1,2-Dimethylimidazole (DMI) and microwaves in the alkylation of carboxylic acids and phenols with dimethyl and diethyl carbonates

Leticia Guerrero R. and Ignacio A. Rivero*

Centro de Graduados, Instituto Tecnológico de Tijuana. Blvd. Industrial S/N, Mesa de Otay. Tijuana, Baja California. CP 22510, México
E-mail: irivero@tectijuana.mx

Abstract

A selective alkylation of carboxylic acids and phenols was optimized with 1,2-dimethylimidazole (DMI) using dimethyl carbonate (DMC) and diethyl carbonate (DEC). The reaction mechanism was determined by the formation of the diethoxy(1,2-dimethyl-1H-imidazolidium-1-yl)methoxy (DEIM) intermediate. The dependence of the amount of DMI on the rate of the ethylation reaction was established, concluding that DMI is a novel and active nucleophilic catalyst. The rate of ethyl benzoate formation is shown. The reactions with DEC require more drastic conditions, while those with DMC are achieved with better efficiency under mild conditions. Solvent free microwave reactions with DMI and DMC or DEC proceed at high temperatures. In the absence of DMI these reactions do not proceed.

Keywords: 1,2 Dimethylimidazole, carbonates, microwaves

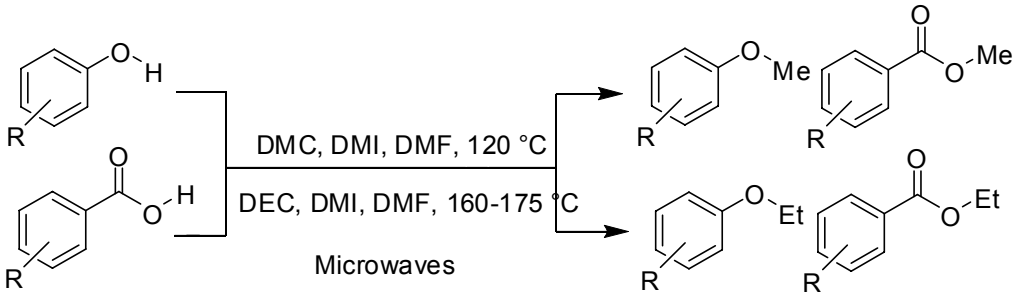
Introduction

The reactivity of dimethyl carbonate (DMC) has been studied by several groups since the early 1980's. Their work was motivated by the report of the first reaction that fulfills "green chemistry" ecological standards,[1] for the synthesis of DMC based on the oxicarbonylation reaction of methanol.[2] This fact was readily recognized, and since the initial report of the procedure an intense research activity has been directed worldwide towards innovative applications of DMC and its higher homologs.

DMC as a methylating reagent, can replace the undesirable and non-selective methyl halides (CH_3X; X=Cl, Br, I) and dimethylsulfate ($CH_3OSO_3CH_3$).[3-6] However the use of DMC as a methylating reagent often requires high temperatures and long reaction times. As a result, autoclaves, sealed tubes[7,8] or the use of asymmetrical carbonates[9] is required. Recently, Shieh and coworkers discovered that 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) can function as an effective nucleophilic catalyst for carboxilic acid esterification.[10]

Large scale microwave-accelerated esterification of carboxylic acids with dimethyl carbonate (DMC) was reported by Shieh et al[11] using a combined strategy, which includes DBU as the catalyst and a commercial microwave continuous-flow reactor.

The same group[12] reported that additional rate enhancement is accomplished by the use of DBU and microwaves in the methylation of phenols, indoles, and benzimidazoles with dimethyl carbonate. We have discovered that 1,2-dimethylimidazole (DMI) can function, like DBU, as a nucleophilic catalyst reacting with DMC or DEC to form a more active alkylating reagent, for carboxylic acids esterification and phenols alkylation (Scheme 1).



Scheme 1

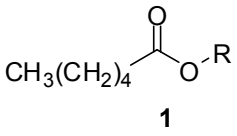
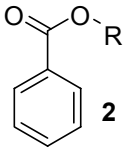
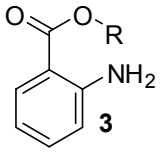
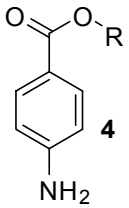
Herein, we report the optimization of both methylation and ethylation of carboxylic acids with DMI, and compare temperatures and reaction times (Table 1 and Table 2). The microwave reactor used is a CEM capable of processing small quantities of substrates controlling time, pressure, and temperature.

Results and Discussion

Esterification of carboxylic acids with DMC and DEC catalyzed by DMI

First, the esterification of benzoic acid with DEC in dimethyl formamide (DMF) at 160 °C in the presence of DMI (1 equiv) to form ethyl benzoate (**2**) was investigated (Table 1, Entry 2). The time and temperature conversion to obtain **2** (R=Et) using DMI was optimized establishing the temperature at which the maximum yield is achieved. Then the reaction times were varied at the same temperature to find the shortest completion time. The kinetic data acquired in our experiment (Figure 1) show 100% conversion after only 12 min. To investigate the dependence of the amount of DMI on the rate of esterification, 0.75, 0.5 and 0.25 equiv of DMI was used in the reaction of benzoic acid with DEC.

Table 1. Esterification of carboxylic acids with DMC and DEC catalyzed by DMI

Entry	Ester	R=Me	R=Et	Yield[a,b] [%]
1	 **1**	120 °C 12 min	165 °C 12 min	98
2	 **2**	120 °C, 12 min	160 °C 12 min	99
3	 **3**	120 °C, 12 min	175 °C 12 min	98
4	 **4**	120 °C, 12 min	160 °C 12 min	98

General Procedure: A CEM designed 10 mL pressurerized sealed vial was charged with substrate (0.1 g), DMI (1 equiv.), DMF (1 mL), and DMC or DEC (1 mL). The reaction products were analyzed by GC-MS until the absence of substrate (time of reaction).

[a] Isolated products yields based on starting material. [b]The identity of the alkylated products was confirmed by ^{1}H and ^{13}C NMR.

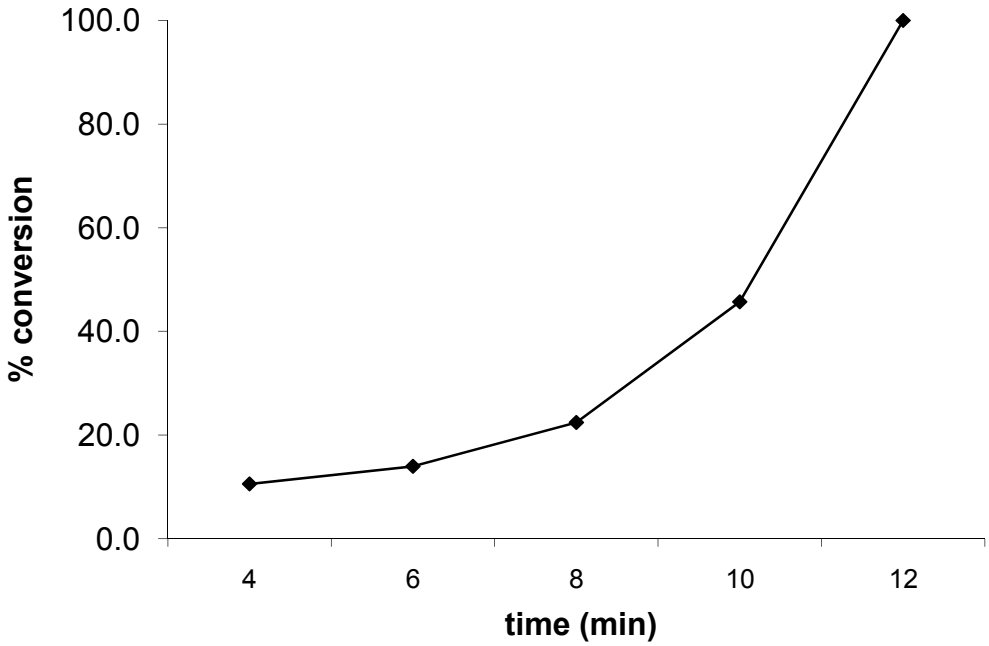
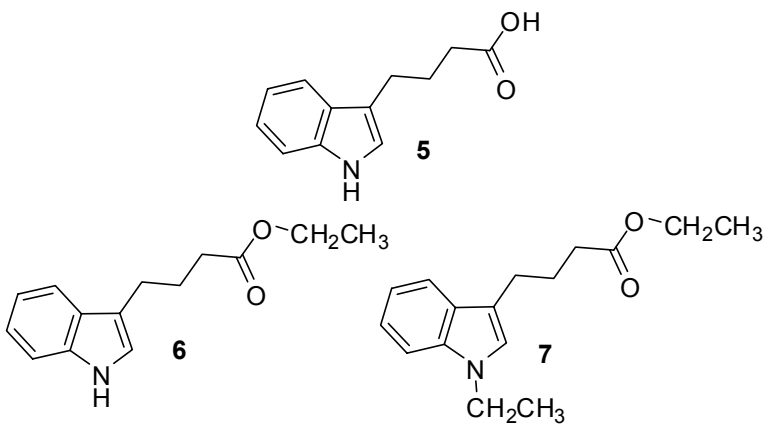


Figure 1. Rate of ethyl benzoate formation with 1 equiv of DMI (μW; 160 °C, 200 W).

The reaction rate dramatically decreased when less than 1 equiv of DMI was used. With 0.25 equiv of DMI, after 30 min of reaction in a microwave reactor, only 47% of ethyl benzoate (**2**) was formed. Esterification with DMI and DEC required at least 160 °C and 12 min to achieve the maximum conversion (Table 1, Entries 2 and 4).

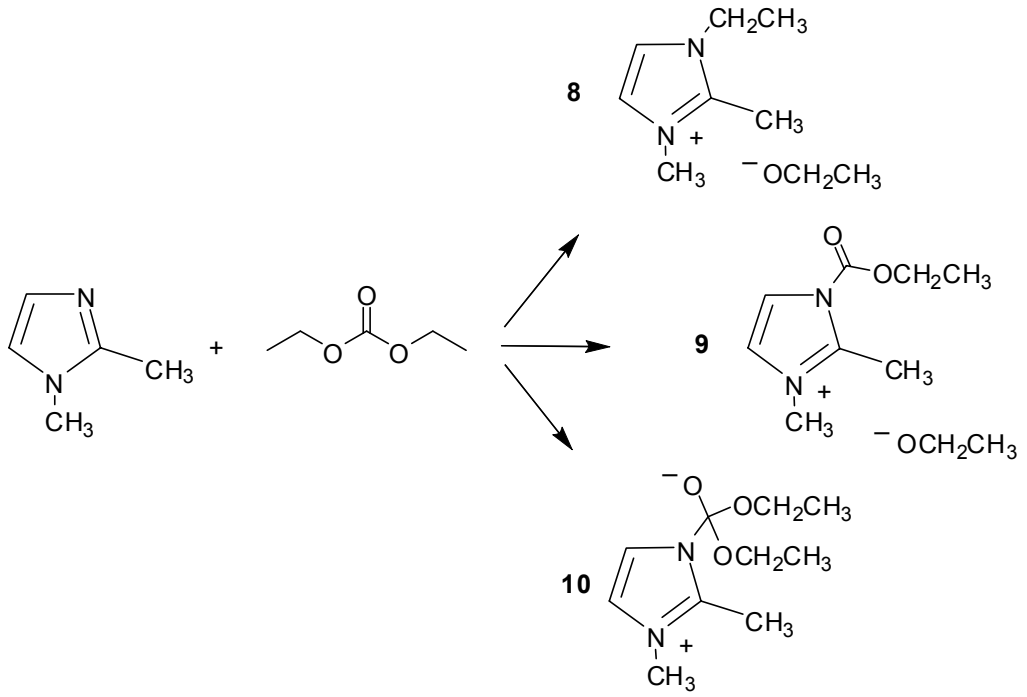
To obtain ethyl 2-aminobenzoate (**3**) from 2-aminobenzoic acid the choice was either to heat at 160 °C for 25 min, or increase the temperature to 175 °C and react for only 12 min to obtain 100% conversion. Reactions with DMC are faster due to the lower boiling points allowing the reactions to be performed at 120 °C in 12 min to obtain the corresponding methyl esters (Table 1, Entries 1 to 4). When a NH functionality was present, as in indole-3-butyric acid (**5**), using one equivalent only the ethylation process at carboxylic acid group occurred (**6**), and with two equiv of DMI, the ethylation of both the carboxylic acid and the indole nitrogen group (**7**) was achieved.

The substrates to obtain the esters in Table 1 by reaction with DMI in a solvent free mixture by microwave irradiation required 20 to 25 °C more than when solvent is used for their total conversion, for either DMC or DEC. The reaction of anthranilic acid with DEC in a solvent free system generated a salt, which turned out to be insoluble when attempts were made to dissolve it for characterization purposes, thus preventing the determination of the reaction parameters in the solvent free system.



Reaction mechanism with DEC and DMI

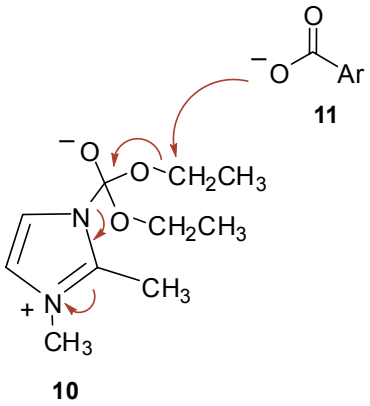
Since diethyl carbonate can act as either a ethylating or a carboxyethylating reagent[13] towards DMI, three possible intermediates, **8**, **9** and **10,** are proposed (Scheme 2). The intermediate **8** involves the reaction of DMI with the ethyl group on DEC to form a *N*–ethylated-DMI salt and the intermediate **9** contain two different ethyl groups; the NMR spectrum only showed one ethyl group. The intermediate **10** is in good agreement with the NMR data.



Scheme 2

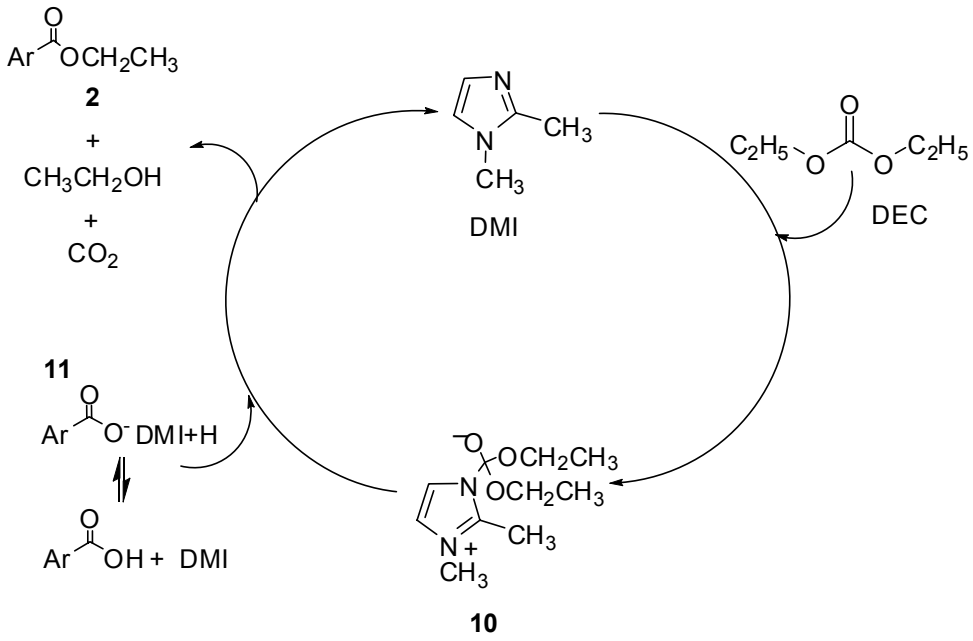
To establish which of these intermediates is formed, a 1:1 equiv solution of DMI and DEC was reacted at different times: 3, 6, 9 and 12 min in a microwave reactor. When monitored by NMR, the signals corresponding to the DEIM increased with the time of the microwaves

irradiation. The identity of the DEIM intermediate was confirmed by IR, ^{1}H NMR, and ^{13}C NMR. The results show that DEIM **10** is formed in 12 min, supporting the postulate that a direct *O*-alkylation of benzoate (**11**) with DEIM (**10**) is the route for the formation of ethyl benzoate (Scheme 3).



Scheme 3

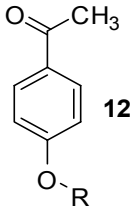
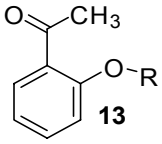
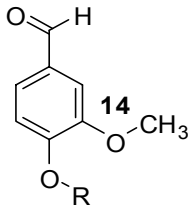
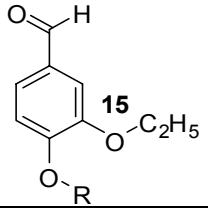
The catalytic cycle consisting of the *N*-acylation of DMI with DEC to form a DEIM intermediate **10,** and subsequent *O*-alkylation of the carboxylate with this intermediate to generate the corresponding ethyl ester (**2**) is shown in Scheme 4. The generation of ethanol and evolution of CO_2 was confirmed by GC-MS.



Scheme 4

We have examined the synthetic utility of DMI reactions through the alkylation of a variety of phenols. Results are summarized in Table 2. In all cases, the isolated yields were excellent and ranged from 98 to 99%. Again, higher temperatures for the alkylation with DEC are required compared to the alkylation with DMC. In some cases more drastic conditions than for carboxylic acid alkylation are required. For products **1** to **3** in Table 2 there is a choice of reaction conditions, either 160 °C for 20 min or 170 °C for only 12 min to obtain 100% conversion.

Table 2. Alkylation of phenols with DMC and DEC catalyzed by DMI

Entry	Product	R=Me	R=Et	Yield[a,b] [%]
1	 **12**	120 °C, 12 min	160 °C 20 min	99
2	 **13**	120 °C, 12 min	160 °C 20 min	98
3	 **14**	120 °C, 12 min	160 °C 20 min	98
4	 **15**	125 °C 6 min	165 °C 20 min	99

General Procedure: A CEM designed 10 mL pressurerized sealed vial was charged with substrate (0.1 g), DMI (1 equiv.), DMF (1 mL), and DMC or DEC (1 mL). The reaction products were analyzed by GC-MS until the absence of substrate (time of reaction).
[a]Isolated products yields based on starting substrate. [b]The identity of the alkylated products was confirmed by ^{1}H and ^{13}C NMR.

Due to steric effects to synthesize 3,4-dietoxy-benzaldehyde (**15**, R=Et), the temperature had to be raised by 5 °C since at 160 °C a 100% conversion could not be achieved in 25 min. To obtain **15** with DEC, the reaction was carried out at 175 °C for 12 min instead of at 165 °C for 20

min. In the same way, the reaction mixture of 3-ethoxy-4-hydroxybenzaldehyde, DMI and DMC to obtain **15** (R=Me), the temperature had to be increased by 5°C to achieve 100% of conversion. All products in Table 2 were reacted by microwave irradiation in a solvent free mixture and required 20 to 25 °C more for their total conversion, than when solvent is used, for either DMC or DEC.

Conclusions

DMI is not reported in the literature as a base or as a proton scavenger but it is used as ionic liquid precursor. We discovered that DMI can function as an effective catalyst for carboxylic acid esterification and alkylation of phenols with dimethyl and diethyl carbonates using microwave irradiation. We proved that alkylation with DMI and DEC involves a stable DEIM (**10**), formed *in situ*, which behaves as a highly activated alkylating reagent. We have demonstrated the synthetic applications of DMI in several carboxylic acids and phenols, optimizing time and temperature for each reaction. Investigation of DMI as a catalyst for *NH*-systems is currently being conducted in our laboratory with positive results.

Experimental Section

General Procedures. Melting points were measured with an Electrothermal 88629 apparatus and are uncorrected. Infrared spectra (IR) were recorded on a Perkin Elmer FT-IR 1600 spectrophotometer. Nuclear magnetic resonance ^{1}H (200MHz) and ^{13}C spectra (50 MHz) were recorded on a Varian Mercury 200 MHz Spectrometer in $CDCl_3$ with TMS as internal standard. Mass spectra were obtained on a Hewlett-Packard 5989 by EI at 70 eV and ESI-MS were performed on a MSD ion Trap in electrospray mode by direct insertion. Microwave equipment was a Discover of CEM Co.

General procedure for esterification

A CEM designed 10 mL pressure-rated vial was charged with benzoic acid (**2**, 0.1 g, 0.8 mmol), DMI (1 equiv), DMF (1 mL), and DMC or DEC (1 mL). The vial was sealed and irradiated at temperatures shown in tables 1 and 2 in a self-tuning single mode CEM Discover^{TM} Focused Synthesizer. The temperatures were measured by an infrared temperature sensor and controlled by automatic modulation of the power. The reaction was monitored by GC-MS until a total conversion to the respective ester or ether was detected. Upon completion, the resulting mixture was cooled to room temperature and diluted with either CH_2Cl_2 or EtOAc and H_2O. The organic layer was washed with H_2O, twice with 2 M HCl or 10% aqueous citric acid, twice with saturated aqueous $NaHCO_3$, and twice with H_2O. The organic layer was dried over Na_2SO_4,

filtered, and concentrated under reduced pressure to afford the pure product **2** (R=Me) as a clear liquid (0.11g. 99%).

Table 3. ^{1}H NMR and GC/MS spectra of esters 1-4, R=Me and R=Et

Entries	Ester	^{1}H NMR spectra (200 MHz), δ[i]	GC/MS (70 eV), m/z
1	$CH_3(CH_2)_4COOR$ 1, R=Me	3.67 (s, 3H, OCH_3), 2.31 (t, 2H, CH_2), 1.70-1.55 (m, 2H, CH_2), 1.31 (m, 4H, $2CH_2$), 0.92 (m, 3H, CH_3)	130 (M^+, 0.5%), 74 ($[M - C_4H_8]^+$, 100)
2	$CH_3(CH_2)_4COOR$ 1, R=Et	4.25 (q, 2H, CH_2), 2.31 (t, 2H, CH_2), 1.70-1.55 (m, 2H, CH_2), 1.31 (m, 4H, $2CH_2$), 1.34 (t, 3H, CH_3), 0.92 (m, 3H, CH_3)	144 (M^+, 1%), 88 ($[M - C_4H_8]^+$, 100)
3	C_6H_5COOR 2,R=Me	8.07-8.01 (m, 2H, Ar), 7.60-7.50 (m, 1H, Ar), 7.48-7.38 (m, 2H, Ar), 3.91 (s, 3H, OCH_3)	136 (M^+, 32%), 105 ($[M - OCH_3]^+$, 100)
4	C_6H_5COOR 2, R=Et	8.07-8.01 (m, 2H, Ar), 7.60-7.50 (m, 1H, Ar), 7.48-7.38 (m, 2H, Ar), 4.40 (q, 2H, CH_2), 1.40 (t, 3H, CH_3)	150 (M^+, 17%), 105 ($[M - OCH_2CH_3]^+$, 100)
5	*o*-$NH_2C_6H_4COOR$ 3, R=Me	7.83 (dd, ^{1}J=8.4 Hz, ^{2}J=1.4 Hz, 1H, Ar), 7.22 (ddd, ^{1}J, ^{3}J=8.4 Hz, ^{2}J=1.4 Hz, 1H, Ar), 6.60 (m, 1H, Ar), 5.76 (bs, 1H, C-NH_2), 3.82 (s, 3H, OCH_3)	151 (M^+, 72%), 120 ($[M - OCH_3]^+$, 31), 119 ($[M - H]^+$, 100)
6	*o*-$NH_2C_6H_4COOR$ 3, R=Et	7.83 (dd, ^{1}J=8.4 Hz, ^{2}J=1.6 Hz, 1H, Ar), 7.22 (ddd, ^{1}J, ^{3}J=8.4 Hz, ^{2}J=1.6 Hz, 1H, Ar), 6.60 (m, 1H, Ar), 5.76 (bs, 1H, C-NH_2), 4.31 (q, 2H, CH_2), 1.36 (t, 3H, CH_3)	165 (M^+, 52%), 137 ($[M - CH_2CH_2]^+$, 31), 119 ($[M - H_2O]^+$, 100)
7	*p*-$NH_2C_6H_4COOR$ 4, R=Me	7.89-7.82 (d, J=8.8 Hz, 2H, Ar), 6.67-6.60 (d, J=8.8 Hz, 2H, Ar), 4.07 (bs, 1H, C-NH_2), 3.85 (s, 3H, OCH_3)	151 (M^+, 52%), 120 ($[M - OCH_3]^+$, 100)
8	*p*-$NH_2C_6H_4COOR$ 4, R=Et	7.89-7.82 (d, J=8.8 Hz, 2H, Ar), 6.67-6.60 (d, J=8.8 Hz, 2H, Ar), 4.31 (q, 2H, CH_2), 4.07 (bs, 1H, C-NH_2), 1.36 (t, 3H, CH_3)	165 (M^+, 41%), 120 ($[M - OCH_2CH_3]^+$, 100)

[i] NMR solvent $CDCl_3$.

Table 4. ^{1}H NMR and GC/MS spectra of ethers 12-15, R=Me and R=Et

Entries	Ester	^{1}H NMR spectra (200 MHz), δ[i]	GC/MS (70 eV), m/z
1	*p*-$ROC_6H_4COCH_3$ 12, R=Me	7.94-7.90 (d, *J*=8.8 Hz, 2H, Ar), 6.94-6.89 (d, *J*=8.8 Hz, 2H, Ar), 3.84 (s, 3H, OCH_3), 2.53 (s, 3H, CO-CH_3)	150 (M^+, 36%), 135 ($[M - CH_3]^+$, 100)
2	*p*-$ROC_6H_4COCH_3$ 12, R=Et	7.93-7.88 (d, *J*=8.8 Hz, 2H, Ar), 6.91-6.87 (d, *J*=8.8 Hz, 2H, Ar), 4.07 (q, 2H, CH_2), 2.53 (s, 3H, OCH_3), 1.42 (t, 3H, CH_3)	164 (M^+, 43%), 149 ($[M - CH_3]^+$, 77), 121 ($[M - CO]^+$, 100)
3	*o*-$ROC_6H_4COCH_3$ 13,R=Me	7.73 (dd, ^{1}J=8.1 Hz, ^{2}J=1.8 Hz, 1H, Ar), 7.45 (ddd, ^{1}J, ^{3}J=8.1 Hz, ^{2}J=1.8 Hz, 1H, Ar), 6.98 (m, 1H, Ar), 3.89 (s, 3H, OCH_3), 2.61 (s, 3H, CO-CH_3)	150 (M^+, 19%), 135 ($[M - CH_3]^+$, 100)
4	*o*-$ROC_6H_4COCH_3$ 13, R=Et	7.73 (dd, ^{1}J=8.1 Hz, ^{2}J=1.8 Hz, 1H, Ar), 7.45 (ddd, ^{1}J, ^{3}J=8.1 Hz, ^{2}J=1.8 Hz, 1H, Ar), 6.98 (m, 1H, Ar), 4.14 (q, 2H, CH_2), 2.64 (s, 3H, CO-CH_3), 1.48 (t, 3H, CH_3)	164 (M^+, 12%), 149 ($[M - CH_3]^+$, 27), 121 ($[M - CO]^+$, 100)
5	3-CH_3O-4-ROC_6H_3CHO 14, R=Me	9.85 (s, 1H, H=CO), 7.49-7.40 (m, 1H, Ar), 6.99 (d, 1H, Ar), 3.97 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3)	166 (M^+, 100%), 151 ($[M - CH_3]^+$, 14)
6	3-CH_3O-4-ROC_6H_3CHO 14, R=Et	9.84 (s, 1H, H=CO), 7.46-7.41 (m, 1H, Ar), 6.97 (d, 1H, Ar), 4.19 (q, 2H, CH_2), 3.93 (s, 3H, OCH_3), 1.51 (t, 3H, CH_3)	180 (M^+, 47%), 151 ($[M - CH_2CH_3]^+$, 100)
7	3-C_2H_5O-4-ROC_6H_3CHO 15, R=Me	9.84 (s, 1H, H=CO), 7.47-7.39 (m, 1H, Ar), 6.98 (d, 1H, Ar), 4.16 (q, 2H, CH_2), 3.95 (s, 3H, OCH_3), 1.49 (t, 3H, CH_3)	180 (M^+, 44%), 151 ($[M - CH_2CH_3]^+$, 100)
8	3-C_2H_5O-4-ROC_6H_3CHO 15, R=Et	9.82 (s, 1H, H=CO), 7.46-7.41 (m, 1H, Ar), 6.97 (d, 1H, Ar), 4.19 (q, 2H, CH_2), 4.16 (q, 2H, CH_2), 1.49 (t, 3H, CH_3), 1.47 (t, 3H, CH_3)	194 (M^+, 42%), 137 ($[M - 2(CH_2CH_3]^+$, 100)

[i] NMR solvent $CDCl_3$

Ethyl-3-(1*H*-indol-3-yl)propanoate (6). A CEM designed 10 mL pressure-rated vial was charged with 3-(1*H*-indol-3-yl)propanoic acid (**5**, 0.8 mmol), DMI (1 equiv), DMF (1 mL), and DEC (1 equiv). Same procedure as above. (96% yield). FTIR(KBr): 3481, 3064, 2936, 1745, 1592, 1254, 1180, 1124, cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 8.01(br, 1H, NH), 7.36-6.95 (m, 4H, Ar-H), 4.52 (q, 2H, CH_2-O), 2.84 (t, 2H, CH_2CO), 2.41 (t, 2H,CH_2-C=), 2.11 (m, 2H, C-CH_2-C), 1.49 (t, 3H, CH_3). EIMS *m/z* (rel. int.): 231(22), 130(100).

Ethyl-3-(1methyl-1*H*-indol-3-yl)propanoate (7). A CEM designed 10 mL pressure-rated vial was charged with 3-(1*H*-indol-3-yl)propanoic acid (**5**, 0.8 mmol), DMI (1 equiv), DMF (1 mL), and DEC (2 equiv). Same procedure as above. (94% yield). FTIR(KBr): 3060, 2938, 1742, 1596, 1250, 1176, 1124 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 8.05(br, 1H, NH), 7.38-6.95 (m, 4H, Ar-H), 4.56 (q, 2H, CH_2-O), 4.14(q, 2H, CH_2-N), 2.88 (t, 2H, CH_2CO), 2.43 (t, 2H,CH_2-C=), 2.15 (m, 2H, C-CH_2-C), 1.48 (t, 3H, CH_3), 1.29 (q, 2H, CH_2-C-N). EIMS *m/z* (rel. int.): 259(20), 158(100).

Diethoxy(1,2-dimethyl-1H-imidazolidium-1-yl)methoxy (DEIM) (10). A CEM designed 10 mL pressure-rated vial was charged with DMI (1 equiv), and DEC (1 equiv). Same procedure as above. (>96% yield). FTIR(KBr): 3350, 3064, 2945, 1656, 1613, 1277, 1050 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 6.85(d, 1H, J= 1.2 Hz, CH=), 6.71(d, 1H, J= 1.2 Hz, CH=), 3.74 (q, 4H, CH_2-O), 3.55 (s, 3H, N-CH_3), 2.35 (s, 3H, =C-CH_3), 1.11(t, 6H, CH_3-C). ESI-MS *m/z*: 451[2M+23Na], 237[M+23Na].

Acknowledgements

We are grateful to Consejo Nacional de Ciencia y Tecnología in México (CONACYT, grant No. SEP-2004-CO1-47835) and Dirección General de Educación Superior Tecnológica (DGEST) for support this project. Leticia Guerrero Thanks to CONACYT for the graduate scholarship. The authors are indebted thanks to Dr Miguel Parra for encouragement.

References

1. Anastas, P.; Warner, J.; *Green Chemistry: Theory and Practice*, Oxford University Press: New York, 1998.
2. (a) Delledonne, D.; Rivetti, F.; Romano, U. *J. Organomet. Chem.* **1995**, *488*, C15-C19. (b) Ikeda, Y.; Sakaihori, T.; Tomishige, K.; Fujimoto, K. *Catal. Lett.* **2000**, *66*, 59. (c) Tomishige, K.; Ikeda, Y.; Skaihori, T.; Fujimoto, K. *Catat.* **2000**, *192*, 355.
3. Trotta, F.; Tundo, P.; Moraglio, G. *J. Org. Chem.***1987**, *52*, 1300.
4. Tundo, P.; Trotta, F.; Moraglio, G. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1070.

5. Lissel, M.; Schmidt, S.; Newman, B. *Synthesis* **1986**, 382.
6. Ono, Y. *Pure Appl. Chem.* **1996**, *68*, 367.
7. Shimizu, I.; Lee, Y. *Synlett* **1998**, 1063.
8. Barcelo, G.; Grenouillat, D.; Senet, J.; Sennyey, G. *Tetrahedron* **1991**, *46*, 1839.
9. Perosa, A.; Selva, M.; Tundo, P.; Zordan, F. *Synlett* **2000**, 272.
10. Shieh, W.; Dell, S.; Repič, O. *J. Org. Chem.* **2002**, *67*, 2188.
11. Shieh, W.; Dell, S.; Repič, O. *Tetrahedron Letters* **2002**, *43*, 5607.
12. Shieh, W.; Dell, S.; Repič, O. *J. Organic Letters* **2001**, *3*, 4279.
13. (a) Bomben, A.; Marques, C. A.; Selva, M.; Tundo, P. *Tetrahedron* **1995**, *51*, 11573. (b) Tundo, P. *Pure Appl. Chem.* **2000**, *72*, 1793. (c) Selva, M.; Marques, C.; Tundo, P. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1323.

