DOI: 10.1002/adsc.201200760

Introducing Catalytic Lossen Rearrangements: Sustainable Access to Carbamates and Amines

Oliver Kreye,[a] Sarah Wald,[a] and Michael A. R. Meier[a,*]

[a] Laboratory of Applied Chemistry, Institute of Organic Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 6, 76131 Karlsruhe, Germany
E-mail: m.a.r.meier@kit.edu (www.meier-michael.com)

Received: August 24, 2012; Revised: October 2, 2012; Published online: December 23, 2012

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201200760.

Abstract: A new, highly efficient and environmentally benign catalytic variant of the Lossen rearrangement is described. Dimethyl carbonate (DMC) as green activation reagent of hydroxamic acids in presence of catalytic amounts of tertiary amine bases {1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,8-biazabicyclo 5.4.0 undec-7-ene (DBU), 1,4-diazabicyclo[2.2.2]octane (DABCO), and triethylamine} and small quantities of methanol initiate the rearrangement. Methyl carbamates were obtained in good to moderate yields when aliphatic hydroxamic acids were employed in this catalytic Lossen rearrangement; under the same conditions aromatic hydroxamic acids yielded anilines. Notably, the mixture of DMC/methanol was recycled several times without observing decreased yields, thus minimizing the produced waste. Moreover, several other organic carbonates were successfully employed in the introduced catalytic Lossen rearrangement procedure.

Keywords: anilines; carbamates; dimethyl carbonate; lossen rearrangement; organocatalysis

Already in 1872, Wilhelm Lossen observed that benzoylated benzhydroxamic acid derivatives rearrange to anilines under basic conditions.[1] More detailed investigations showed that products having an activated hydroxy group undergo a facile rearrangement to isocyanates as intermediates, followed by degradation to primary amines in the presence of water, whereas carbamates and urea derivatives will be formed under non-aqueous conditions.[2] With respect to various promising modern procedures and interesting applications of the Lossen rearrangement, our motivation was to find a catalytic and thus more sustainable and environmentally benign procedure for the rearrangement of hydroxamic acids. We thus thought of dimethyl carbonate (DMC) as a suitable *in situ* activation reagent for a catalytic Lossen rearrangement. Particularly during the last years, DMC has received attention as a non-toxic phosgene substituent as well as a green solvent.[3] Additionally, numerous procedures for the synthesis of DMC avoiding phosgene and its derivatives have been described.[4] Moreover, DMC is frequently used as reagent in several organic chemistry procedures as well as in polymer chemistry for the synthesis of polycarbonates.[5] To achieve an *in situ* activation of hydroxamic acids with DMC, catalytic amounts of tertiary amine bases should be suitable for two main reasons: (i) methanolate, which is released from DMC in the progress of the reaction, should regenerate the protonated amine bases, and (ii) such amine bases would act as esterification catalysts in the activation of the hydroxamic acids. A Lossen rearrangement in such a catalytic manner was never described, although the reaction has been known for more than 140 years. Generally, the development of catalytic procedures are of extraordinary importance regarding sustainability, since they have the potential to reduce the amount of produced waste and can significantly increase not only the rate of the reaction, but also its scope.

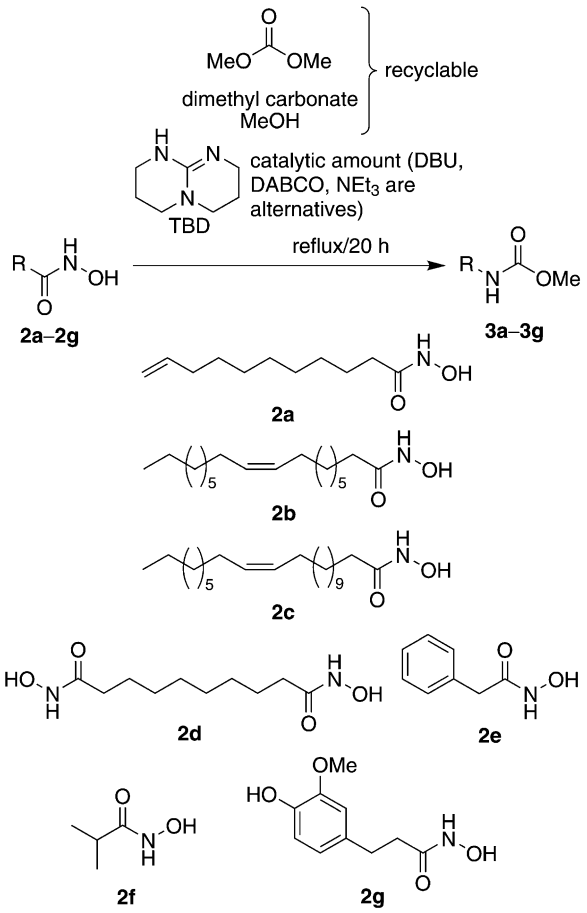
Recently, we introduced a strategy for the preparation of symmetric and asymmetric carbonates as well as polycarbonates using 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) catalyzed transesterifications with different alcohols.[6] Currently, TBD, a strong guanidine base, is gaining more and more interest in organic synthesis.[7] Having these results in mind, we explored if catalytic quantities of TBD or other amine bases have the potential to activate hydroxamic acids with DMC *in situ* to form highly reactive mixed anhydrides, which should be suitable intermediates for the Lossen rearrangement. Initially, the catalytic Lossen rearrangement was studied by employing different fatty acid-derived hydroxamic acids. Herein, the hy-

droxamic acid derived from 10-undecenoic acid **2a** was used as a model substance. Generally, there is a high interest in a simple and environmentally benign pathway to obtain amine derivatives of undecenoic acid and other renewable building blocks as intermediates for renewable polyurethanes, -ureas and -amides.

In a first try, **2a** was reacted with DMC (20 equiv.) and TBD (0.2 equiv.) under refluxing conditions for one day; the rearrangement occurred, but the desired methyl carbamate **3a** was obtained in a low yield of 15%. The main product, with a yield exceeding 50%, was 1,3-di(dec-9-enyl)urea **4a**. Probably, the urea formation is a result of too small amounts of methanol, which acts as a nucleophile to form the carbamate. Thus, we repeated the experiment in the presence of additional methanol (5.0 equiv.) and, as expected, the yield of the urea product decreased dramatically (< 10%) and methyl carbamate **3a** was isolated in a yield of 40%. However, due to the high amount of methanol, TBD also catalyzed the formation of methyl 10-undecenoate (yield 20%). After additional investigations and optimization of the reaction conditions, we found that the best results can be obtained when DMC and methanol were used in a 10:1 ratio with 0.2 equiv. of TBD. The Lossen rearrangement of **2a** with DMC (20 equiv.), methanol (2.0 equiv.) and TBD (0.2 equiv.) gave methyl carbamate derivative **3a** as a colorless oil in an isolated yield of 65% after heating to reflux for 20 h (Scheme 1, Table 1).

The side product 1,3-di(dec-9-enyl)urea **4a** was obtained in low yield (12%). In following experiments, the hydroxamic acids of oleic acid **2b** and erucic acid **2c** were investigated in the rearrangement. Similar results were achieved with yields of 62% (**3b**, colorless oil) and 65% (**3c**, colorless wax) after purification by column chromatography. In the case of **2c**, higher amounts of DMC and methanol were applied due to the low solubility of **2c**. The fatty acid-based dihydroxamic acid **2d** was rearranged to dimethyl carbamate derivative **3d**. A major drawback of aliphatic dihydroxamic acids is their poor solubility in common organic solvents. Thus, high amounts of DMC and methanol were used for the rearrangement of **2d.** Pure **3d** was obtained as a colorless solid in a relatively low yield of 34% (38% with 0.6 equiv. TBD). However, if DMSO is used as co-solvent and the amounts of DMC and methanol are reduced to half, the yield of **3d** increases significantly to 66%.

Furthermore, the tertiary amine base-catalyzed Lossen rearrangement with DMC with diverse aliphatic hydroxamic acids **2e–2g** gave similar yields of methyl carbamates **3e–3g** (Scheme 1, Table 1). In the case of **2g** we observed that half of the product was methylated at the phenolic hydroxy group. However, this result was in agreement with the well-known methylation reaction of DMC with phenols.[5a,b,8]



Scheme 1. Tertiary amine base-catalyzed Lossen rearrangements of hydroxamic acids **2a–2g** with dimethyl carbonate to obtain methyl carbamates **3a–3g**.

Table 1. Results of the catalytic Lossen rearrangement of hydroxamic acids **2a–2g** to yield **3a–3g**.

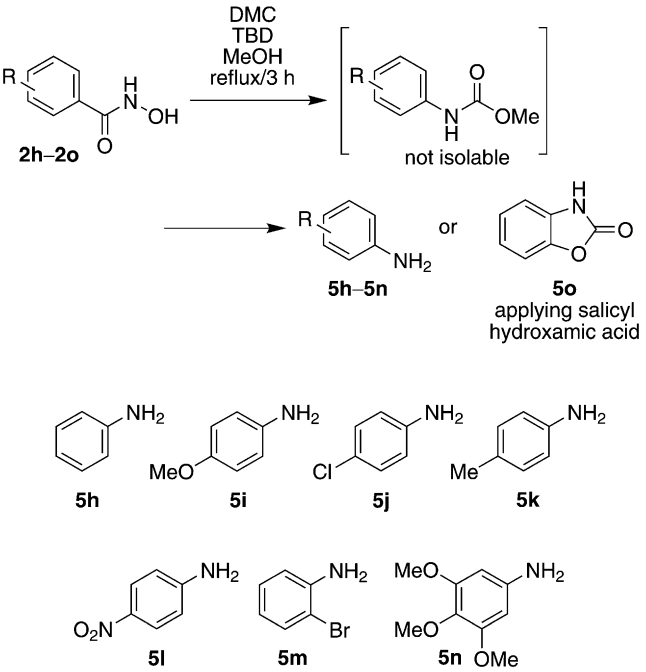
Entry	DMC equiv.]	MeOH [equiv.]	TBD [equiv.]	Product	Yield [%]
1	20	2	0.2	**3a**	65
2	20	2	0.2	**3b**	62
3	40	4	0.4	**3c**	65
4	200	20	0.4	**3d**	34 (38[a], 66[b])
5	20	2	0.2	**3e**	73
6	20	2	0.2	**3f**	65
7	20	2	0.4	**3g**	~76[c]

[a] *Conditions:* 0.6 equiv. TBD were used.
[b] *Conditions:* DMC (100 equiv.), methanol (10 equiv.), TBD (0.6 equiv.) and DMSO ($c = 0.24$ mol/L) as co-solvent.
[c] About half of the product was methylated at the phenol group as determined *via* NMR. Due to same retention, a separation of both products by column chromatography was not possible.

Table 2. Conversion C [%] and product formation P [%] for the catalytic Lossen rearrangement of **2a** to **3a** with different catalysts at different catalyst loadings.[a]

Catalyst	[mol%]	4 h		24 h	
		C	**P**	**C**	**P**
TBD	20	100	76	100	81
	10	99	69	100	79
	5.0	63	13	85	18
DBU	20	100	59	100	78
	10	95	29	98	49
	5.0	57	5	80	10
DABCO	20	99	41	100	78
	10	95	45	100	68
	5.0	75	9	85	20
NEt_3	20	90	4	100	58
	10	69	2	94	32

[a] *Conditions:* DMC (20 equiv.), methanol (2.0 equiv.), reflux; ^{1}H NMR spectroscopy was applied to determine the conversion of **C** and formation of product **P** *via* integral correlation (an experimental error of ±5% due to the use of reaction mixtures should be considered).



Scheme 2. Direct synthesis of aniline derivatives **5h–5n** and cyclic carbamate derivative **5o** by base-catalyzed Lossen rearrangements of aromatic hydroxamic acids **2h–2o**.

Having established the broad scope of this reaction, we tried to minimize the amount of catalyst. In a test series, different quantities (20, 10 and 5.0 mol%) of TBD, DBU, DABCO, and triethylamine were employed to investigate the rearrangement of **2a** to **3a** (Table 2). The conversions and product formation were obtained by integral correlations of ^{1}H NMR spectra of the crude reaction mixtures after specified time periods (1, 4, 24 and 48 h). We found that TBD, DBU and DABCO showed similar activity at 20 and 10 mol% of catalyst loading, whereas 5 mol% and less catalyst led to lower activity. Triethylamine in amounts of 20 and 10 mol% showed significantly increased reaction times in comparison to the above-mentioned catalysts, but we believe it is important to report these results, since triethylamine is cheap, easy to remove, and the amount of product formed after longer reaction times is satisfying. These experiments thus clearly show that a variety of bases catalyze this rearrangement and that catalyst loadings of 10%, a typical value for organocatalysis, show good results.

To further broaden the scope of this new and catalytic rearrangement procedure, we also investigated aromatic hydroxamic acids. In a first reaction, *N*-hydroxybenzamide **2h** was treated with DMC, methanol and TBD under the same conditions as described above for the aliphatic hydroxamic acids and after only three hours TLC showed full conversion. However, instead of the expected methyl carbamate derivative **3h**, we obtained aniline **5h** in 81% yield (Scheme 2, Table 3). Presumably, aromatic methyl carbamates are not stable under the applied basic reaction conditions and degrade in the presence of TBD and methanol and/or water to anilines.

Table 3. Yields of aniline derivatives **5h–5n**.

Entry	DMC [equiv.]	MeOH [equiv.]	TBD [equiv.]	Product	Yield [%]
1	20	2	0.2	**5h**	81
2	20	2	0.2	**5i**	65
3	20	2	0.2	**5j**	83
4	20	2	0.2	**5k**	78
5	20	-	0.05[a]	**5l**	72
6	20	2	0.2	**5m**	73
7	20	2	0.2	**5n**	81
8	20	2	0.4[b]	**5o**	77

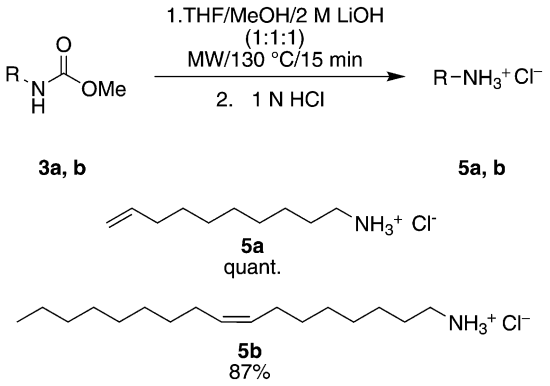
[a] *Conditions:* reaction time was 20 h.
[b] *Conditions:* reaction time was seven hours.

Further investigations showed that also DBU, DABCO and triethylamine reacted in the same way and isolation of the methyl carbamates was not possible. Afterwards, we tested if electron-donor and electron-acceptor substituents at the aromatic core would have an influence on the reaction. Also here, the hydroxamic acid of *para*-methoxybenzoic acid **2i** was fully converted to *p*-anisidine **5i** in an isolated yield of 65% without detection of the corresponding methyl carbamate derivative. Moreover, *para*-chloro- and *para*-methylbenzhydroxamic acids **2j** and **2k** were directly converted to the corresponding aniline derivatives **5j** and **5k** in high yields. In the case of the rearrangement of *para*-nitrobenzhydroxamic acid **2l**, applying the standard conditions with DMC (20 equiv.),

methanol (2.0 equiv.) and TBD (0.2 equiv.), the main product was not *para*-nitroaniline **5l**. In this case we observed that the TBD-catalyzed esterification with methanol was faster than the rearrangement and thus, methyl *p*-nitrobenzoate was isolated in a yield of about 60%. Although the same experiment without methanol and smaller amount of TBD (0.05 equiv.) required longer reaction times, the product **5l** was obtained in a good yield of 72% after heating to reflux for 20 h. In a further experiment with *ortho*-bromobenzhydroxamic acid **2m** rearranged with the standard procedure and *ortho*-bromoaniline **5m** was obtained in a yield of 73%. Also the trisubstituted 3,4,5-trimethoxybenzhydroxamic acid **2n** rearranged completely after three hours and 3,4,5-trimethoxyaniline **5n** was isolated in a yield of 81%. An indication that methyl carbamtes are intermediates in the rearrangement of aromatic hydroxamic acids is the result of the rearrangement of salicylhydroxamic acid **2o**. Instead of the expected 2-aminophenol, the cyclic carbamate derivative **5o** was obtained in a yield of 77%. One would expect that phenols will be methylated under these conditions. Obtaining **5o** thus indicates that the Lossen rearrangement is faster than the methylation; the intermediately obtained methyl carbamte is not hydrolyzed, but the formation of the five-membered carbamate **5o** is favored.

Moreover, a catalyst screening in the rearrangement of *N*-hydroxybenzamide **2h** to aniline **5h** was performed and similar results as in the case of aliphatic hydroxamic acid **2a** were observed with the exception that the rearrangement was generally considerably faster. It is important to mention that longer reaction times (>7 h) led to the formation of mono- and dimethylated anilines, as a well-known methylation reaction of DMC in the presence of TBD, DBU and DABCO.[5a,b,6,8] Even in the case of triethylamine, after two days reaction time, a low yield of methylated aniline was detected *via* ^{1}H NMR.

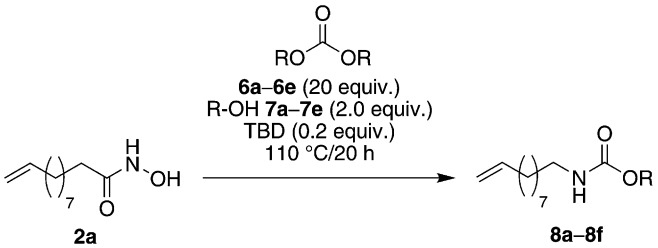
Since one of our goals is the synthesis of renewable amine derivatives, some of the obtained aliphatic methyl carbamates were hydrolyzed to primary amines. In contrast to aromatic methyl carbamates, which were hydrolyzed immediately under the influence of the tested tertiary amine bases in the reaction mixture, aliphatic methyl carbamates are rather stable. Nonetheless, there are many procedures describing the cleavage of methyl carbamates, but usually toxic and expensive reagents are required.[9] For a sustainable synthesis of fatty amines, we tried to cleave the carbamates by applying aqueous alkali solutions, for example, 2 M LiOH and 4 M KOH, mixed with organic solvents such as methanol or THF under refluxing conditions. Long reaction times (>4 days) were required under these conditions. To reduce the time of hydrolysis, we successfully applied a microwave heating procedure described by Lehmann and



Scheme 3. Microwave assisted hydrolysis of methyl carbamates **3a** and **3b** under basic conditions to obtain primary amine hydrochlorides **5a** and **5b**.

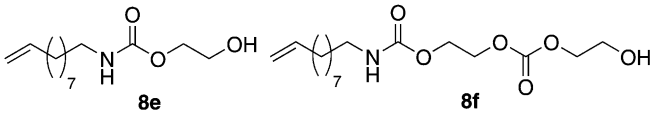
Scobie (Scheme 3).[9d] Thus, fatty acid methyl carbamates **3a** and **3b** were dissolved in a mixture of THF, methanol and 2 M LiOH (1:1:1) and heated in the microwave synthesizer to 130 °C for only 15 min. Complete hydrolysis was detected *via* TLC and after aqueous work-up, the amines **5a** and **5b** were obtained as hydrochlorides in quantitative yield for **5a** and 87% for **5b**. Subsequently, we found that the microwave-supported hydrolysis with the same *ratio* of THF, methanol and 2 M LiOH can also applied successfully in a high pressure reactor at 10 bar and a temperature of 150 °C.

Finally, in order to broaden the scope of the introduced rearrangement procedure, several other organic carbonates were employed in this catalytic Lossen rearrangement providing access to diverse carbamates. It is worth mentioning here that dialkyl carbonates can be easily prepared from DMC by the reaction of alcohols in the presence of TBD.[6] The reaction of hydroxamic acid **2a** with diethyl carbonate **6a**, ethanol **7a** and TBD in same *ratios* and identical conditions as described for DMC, afforded the corresponding ethyl carbamate derivative **8a** in a good yield of 77% (Scheme 4, Table 4). Also diallyl and dibenzyl carbonates **6b** and **6c** reacted with **2a** to furnish the corresponding allyl and benzyl carbamates **8b** and **8c** in yields of 68 and 74%, respectively. These results demonstrate that this approach can be a very useful tool



Scheme 4. Catalytic Lossen rearrangement of hydroxamic acid **2a** with carbonates **6a–6e**.

Table 4. Yields of carbamates **8a–8f**.



8e **8f**

Entry	R	Product	Yield [%]
1	Et	**8a**	77
2	All	**8b**	68
3	Bn	**8c**	74
4	Ph	**8d**	62
5	$-CH_2CH_2-$	**8e**	21
		8f	33

to synthesize urethane-protected amines from carboxylic acids, representing a simple and environmentally benign alternative to commonly used strategies; the obtained allyl carbamates (Alloc) and benzyl carbamates (Cbz or Z) are frequently used as protecting groups for amine functionalities in peptide or related chemistry.[9a] Furthermore, the application of diphenyl carbonate **6d**, as an example of a diaryl carbonate derivative, in the presence of phenol **7d** gave the corresponding phenyl carbamate **8d** in 62% yield. Interestingly, the rearrangement of **2a** with ethylene carbonate **6e** in the presence of ethylene glycol **7e** afforded two major products. The expected product **8e** was obtained only in a low yield of 21% and the main product with an isolated yield of 33% was identified to be carbonate **8f** formed by additional transesterification of **8e** with excess of ethylene carbonate. Although a more detailed study would be required in this case, generally, longer reaction times should increase the yield of **8f**, whereas **8e** should be the major product when applying shorter reaction times.

In conclusion, a novel procedure of the Lossen rearrangement is described utilizing dialkyl or diaryl carbonates as *in situ* activating reagents for hydroxamic acids. The reaction is catalyzed by tertiary amine bases. The best results were obtained by refluxing hydroxamic acids in a dialkyl carbonate/corresponding alcohol mixture (*ratio* 10:1) with 0.2 or 0.1 equivalents of the mentioned tertiary amine bases for approximately 20 h to obtain alkyl carbamates in isolated yields between 52 and 77%, which are comparable to conventionally performed Lossen rearrangements. As shown for some aliphatic derivatives, these yields can further be improved by optimizing the reaction conditions for the different derivatives. By applying aromatic hydroxamic acids, the rearrangement was faster and the methyl carbamates were directly hydrolyzed to anilines. The isolated yields of anilines were in a range of 65 to 83%. The results illustrate that this new catalytic procedure is applicable to various aliphatic and aromatic hydroxamic acids. The reaction proceeded under quite mild conditions and thus, many functional groups shown in the rearrangement of aromatic hydroxamic acids are tolerated. Moreover, the experience that every dialkyl or diaryl carbonate can be used to give the corresponding alkyl or aryl carbamate makes this process very versatile. Compared to a conventional Lossen rearrangement procedure, which requires stoichiometric amounts of base, an activating reagent (i.e., acetyl chloride or acetic anhydride), and an additional purification step, our new catalytic variant is certainly easier applicable and fully along the lines of green chemistry. Very importantly, it was also possible to recycle the reagent (solvent) mixture of DMC/methanol several times by simple distillation without observing decreased yields. The rearrangement of **2a** showed the formation of methyl carbamate **3a** in nearly identical yields after three recycling cycles. All in all, the introduced Lossen rearrangement procedure is clearly demonstrated to be a synthetically very useful tool being environmentally friendly, catalytic, and a mild method providing access to various structurally diverse carbamates and amines.

Experimental Section

Representative Procedure for Tertiary Amine Base-Catalyzed Lossen Rearrangements with Dialkyl(aryl) Carbonates

The hydroxamic acid derivatives **2a–2n** (100 mmol) were dissolved in dialkyl or diaryl carbonate (2.00 mol, 20 equiv.) and the corresponding alcohol (phenol) (200 mmol, 2.0 equiv.). The mixtures were heated to reflux and TBD (2.79 g, 20.0 mmol, 0.2 equiv.; or DBU, DABCO, triethylamine as alternative bases) was added. After TLC and GC-MS revealed full conversions (usually after 20 h for aliphatic hydroxamic acids and 3–5 h for aromatic hydroxamic acids) the reaction mixtures were evaporated to dryness. The crude products were purified by column chromatography to obtain the pure methyl carbamate derivatives **3a–3g** (from aliphatic hydroxamic acids **2a–2g**), aniline derivatives **5h–5n** (from aromatic hydroxamic acids **2h–2n**) and miscellaneous carbamates **8a–8f**.

Acknowledgements

We kindly thank Laetitia Martin from the École nationale de supérieure de chimie (ENSC) de Lille (France) for the synthesis of some hydroxamic acids and for the investigation of first rearrangement experiments during her practical course in our group. For some optimizations, we kindly thank Alexander Prohammer from the Karlsruhe Institute of Technology (KIT), who also performed a practical course in our group. We also thank Madlen Schreiner for measuring the melting points. We kindly acknowledge the analytical department, especially Angelika Kernert, Ingrid Roßnagel and Pia Lang for their support in NMR and FAB-MS measurements.

Last but not least, we kindly acknowledge financial support from the German Federal Ministry of Food, Agriculture and Consumer Protection (represented by the Fachagentur Nachwachsende Rohstoffe; FKZ 22023008; collaborative project: SynRg®).

References

[1] For reviews of hydroxamic acids and Lossen rearrangements see: a) H. L. Yale, *Chem. Rev.* **1943**, *33*, 209; b) L. Bauer, O. Exner, *Angew. Chem.* **1974**, *86*, 419; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 376; c) W. Lossen, *Justus Liebigs Ann. Chem.* **1872**, *161*, 347.

[2] Current publications regarding Lossen rearrangements and applications: a) G. Giacomelli, A. Porcheddu, M. Salaris, *Org. Lett.* **2003**, *5*, 2715; b) J. C. S. Woo, E. Fenster, G. R. Dake, *J. Org. Chem.* **2004**, *69*, 8984; c) C. Y. Ho, E. Strobel, J. Ralbovsky, R. A. GalemmoJr, *J. Org. Chem.* **2005**, *70*, 4873; d) A. Massaro, A. Mordini, G. Reginato, F. Russo, M. Taddei, *Synthesis* **2007**, 3201; e) E. Riva, S. Gagliardi, C. Mazzoni, D. Passarella, A. Rencurosi, D. Vigo, M. Martinelli, *J. Org. Chem.* **2009**, *74*, 3540; f) P. Dubé, N. F. F. Nathel, M. Vetelino, M. Couturier, C. L. Aboussafy, S. Pichette, M. L. Jorgensen, M. Hardink, *Org. Lett.* **2009**, *11*, 5622; g) L. Duchářčková, J. Roithová, *Chem. Eur. J.* **2009**, *15*, 13399; h) B. Vasantha, H. P. Hemantha, V. V. Sureshbabu, *Synthesis* **2010**, 2990; i) S. Han, Z. Xue, Z. Wang, T. B. Wen, *Chem. Commun.* **2010**, *46*, 8413; j) X. Wu, Z. Wu, Y. Yang, S. Han, *Chem. Commun.* **2012**, *48*, 1895; k) S. Pichette, S. Aubert-Nicol, J. Lessard, C. Spino, *Eur. J. Org. Chem.* **2012**, 1328.

[3] Dimethyl carbonate as green solvent. For reviews see: a) P. Tundo, F. Aricò, A. E. Rosamilia, S. Grego, L. Rossi, *NATO Science for Peace and Security Series C: Environmental Security*, **2008**, 213; b) A. Mohammad, Inamuddin, in: *Green Solvents I: Properties and Applications in Chemistry*, Springer, Dordrecht, Heidelberg, London, New York **2012**, chap. 12, p 363; recent advances of dimethyl carbonate as green solvent in organic reactions: c) J. Cornely, L. M. Su Ham, D. E. Meade, V. Dragojlovic, *Green Chem.* **2003**, *5*, 34; d) H. Bilel, N. Hamdi, F. Zagrouba, C. Fischmeister, C. Bruneau, *Green Chem.* **2011**, *13*, 1448; e) K. Inamoto, C. Hasegawa, K. Hiroya, Y. Kondo, T. Osako, Y. Uozumi, T. Doi, *Chem. Commun.* **2012**, *48*, 2912.

[4] Recent advances in the synthesis of dimethyl carbonate: a) M. Sankar, S. Satav, P. Manikandan, *ChemSusChem* **2010**, *3*, 575; b) Z.-F. Zhang, Z.-W. Liu, J. Lu, Z.-T. Liu, *Ind. Eng. Chem. Res.* **2011**, *50*, 1981; c) D. Ballivet-Tkatchenko, F. Bernard, F. Demoisson, L. Plasseraud, S. R. Sanapureddy, *ChemSusChem* **2011**, *4*, 1316; d) C. Yan, B. Lu, X. Wang, J. Zhao, Q. Cai, *J. Chem. Technol. Biotechnol.* **2011**, *86*, 1413; e) D.-W. Kim, D.-O. Lim, D.-H. Cho, J.-C. Koh, D.-W. Park, *Catal. Today* **2011**, *164*, 556; f) J.-Q. Wang, J. Sun, C.-Y. Shi, W.-G. Cheng, X.-P. Zhang, S.-J. Zhang, *Green Chem.* **2011**, *13*, 3213; g) C. Zhang, B. Lu, X. Wang, J. Zhao, Q. Cai, *Catal. Sci. Technol.* **2012**, *2*, 305.

[5] Chemistry of dimethyl carbonate. For reviews, see: a) A.-A. G. Shaikh, S. Sivaram, *Chem. Rev.* **1996**, *96*, 951; b) P. Tundo, M. Selva, *Acc. Chem. Res.* **2002**, *35*, 706. Recent advances in synthetic approaches applying dimethyl carbonate: c) M. Hatano, S. Kamiya, K. Moriyama, K. Ishihara, *Org. Lett.* **2011**, *13*, 430; d) Y. Pei, H. Li, H. Liu, Y. Zhang, *Ind. Eng. Chem. Res.* **2011**, *50*, 1955; e) Z. Chen, D. Wu, *Ind. Eng. Chem. Res.* **2011**, *50*, 12343; f) Y. Gan, Y. Zhang, C. Xiao, C. Zhou, Y. Zhao, *Carbohydr. Res.* **2011**, *346*, 389; g) C. Hou, Y. Chen, W. Chen, W. Li, *Carbohydr. Res.* **2011**, *346*, 1178; h) M. Malyaadri, K. Jagadeeswaraiah, P. S. Sai Prasad, N. Lingaiah, *Appl. Catal. A* **2011**, *401*, 153; i) W. Zhu, X. Huang, C. Li, Y. Xiao, D. Zhang, G. Guan, *Polym. Int.* **2011**, *60*, 1060; j) F. Aricò, U. Toniolo, P. Tundo, *Green Chem.* **2012**, *14*, 58; k) M. Selva, V. Benedet, M. Fabris, *Green Chem.* **2012**, *14*, 188; l) G. Righi, P. Bovicelli, M. Barontinic, I. Tirotta, *Green Chem.* **2012**, *14*, 495; m) F. Aricò, P. Tundo, A. Maranzana, G. Tonachini, *ChemSusChem* **2012**, *5*, 1578; n) C. R. McElroy, F. Aricò, P. Tundo, *Synlett* **2012**, 1809.

[6] H. Mutlu, J. Ruiz, S. C. Solleder, M. A. R. Meier, *Green Chem.* **2012**, *14*, 1728.

[7] For reviews about applications of TBD and other guanidine bases, see: a) U. Schuchardt, R. Sercheli, R. M. Vargas, *J. Braz. Chem. Soc.* **1998**, *9*, 199; b) J. E. Taylor, S. D. Bull, J. M. J. Williams, *Chem. Soc. Rev.* **2012**, *41*, 2109; applications of TBD as organocatalyst: c) M. K. Kiesewetter, M. D. Scholten, N. Kirn, R. L. Weber, J. L. Hedrick, R. M. Waymouth, *J. Org. Chem.* **2009**, *74*, 9490; d) O. Mahé, D. Frath, I. Dez, F. Marsais, V. Levacher, J.-F. Brière, *Org. Biomol. Chem.* **2009**, *7*, 3648; e) P. Hammar, C. Ghobril, C. Antheaume, A. Wagner, R. Baati, F. Himo, *J. Org. Chem.* **2010**, *75*, 4728; f) F. Saliu, B. Rindone, *Tetrahedron Lett.* **2010**, *51*, 6301; g) M. Terada, K. Ando, *Org. Lett.* **2011**, *13*, 2026; h) D. Tang, D.-J. Mulder, B. A. J. Noordover, C. E. Koning, *Macromol. Rapid Commun.* **2011**, *32*, 1379; i) X. Fu, C.-H. Tan, *Chem. Commun.* **2011**, *47*, 8210; j) D. Lanari, R. Ballini, S. Bonollo, A. Palmieri, F. Pizzo, L. Vaccaro, *Green Chem.* **2011**, *13*, 3181; k) Á. Martínez-Castañeda, H. Rodríguez-Solla, C. Concellón, V. del Amo, *Org. Biomol. Chem.* **2012**, *10*, 1976; l) S. Bonollo, D. Lanari, J. M. Longo, L. Vaccaro, *Green Chem.* **2012**, *14*, 164; m) S. Matsukawa, S. Fujikawa, *Tetrahedron Lett.* **2012**, *53*, 1075.

[8] Methylation reactions of DMC with phenols: a) R. Luque, J. M. Campelo, T. D. Conesa, D. Luna, J. M. Marinas, A. A. Romero, *New J. Chem.* **2006**, *30*, 1228; b) M. Selva, A. Perosa, *Green Chem.* **2008**, *10*, 457.

[9] For an overview about the cleavage of methyl carbamates see: a) P. G. M. Wuts, T. W. Greene, *Protective Groups in Organic Synthesis*, 4th edn., John Wiley & Sons, New York, **2006**, p 708; recent literature about hydrolysis of methyl carbamates: b) W. Liu, M. Buck, N. Chen, M. Shang, N. J. Taylor, J. Asoud, X. Wu, B. B. Hasinoff, G. I. Dmitrienko, *Org. Lett.* **2007**, *9*, 2915; c) T. Nemoto, T. Harada, T. Matsumoto, Y. Hamada, *Tetrahedron Lett.* **2007**, *48*, 6304; d) F. Lehmann, M. Scobie, *Synthesis* **2008**, 1679.

