirred for 5 min and decanted. The precipitate obtained was washed with *n*-hexane to give the desired product **4** in 95% yield (see ESI† for the ^{1}H- ^{13}C-NMR and mass spectra).

General procedure for 1,6-Michael addition on isoxazole–oxindole styrene (4)

To a solution of styrene derivative **4** (20 mg, 0.055 mmol) in ethanol (2 mL), was added the nucleophile with active methylene group (0.085 mmol, 1.5 equiv.) at room temperature followed by DMAP (2 mg, 0.016 mmol, 30 mol%). The mixture was stirred at room temperature for 5–10 h. After completion of the reaction (TLC), ethanol was evaporated under reduced pressure to give the crude compound which was purified by silica gel column chromatography. Elution of the column with EtOAc : petroleum ether gave the desired products in 87–98% yields (see ESI† for the ^{1}H- ^{13}C-NMR and mass spectra).

Procedure for one-pot synthesis of quaternary centred isoxazol–oxindole hybrids (8 and 9)

To a solution of isatin (20 mg, 0.0135 mmol), 3,5-dimethyl-4-nitroisoxazole (28 mg, 0.197 mmol) in ethanol (2 mL) malononitrile (8 mg, 0.315 mmol) followed by DMAP (4 mg, 0.032 mmol, 30 mol%) and the mixture was stirred at room temperature for 3 h (monitored by TLC). Then the solvent was evaporated under reduced pressure and crude compound obtained was purified by silica gel column chromatography. Elution of the column with EtOAc : petroleum ether gave desired products in 99% yields (see ESI† for the ^{1}H, ^{13}C and mass spectral data).

Acknowledgements

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