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# Dibutyltin oxide catalyzed aminolysis of oxalate to carbamate, oxamate and derivatives of imidazolidine trione

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**Catalytic aminolysis of oxalates by simple and substituted ureas has been shown to give carbamates, oxamates and derivatives of imidazolidine trione. Various substituted ureas and oxalates were screened to verify the applicability of the protocol. The role of dibutyltin oxide as catalyst, effect of solvent and reaction conditions on product distribution pattern has been discussed.** 

**Keywords:** urea; oxalate; carbamate; oxamate; derivative of imidazolidine trione; transfunctionalyzation; aminolysis

## Introduction

Organic molecules containing amide (peptide bond) and heterocyclic *N*-containing functionality are important in the synthesis of drug intermediates.[1] The ever increasing need for the development of new drugs with multiple functionality demands that more efficient protocols be developed in their synthesis.[2] In this connection catalysts can play an important role in the development of new routes for fine chemical synthesis. One such example is in the synthesis of amide from amine, which involves insertion of carbonyl functionality in amines.

In the present work we report trans-functionalization between simple as well as substituted urea with oxalate to synthesize carbamate and oxamate which on further condensation yield derivative of imidazolidine trione. This reaction can be viewed as an addition of two reactions, viz. aminolysis of oxalate and alcoholysis of urea (Scheme 1). Here oxalate and urea functionality is converted into oxamate and carbamate functionality without generating amine and alcohol usually expected in aminolysis of oxalate[3] and alcoholysis of urea respectively.[4]

Trans-functionalization is an efficient way to generate organic intermediates considering the fact that value-added products can be synthesized using this methodology, for example some of us have earlier shown the efficiency of this protocol wherein carbamates were synthesized with atom economy from substituted ureas and carbonates.[5]

Oxamate functionality has been found to play a vital role in many drugs, e.g. oxamate derivatives are used as orally active antiallergic agents.[6] Oxamate functionality has been also found to play a vital role as a potent antimalarial drug. The drug has been shown to inhibit the activity of plasmodium falciparum lactate dehydrogenase (pfLDH), a key enzyme responsible for metabolizing glucose in malarial parasite. *N*-substituted 3-pyrrolines exhibit neuritogenic activity and are reported to be synthesized from oxamate as one of the starting materials.[7] Oligonucleotides are often functionalized with oxamate[8] and carbamate[9] and are useful in medicinal chemistry.

Carbamates and oxamates are conventionally prepared from amines employing hazardous reagents such as phosgene/acetylchloride[10] and oxalylchloride[11] derivatives, respectively. A method of preparation of oxamate from diisopropyl oxalate has been reported; however, synthesis of this reagent involves costly ruthenium catalyst.[12] *N*-substituted oxamates can be synthesized from *N*-Boc ethyl oxamate via Mitsunobu couplings.[13] Aminolysis of oxalate by amine produce oxamate, e.g. refluxing a mixture of aniline and diethyloxalate in toluene for 45 min; oxamates are obtained in 75–90% yield. Less reactive anilines such as fluro, chloro, nitro and cyano anilines, however, required ethoxycarbonyl ethanoyl chloride for conversion to oxamate.[3] One-pot cerium-based catalytic synthesis by air oxidation of acetoacetamide has also been reported to yield oxamates in over 70% yields; however, the synthesis of catalyst is cumbersome in this case.[14]

Imidazolidine trione and their derivatives are useful in the synthesis of high-performance polymers because of their high decomposition temperature and mechanical and thermal resistant properties, and find numerous applications, e.g. in the synthesis of polyester resin,[15] polyurethanes and polyacrylates[15] and in increasing the crease-proof properties of cotton fabrics.[16]

In the present work we wish to report a greener approach replacing the reagent-based approach for the synthesis of carbamate, oxamate and derivatives of imidazolidine trione from ureas and oxalates in the presence of dibutyltin oxide (DBTO) catalyst.

## DBTO as Catalyst

A non-catalytic reaction between *N*,*N*′-dimethyl urea (DMU) and diethyloxalate (DEO) was examined initially to understand their interactions. It was observed that at 140 °C and under non-catalytic conditions, 26% of methyl urea was found to be converted at the end of 14 h reaction time forming 24% yield of *N*-methyl ethyl carbamate, 24.5% yield of *N*-methyl ethyl oxamate and

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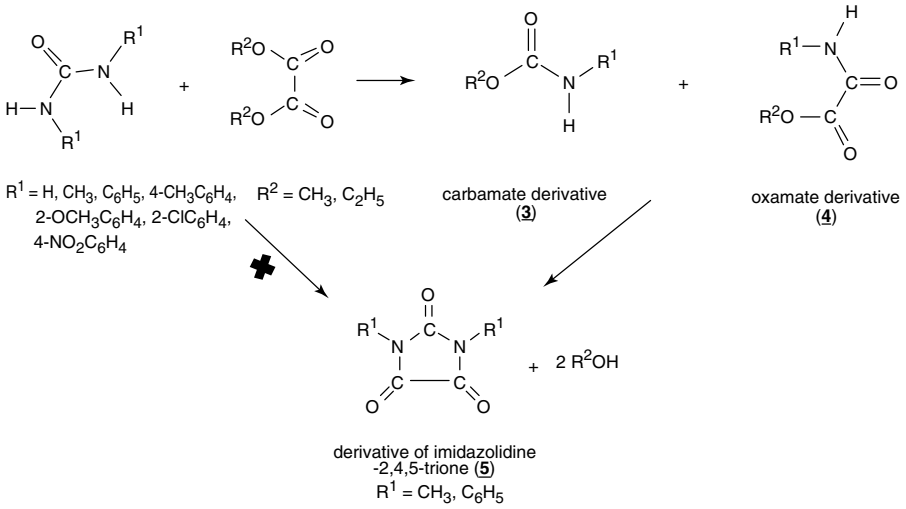



**Scheme 1.** DBTO catalyzed aminolysis of oxalate.

**Table 1.** Solvent effect[a]

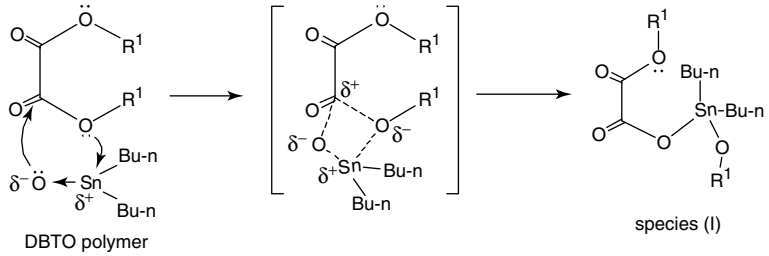
| Sample no. | Solvent | Conversion urea[b] (%) | Yield[b] (%) (3b) | (4b) | (5b) |
|---|---|---|---|---|---|
| 1 | DEO | 100 | 2.7 | 3.2 | 94.1 |
| 2 | DMF | 75.5 | 74 | 74 | 1 |
| 3 | NMP | 67 | 64 | 66 | 1 |
| 4 | Tetraglyme | 48.5 | 44 | 44.6 | 3 |
| 5[c] | DEO | 26 | 24 | 24.5 | 1.1 |
| 6[c] | DMF | 58 | 55.3 | 54 | 2.5 |

[a] Reaction conditions: DMU: 5.68, mmol; DEO, 34.2 mmol; DBTO, 0.806 mmol; time, 14 h; solvent, 10 ml; temperature, 140 °C. [b] Conversions and yield are calculated from GC analysis. [c] In the absence of DBTO.

1.1% yield of 1,3-dimethylimidazolidine-2,4,5-trione according to stoichiometry shown in Scheme 1 (see Table 1, entry 5). Dimethyl urea is considered to be weakly basic in nature ($pK_a = 18.3$)[17] and is believed to catalyze base-assisted aminolysis of acetate functionality in oxalate, giving rise to carbamate and oxamate, which further cyclize to derivatives of imidazolidine trione (also discussed later). Such a base-catalyzed aminolysis of carbonate by dimethyl urea has been reported previously.[18] In the presence of DBTO, excellent yields of 1,3-dimethylimidazolidine-2,4,5-trione (see Table 1, entry 1, 94.1%) were obtained with a small amount of carbamate and oxamate (~3% yield) remaining unconverted at this stage. Time sampling of the DBTO-catalyzed reaction revealed that carbamate and oxamate were formed as intermediates which condense further, forming 1,3-dimethylimidazolidine-2,4,5-trione with elimination of alcohol. It also eliminates the possibility of direct condensation of dimethyl urea and oxalate giving rise to 1,3-dimethylimidazolidine-2,4,5-trione (see Scheme 1) under the experimental conditions. Tin (IV) compounds have often been used as catalysts in esterification and transesterification reactions in organic synthesis.[19] Generally, the acidity of tin in organotin compounds is not enough to catalyze organic reactions of general interest; however, the acidity of tin can be increased by attaching electron-withdrawing groups to the tin.[20] The structure of DBTO is polymeric in nature having Lewis acidic Sn centers and oxygen, which represents basicity centers.[21] Accordingly, DBTO is expected to activate oxalate via hard–hard interaction between tin and alkoxy oxygen of oxalates as well as between oxygen of DBTO and carbonyl carbon of oxalate, as shown in Scheme 2. The activated oxalate (species I) is thus prone to be attacked by substituted urea, giving rise to carbamate and oxamate. Thus the amphoteric nature of DBTO seems to be playing an important role in activating DEO.

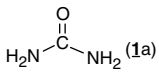
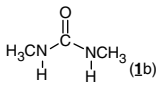
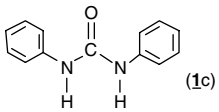
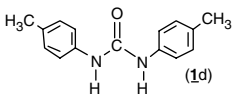
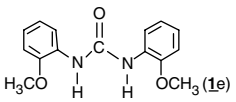
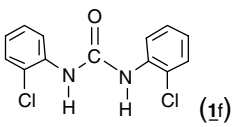
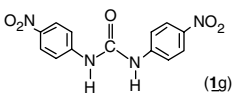
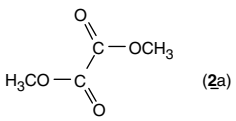
## Solvent Screening

The role of solvents was investigated and for this purpose polar solvents such as tetraethylene glycol dimethyl ether (tetraglyme), *N*-methyl pyrrolidin (NMP) and dimethyl formamide (DMF) were screened. Reactions were also run in the absence of catalyst using DMF as solvent to check the activity due to basic nature solvent. Table 1 represents the results of solvent screening experiments. The activity of DBTO as catalyst was found to be the highest in DEO, which was used as a solvent and as one of the reactants in this case (see Table 1, entry 1). It may be noted here that high catalytic activity of DBTO obtained in this case is partly due to the higher concentration of reactant, DEO (also acting as solvent), compared with that prevailing when DMF, NMP or tetraglyme are used as solvent. The solvents used are arranged in the decreasing order of DBTO activity and follow the sequence DMF > NMP > tetraglyme (see Table 1, entries 2–4). In the absence of DBTO, DMF seems to assist aminolysis of DEO by methyl urea, as 58% conversion of methyl urea (Table 1, entry 6) is obtained in this case as against only 26% when DEO is used as solvent (Table 1, entry 5). The non-catalytic reaction was found to be almost selective towards carbamate and oxamate. It may be noted that DBTO produces 1,3-dimethylimidazolidine-2,4,5-trione as a major product when DEO is used as a solvent, whereas when polar solvents are used, the 1,3-dimethylimidazolidine-2,4,5-trione yield is less than 3% and the highest yields of carbamate and oxamate are obtained (see Table 1, entry 2–4). Hence, it may be argued that acidic sites of tin might be responsible for catalyzing condensation of carbamate and oxamate, which might be deactivated due to basic nature of polar solvents, thereby decreasing the yield of 1,3-dimethylimidazolidine-2,4,5-trione.




**Scheme 2.** Plausible interaction of DBTO and oxalate.

**Table 2.** Reaction of urea and oxalate catalyzed by DBTO under pot conditions[a]

| Sample no. | Substrate | Urea conversion[b] (%) | Yield[b] (%) (**3**) | Yield[b] (%) (**4**) | Yield[b] (%) (**5**) |
|---|---|---|---|---|---|
| 1 |  (**1a**) | 65 | 63.5 | 63 | 00[c] |
| | | 100 | 84.3; 80* | 84; 80* | |
| | | | (3a) | (4a) | |
| 2 |  (**1b**) | 80 | 2.8 | 2.5 | 77 |
| | | 100 | 9 | 9.5 | 90; 85* |
| | | | (3b) | (4b) | (5b) |
| 3 |  (**1c**) | 55 | 30.8 | 30 | 24 |
| | | 100 | 31.9 | 32 | 68; 63* |
| | | | (3c) | (4c) | (5c) |
| 4 |  (**1d**) | 80 | 79 | 79.5 | 00 |
| | | 100 | 99.5; 95* | 99; 93* | |
| | | | (3d) | (4d) | |
| 5 |  (**1e**) | 71 | 69 | 70 | 00 |
| | | 100 | 99.2; 90* | 99; 94* | |
| | | | (3e) | (4e) | |
| 6 |  (**1f**) | 38 | 36 | 36 | 00[d] |
| | | 80 | 74.5; 70* | 74; 69* | |
| | | | (3f) | (4f) | |
| 7 |  (**1g**) | 0 | 0 | 0 | 0 |
| 8[e] |  (**2a**) | 60[f] | 47 | 48 | 12 |
| | | 100 | 77; 72* | 77; 73* | 22;18* |
| | | | (3i) | (4i) | (5b) |

[a] Pot reaction condition: urea, 5.68 mmol; oxalate, 34.2 mmol; DBTO, 0.806 mmol; time, 12 h; temperature, 140 °C. [b] Conversions and yields are calculated from gas chromatography analysis, yields are based on urea conversions. The first entry shows conversion for 2 h reaction time. [c] Approximately 15% yield of $H_5C_2OCONHOCOC_2H_5$ (diethyl iminodicarbonate **6** as a side product was realized in this case. [d] Approximately 5% yield of $ClC_6H_4NHCOCONHC_6H_4Cl$ [$N^1$,$N^2$-bis(2-chlorophenyl) oxalamide **10**] as a side product was detected. [e] Dimethyl urea: 5.68 mmol, and dimethyl oxalate, 34.2 mmol, as reactants. [f] Conversion of methyl urea. * Isolated yield.

### Substrate Screening

The reactivity pattern of aliphatic and aromatic urea towards aminolysis of oxalate under pot conditions was investigated and the results are presented in Table 2 (the first entry under each substrate heading represents the result obtained at 2 h contact time). Aliphatic urea such as simple urea showed a completely different reactivity pattern both under pot and under autogenous pressure conditions (also discussed later). In the initial period of the reaction (2 h contact time), carbamate and oxamate are formed as major products, which upon cyclization yield derivatives of imidazolidine-2,4,5-trione only for methyl and phenyl substituted ureas (entries 2, 3 and 8), while for remaining ureas, carbamate and oxamate were selectively formed (entries 1, 4–7). It was observed that simple urea as substrate yields diethyl iminodicarbonate (~15 wt% yield, Table 2, entry 1, see footnote to Table 2), along with

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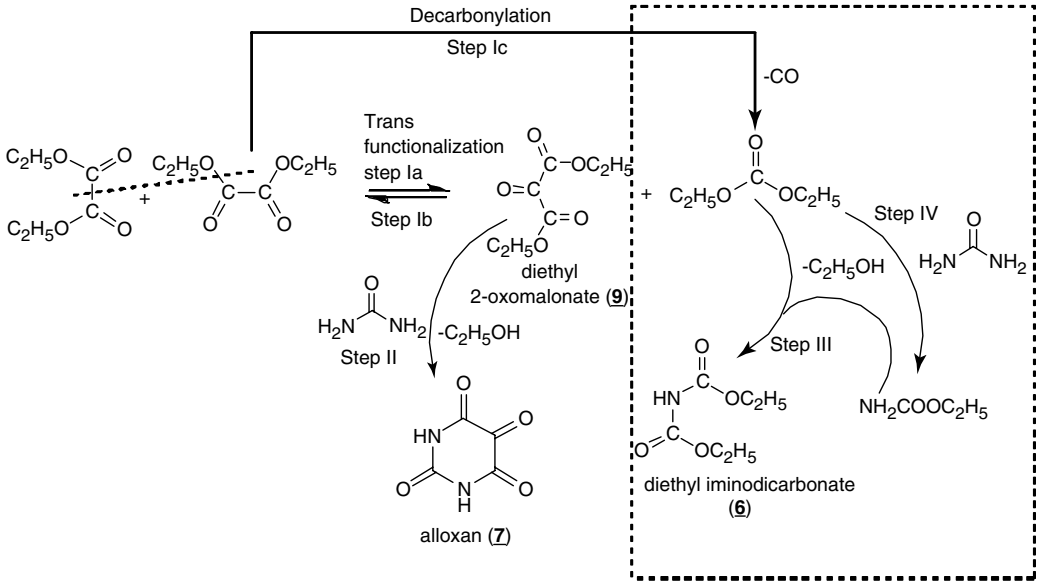



**Scheme 3.** DBTO-catalyzed urea and oxalate reaction under autogenous pressure; the box shows the reactions taking place also under pot conditions.

expected carbamate and oxamate (~84% yield). The key step here is the catalytic decarbonylation of DEO in the presence of DBTO to diethyl carbonate and CO. In order to confirm this step (see step Ic in Scheme 3), the reaction was monitored to check the liberation of CO, which was qualitatively detected by exposing the gas phase to a filter paper strip soaked with $PdCl_2$ solution. The $PdCl_2$ solution-soaked paper strip turned black, indicating the presence of CO in gas the phase. Scheme 3 shows that diethyl carbonate (DEC) reacts with urea according to a known route to yield ethyl carbamate,[5] which in turn reacts with one more molecule of DEC, giving rise to diethyl iminodicarbonate (see Table 2, entry 1, compound **6**). The data in Table 2 shows that methyl urea is more reactive as compared with simple urea (entries 1 and 2), while for aromatic ureas it was found that electron-donating substituents on the ring enhance the reactivity of diphenyl urea, while electron-withdrawing substituents reduce its reactivity.[22] Reaction of *o*-chloro diphenyl urea give rise to $N^1$,$N^2$-bis(2-chlorophenyl)oxalamide (**10**) as a side product (~5%) along with expected carbamate and oxamate (entry 6). *p*-Nitro diphenyl urea was found to be extremely unreactive towards aminolysis of oxalate due to the strong electron-withdrawing nature of *p*-$NO_2$ functionality, which reduces the nucleophilicity of the attacking urea. As expected, dimethyl oxalate is less reactive compared with diethyl oxalate towards aminolysis by methyl urea (entry 2 and 8), due to poor leaving group ability of $^{\ominus}OCH_3$ compared with $^{\ominus}OC_2H_5$. Further condensation of carbamate and oxamate to 1,3-dimethylimidazolidine-2,4,5-trione is facilitated by higher basicity of $^{\ominus}OC_2H_5$ compared with $^{\ominus}OCH_3$. Thus, carboxylation of methyl urea by diethyl oxalate results in almost quantitative formation of 1,3-dimethylimidazolidine-2,4,5-trione compared with dimethyl oxalate (see entries 2 and 8). The reactivity pattern of aromatic carbamate and oxamate towards cyclization shows that substituents on amides have a pronounced hindrance effect, which decreases the reactivity towards cyclization. Accordingly, cyclization of phenyl carbamate and phenyl oxamate yields ~68% 1,3-diphenylimidazolidine-2,4,5-trione (entry 3), while on the other hand substituted derivatives of aromatic carbamate and oxamate were found to be completely unreactive towards cyclization (entries 4–7).

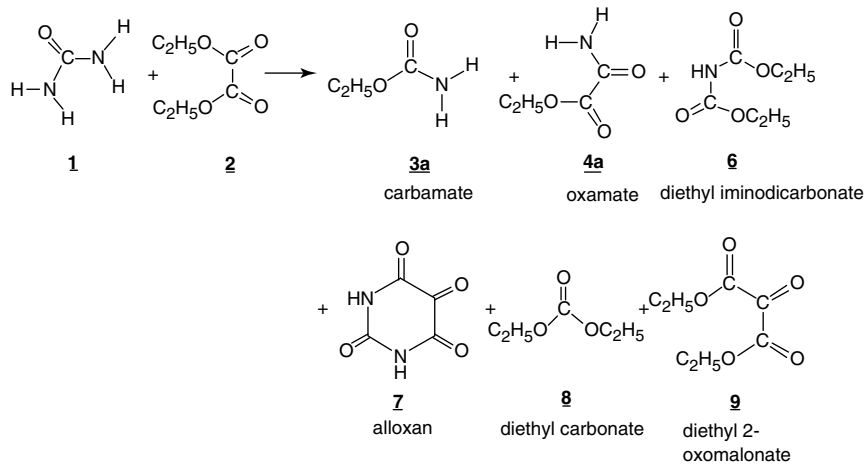
## Reaction under Autoclave Conditions

The reaction between simple urea and oxalate was also explored under autogenous pressure conditions in the presence of DBTO as catalyst. Initially simple urea and diethyl oxalate were made to react in the presence of catalytic amount of DBTO at 140 °C and for 12 h. The GC and GC-MS analysis of the reaction mixture indicated the presence of ethanol, diethyl oxomalonate, diethyl carbonate, alloxan and diethyl iminodicarbonate (see Table 3, entry 1), along with ethyl carbamate and ethyl oxamate. It can be seen from Table 3 (entry 1), that an appreciable amount of ethyl carbamate and ethanol is produced in this reaction as compared with the same reaction under pot conditions (see Table 3, entry 1). The plausible pathway for the formation of four additional products (viz. diethyl carbonate, diethyl oxomalonate, alloxan and diethyl iminodicarbonate) along with the usual carbamate and oxamate is depicted in Scheme 3. It is shown in this scheme that intermolecular transfunctionalyzation of DEO results in diethyl 2-oxomalonate (**9**) and diethyl carbonate formation (see step Ia, Scheme 3). We have not been able to find any report on this reaction and hence carried out a separate reaction in the absence of urea to confirm the feasibility. It was observed that DEO in presence of DBTO as catalyst and under autogenous pressure but in absence of urea (see Table 3, entry 2 for details) indeed gave small quantities (~5%) of diethyl 2-oxomalonate along with DEC. DEC is also formed by decarbonylation of DEO (step Ic, Scheme 3). The formation of CO under autogenous condition has been confirmed by the $PdCl_2$ test described earlier. At this stage it is interesting to note that generally dialkyl carbonate can be produced from dialkyl oxalate via an energy-intensive decarbonylation step. Usually expensive Pd catalyst[23] or highly reactive and unstable phosphonium salts have been employed for decarbonylation of DEO to DEC.[24] We believe that, in the present case, transfunctionalyzation of two molecules of DEO give rise to diethyl oxomalonate and DEC while, in the presence of urea, diethyl oxomalonate produces alloxan (~2%, Table 3, entry 1 and Scheme 3, step II) thereby preventing the reverse reaction (step Ib). The other reaction between diethyl carbonate and urea to yield carbamate is known (step IV),[5] and accordingly more



**Table 3.** Urea and oxalate reaction under autogenous pressure[a]




| | Substrate | | Conversion of urea (%) | Product yield[b] (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Urea (**1**) | Oxalate (**2**) | | (**3**) | (**4**) | (**6**) | (**7**) | (**8**) | (**9**) |
| 1 | H | $C_2H_5$ | 100 | 60 | 30 | 2.5 | 2 | ~3 | 2.5 |
| 2 | – | $C_2H_5$ | – | – | – | – | – | 5 | 5 |

[a] Urea, 66.7 mmol; DEO, 154.8 mmol; DBTO, 5.64 mmol; time, 12 h; temperature,140 °C; autogenous pressure. [b] Conversions and yields are calculated from gas chromatography analysis; ethanol is also formed at ~24% yield, but is excluded from percentile calculations for the sake of convenience.

ethyl carbamate is produced, which seems to be the reason for formation of substantial quantities of ethyl carbamate in this case. It is shown that aminolysis of DEC by ethyl carbamate produces diethyl iminodicarbonate (**6**, see step III, Scheme 3). This reaction is also unknown in the literature. It may be noted here that diethyl iminodicarbonate is formed in pot as well as under autoclave conditions; however, since under pot conditions either diethyl 2-oxomalonate or alloxan are not detected, we presume that diethyl carbonate (which is the precursor to diethyl iminodocarbonate formation) is produced by two different routes (steps 1a and 1c), as shown in Scheme 3.

## Conclusions

Here we report an efficient but simple catalytic route that can replace the toxic reagent-based route employed in the transformation of amines to carbamates, oxamates and derivatives of imidazolidine trione. Our results show that simple urea does not yield imidazolidine trione under the experimental conditions employed and in this case carbamate and oxamate are produced along with diethylimino dicarbonate as a side product. A derivative of imidazolidine trione is produced when methyl and phenyl urea are used as substrates, and other substituted ureas give rise to mainly carbamate and oxamate. Yields of carbamates, oxamates and substituted imidazolidine trione can be manipulated by choice of the solvent. The possibility of producing important organic intermediates such as dialkyl carbonate, oxomalonate and imino dicarbonate is an interesting outcome of the work.

## Experimental Section

Substituted ureas were synthesized by a reported procedure.[25] Some solvents (DMO, NMP and tetraglyme) were procured from Aldrich USA, other solvents (DEO and DMF) were purchased from SD Fine Chemicals India, while DBTO was purchased from Merck, India and was used as such.

A typical procedure for synthesis of substituted imidazolidine trione is as follows: 5 g (34.2 mmol) of DEO was taken in a two-neck 25 ml round-bottom flask equipped with a reflux condenser and magnetic bar for stirring under argon atmosphere. To this 0.5 g (5.68 mmol) dimethyl urea and 0.2 g (0.806 mmol) of DBTO were added. The system was flushed with argon and then immersed in the oil bath preheated to 140 °C temperature. Internal reaction temperature as well as that of the oil bath was maintained by temperature controller. The standard reaction was carried out for 12 h and time sampling was done at periodical intervals. For reaction under autogenous pressure, a similar procedure to that mentioned for atmospheric pressure condition was followed, except instead of a glass reactor a 50 $cm^3$ Par autoclave (USA make) was used with a urea charge of 66.7 mmol, DEO charge of 154.8 mmol and DBTO charge of 5.64 mmol. Contents of the autoclave were flushed with 50 psig of nitrogen gas pressure, two or three times before starting the reaction under autogenous condition. The liquid phase was quantitatively analyzed on a Hewlett Packard 6890 series gas chromatograph equipped with a BP10, 30 m × 0.32 mm i.d. capillary column. The products were separated from the organic phase by flash chromatography on a 4 g normal phase silica RediSep column employing *n*-hexane–ethyl acetate as the eluent with gradient programming. Flash chromatography was performed using CombiFlash Companion, supplied by Teledyne ISCO, USA. All the compounds were known and characterized by comparing their reported $^{13}C$ NMR, $^{1}H$ NMR and GC-MS data [**3a,e**thyl carbamate; **3b**, ethyl *N*-methylcarbamate; **3c,e**thyl *N*-(phenyl)carbamate; **3i**, methyl *N*-methylcarbamate;[18,26] **4a**, ethyl oxamate; **4b**, ethyl *N*-methyloxamate; **4c**, ethyl *N*-(phenyl) oxamate[26a,b,27];**5b**, 1,3-dimethylimidazolidine-2,4,5-trione;[28] **5c**,

1,3-diphenylimidazolidine-2,4,5-trione;[29] **3d**, ethyl *N*-(4-methylphenyl) carbamate; **3e**, ethyl *N*-(2-methoxyphenyl)carbamate; **3f**, ethyl *N*-(2-chlorophenyl)carbamate;[30] **4d**, ethyl *N*-(4-methylphenyl) oxamate; **4e**, ethyl *N*-(2-methoxyphenyl)oxamate;[11a] **4f**, ethyl *N*-(2-chlorophenyl)oxamate;[3] **4i**, methyl *N*-methyloxamate;[12] **6**, diethyl iminodicarbonate;[31] **10**, $N^1$,$N^2$-bis(2-chlorophenyl)oxalamide (GC-MS).[32] The $^1$H NMR and $^{13}$C NMR spectra in $CDCl_3$ were recorded on a 200 and 500 MHz Brucker instrument. Infrared (IR) spectra were recorded on a Perkin-Elmer system 2000 infrared spectroscope. Samples for IR spectroscopy were prepared employing a potassium bromide under normal mode. GC-MS analysis was carried out on an instrument supplied by Agilent, model 6890/5973N GC mass selective detector using an HP-5 MS capillary column.

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