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PAPER

# Ambient carboxylation on a supported reversible CO<sub>2</sub> carrier: ketone to $\beta$ -keto ester

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A reversible CO<sub>2</sub> carrier (RCC) has been developed to perform carboxylation of ketone to  $\beta$ -ketoester under ambient CO<sub>2</sub> pressure and temperature. RCC has been synthesized by immobilizing 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) on methylhydrosiloxane support and reacting with CO<sub>2</sub> with 100% degree of functionalisation. RCC is found to be recyclable and shows retention of activity in 5 recycles. CO<sub>2</sub> absorption under ambient temperature and desorption at 120 °C renders the material suitable for carrying out carboxylation reactions at 25 °C with excellent yields. The yield of the reaction can reach up to 100% with TON 200 in 4 h. The extent of the reaction primarily depends upon enol content of the substrate.  $\beta$ -Ketoacid produced during the reaction can be isolated and converted to its corresponding methyl ester derivative by reacting with methyl iodide.

## Introduction

Chemical fixation of CO<sub>2</sub><sup>1</sup> is severely limited<sup>2</sup> for practical applications, as often high pressure of CO<sub>2</sub> is required to accomplish the reaction.<sup>3</sup> The challenge is to develop materials or catalysts that are capable of activating CO<sub>2</sub> under low pressure (preferably at 1 atm), and incorporating CO<sub>2</sub> into organic molecules catalytically. Imidines, particularly guanidines are well known for reacting with CO<sub>2</sub> reversibly, even at 1 atm pressure.<sup>4</sup> Taking advantage of this property of amidines and guanidines, some potential uses have already been recognized.<sup>5</sup> In this context, carboxylation of organic molecules containing active methylinic protons were also carried out with low to moderate yields using DBU and CO<sub>2</sub> under 1 atm of pressure in DMSO.<sup>6</sup> The reactions are a significant contribution of using CO<sub>2</sub> for fine chemical synthesis under low pressure. However there are certain areas of concern which can be further addressed. Low yields and use of a large amount of DBU, which interferes with the product separation, are the major challenges. Another disadvantage of the method is the use of free bases without any support, which releases CO<sub>2</sub> at a very low temperature and this may turn out to be unsuitable for carrying out the chemical reactions at high temperature.<sup>7</sup> Therefore, in order to overcome the aforementioned problems,

development of RCC that can absorb CO<sub>2</sub> under low pressure, ideally at 1 atm, and release at relatively high temperature for accomplishing chemical reactions is an important area of research.

In this context, supported CO<sub>2</sub> sorbents can be very useful materials for performing chemical reactions. There are few reports involving reversible binding of CO<sub>2</sub> on the supported amines.<sup>8</sup> For example, polystyrene and other polymer supported DBU react with CO<sub>2</sub> reversibly and even at temperature as high as 120 °C.<sup>9</sup> However, reactions using these DBU supported polymers are not reported. Certain transition metal based RCCs are known, which are able to execute chemical reactions. However, low efficiency and stoichiometric reactions are the major disadvantages.<sup>10</sup> Thus, RCC catalysts that can efficiently incorporate CO<sub>2</sub> at low pressure are still elusive.

We report here the synthesis and use of methylhydrosiloxane dimethyl siloxane copolymer (trimethylsiloxane terminated) (HMS) supported DBU, HMS-DBU, which absorbs CO<sub>2</sub> almost 100 mol% with respect to the available functional groups. The material obtained after the reaction with CO<sub>2</sub> is denoted here as HMS-DBU-CO<sub>2</sub>, which acts as RCC. To the best of our knowledge, similar supported DBU has not been studied before and thus gives us an immense opportunity to explore. Here, we have shown the practical utility by performing the chemical transformations, namely, ketone to  $\beta$ -keto ester under ambient temperature and CO<sub>2</sub> pressure. Moderate to quantitative yield with turnover number (TON) of ~200 within 4 h was observed when 0.25 g of RCC in methanol was reacted with ketone in the presence of CO<sub>2</sub> and MeI. An additional advantage of the RCC was easy catalyst separation with equivalent efficiency as that of free base, and no need for further purification of the products.

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Overall, the process has potential to be recognized as a smart green process.<sup>11</sup>

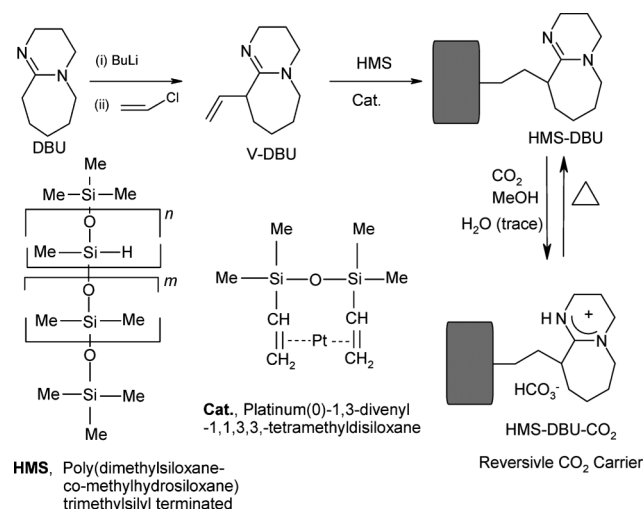
## Results and discussion

Synthesis of the RCC is described in Scheme 1. At first, incorporation of a vinyl group at the 6 position of DBU (V-DBU) was performed according to a literature reported procedure.<sup>12</sup> V-DBU, a colorless liquid, shows a characteristic <sup>1</sup>H NMR peak at  $\delta$ , 5.51 ppm, which corresponds to olefinic proton, and the peak is distinctly different from DBU<sup>13</sup> as well as from vinyl chloride ( $\delta$ , 6.74 ppm). FTIR of vinyl chloride gas shows that the corresponding  $\nu_{C-Cl}$  appeared at 717  $\text{cm}^{-1}$  completely disappeared in V-DBU while peak at 1450  $\text{cm}^{-1}$  corresponding to  $\nu_{CH=CH_2}$  was retained.<sup>14</sup> Additionally, molecular ion peak observed at  $m/z$  177.41 clearly indicates the formation of V-

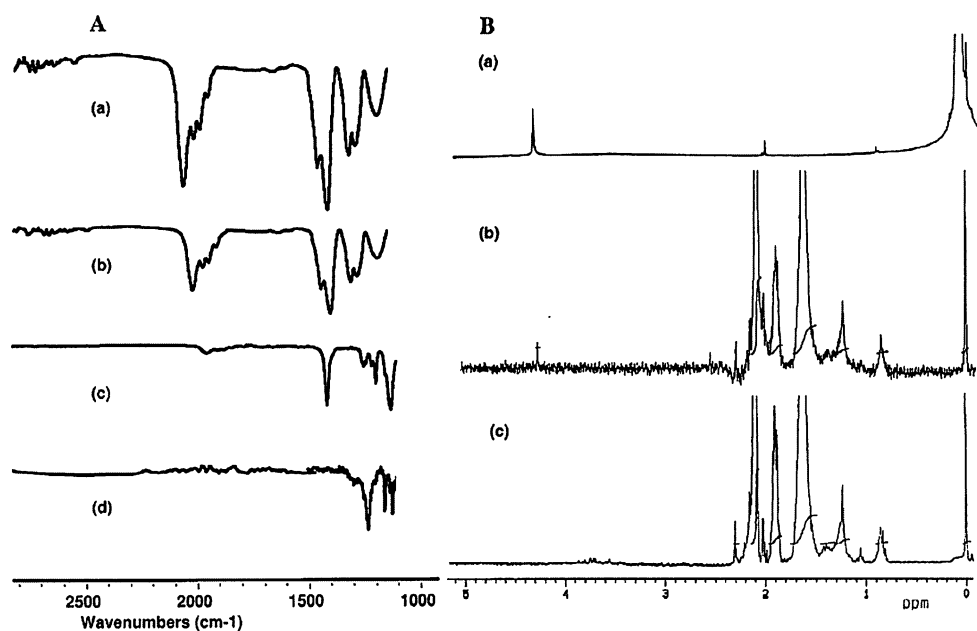
DBU. Finally, V-DBU was reacted with HMS using platinum-vinyl dimethyl siloxane as a catalyst. Progress of the synthesis of HMS-DBU was monitored by FTIR and <sup>1</sup>H NMR as shown in Fig. 1. Disappearance of the Si-H peak at 2157  $\text{cm}^{-1}$  in FTIR spectrum and  $\delta$  4.7 ppm in <sup>1</sup>H NMR spectrum confirmed the formation of HMS-DBU.<sup>9b</sup> Additionally vinyl stretching frequency (C=C) at 1450  $\text{cm}^{-1}$  gradually vanished during the reaction, further confirming the complete functionalization of HMS.<sup>15</sup> Nitrogen elemental analysis showed 0.22% of N (w/w) in HMS-DBU, which was used to calculate the degree of functionalization.

HMS-DBU was found to absorb CO<sub>2</sub> in methanol under ambient temperature when CO<sub>2</sub> was bubbled through the mixture under 1 atm of pressure for 2 h and form HMS-DBU-CO<sub>2</sub> or RCC. Finally, the RCC was obtained after filtration followed by drying. Appearance of a new IR peak at 1647  $\text{cm}^{-1}$  and <sup>13</sup>C NMR peak at 161 ppm confirms the formation of RCC.<sup>13</sup> Absence of a peak at around 120 ppm in the <sup>13</sup>C NMR spectrum indicates that there is no surface adsorbed CO<sub>2</sub> in the material.<sup>3a</sup> Addition of HCl to RCC evolved CO<sub>2</sub>, assuring the incorporation of CO<sub>2</sub> into the matrix. As checked, sequential increase of mass was observed during synthesis of RCC: 6.6 g HMS to 6.69 g HMS-DBU and finally to 6.73 g HMS-DBU-CO<sub>2</sub>.

HMS-DBU shows reversible binding with CO<sub>2</sub> as it absorbs CO<sub>2</sub> at 1 atm and ambient temperature and releases at high temperature. Thermogravimetric analysis (TGA) of RCC reveals that desorption occurs at 120 °C, which is significantly different from the DBU-CO<sub>2</sub> (55 °C),<sup>16</sup> ruling out the possibility of surface adsorption. Total desorption with weight loss of 0.6% (w/w) was observed with 0.6% weight loss of the RCC as calculated by using TGA. Complete desorption was also confirmed by FTIR and <sup>13</sup>C NMR spectra. Astonishingly, the amount of DBU present, as per %N analysis, is proportional to the moles of CO<sub>2</sub> absorbed, calculated from the weight gain of the materials as well as to the

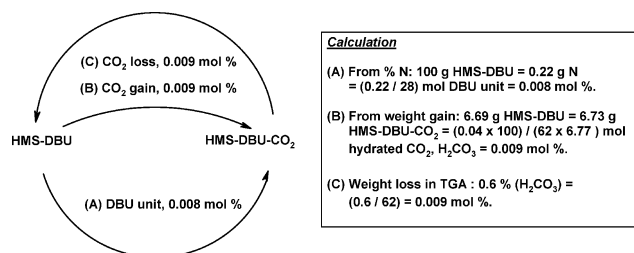


**Scheme 1** Preparation of RCC.



**Fig. 1** HMS-DBU formation. A) FTIR (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h. B) <sup>1</sup>H NMR (a) 0 h, (b) 2 h, (c) 4 h.

weight loss of the RCC by TGA, described in Scheme 2. There is 1 : 1 mole ratio retained between DBU and CO<sub>2</sub> adsorbed.<sup>16</sup> This correlates to 100% functionalization of the support. As observed experimentally, 6.73 g of RCC when heated at 120 °C for 1 h, 6.687 g of HMS-DBU was obtained, corresponding to 100% CO<sub>2</sub> loss. Adsorption-desorption for 5 cycles show equal efficiencies in every cycle.



Scheme 2 Weight gain-loss proportionality.

To show the effectiveness of RCC as good catalyst we have carried out the synthesis of  $\beta$ -ketoesters from ketones involving CO<sub>2</sub> for variety of substrates that are listed in Table 1. Substrates are chosen on the basis of having enolizable methylene protons ( $-^*CH_2-$ ). The reaction begins with purging CO<sub>2</sub> in the solution of RCC, ketone and CH<sub>3</sub>I under ambient temperature (maintained at 25–27 °C) while stirring of the reaction mixture continued for 4 h. The reaction was monitored through FTIR and <sup>1</sup>H NMR following the peaks corresponding to  $\nu(COOME)$  and  $\alpha$ -H respectively. Thus for cyclohexanone FTIR peak at 1750 cm<sup>-1</sup> and <sup>1</sup>H NMR peak at 2.53 ppm ( $\delta$ ) could be designated for  $-COOME$  and  $\alpha$ -C–H respectively, signifying incorporation of CO<sub>2</sub> into cyclohexanone.

Table 1 clearly shows the high efficiency of the reaction for most of the substrates (entries 1–6, except entry 3). For entry 3 there is significant drop in efficiency due to acidity loss on the adjacent carbon as the carbonyl group is already involved in enol tautomerism with carboxymethyl group. There is a slightly lower yield observed in case of 2-cyclopentanone, entry 5, perhaps due to the sterics of the cyclopentanone ring. Noticeably, the success of the reaction primarily depends on the enol content<sup>17</sup> of the ketones. The literature values of keto  $\leftrightarrow$  enol equilibrium constants (in aqueous solutions) are given for comparison. For example, cyclohexanone showed a lower rate of carboxylation than 2-indanone (entry 6, 7). Due to lower enol content, 1-indanone shows inferior reactivity compared to 2-indanone (entry 4, 7). However, 1-indanone could be carboxylated forcibly by using high DBU ratios. The results are comparable with the reported values.<sup>6b</sup> Conversely, efficiency of RCC is found to be limited to the highly deactivated ketones where enol content is too low, e.g. in case of acetone (entries 8–11) and its derivatives. Acetophenone and their analogues with both electron donating and withdrawing groups could not be carboxylated by RCC. Nonetheless, acetophenones (entries 9–11) are observed to undergo reaction at higher pressure and prolonged reaction time. Through testing different acetophenones with electron withdrawing and donating groups, the difference in productivity is observed, (entry 10–12). *p*-Chloro acetophenone (entry 10) seems to behave like *p*-methoxy one, showing the +R effect of aromatic Cl. RCC was found to be incapable of

carboxylating a 2nd time on the same carbon, possibly due to steric reasons. Thus, methyl-2-cyclohexanonecarboxylate is observed to carboxylate at  $\alpha'$ , entry 3.

To estimate the activity of catalyst we have tried to express the efficiency in terms of 'turn over number'. Considering 0.22% N (from elemental analysis), 96  $\mu$ mol g<sup>-1</sup> of active sites are present in RCC. This dictates TON of  $\sim$ 200 in 4 h in case of cyclohexanone.

A plot of time *versus* yield shows a rapidly progressing reaction for highly activated substrates. Thus according to Fig. 3, cyclohexanone and 2-indanone are found to be undergoing fast conversion whereas reaction with methylcyclohexanone-2-carboxylate is comparatively sluggish. Prolonged reaction for this substrate does not help under the present reaction conditions.

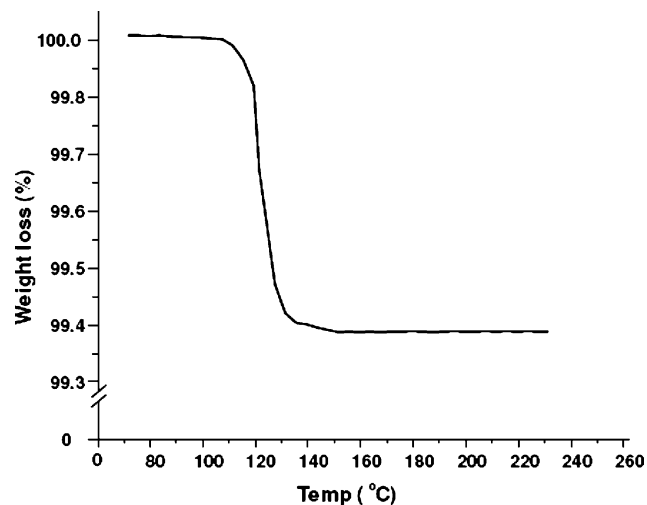


Fig. 2 TGA of RCC (HMS-DBU-CO<sub>2</sub>). N<sub>2</sub>, 10 °C min<sup>-1</sup>.

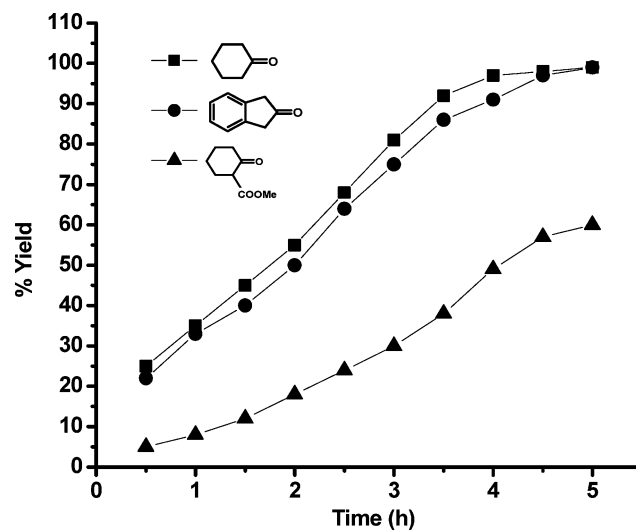

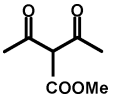

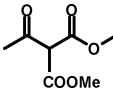

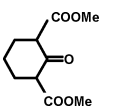

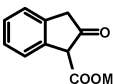



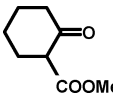

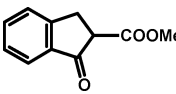

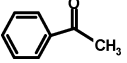
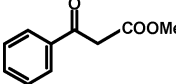
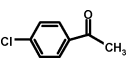
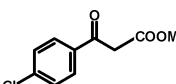
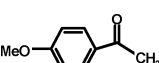
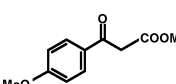
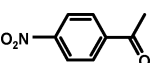
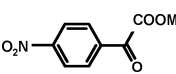


Fig. 3 Change in yield with time showing progress of reaction. CO<sub>2</sub> 1 atm, in methanol, cat HMS-DBU-CO<sub>2</sub> 0.25 g, room temp, 4 h.

While studying the effect of pressure, we observed that the reaction proceeds faster with increasing pressure. As explained in Fig. 4, cyclohexanone could even be 100% converted in

**Table 1** Carboxylation of ketones using RCC

Entry	Substrate	K <sup>a</sup>	Product	TON	Yield (%)
1		$2.3 \times 10^{-1}$ <sup>20a</sup>		206	99 <sup>b</sup>
2		$7.0 \times 10^{-2}$ <sup>20a</sup>		207	99
3		Not known		41	32
4		$1.5 \times 10^{-4}$ <sup>20b</sup>		208	99
5		$1.3 \times 10^{-5}$ <sup>20d</sup>		200	96
6		$4.2 \times 10^{-7}$ <sup>20c</sup>		204	98
7		$3.3 \times 10^{-8}$ <sup>20e</sup>		188	90
8		$2.4 \times 10^{-9}$ <sup>20f</sup>	—	—	-no-
9		$1.1 \times 10^{-8}$ <sup>20g</sup>		61	29
10		$9.77 \times 10^{-9}$ <sup>20g</sup>		38	18
11		$1.35 \times 10^{-9}$ <sup>20g</sup>		25	12
12		—		21	9

<sup>a</sup> K, keto  $\leftrightarrow$  enol equilibrium constant, ref. 20 <sup>b</sup> Yields are absolute. CO<sub>2</sub> 1 atm, in methanol, cat HMS-DBU-CO<sub>2</sub> 0.25 g, room temp.

half the time if pressure increased from 1 to 10 atmosphere. Likewise, reaction rate for methylcyclohexanone-2-carboxylate becomes almost doubled when pressure was raised from 1 to 10 atmospheres. Unlike the previously observed reactions where pressure has subtle effect on reaction yield<sup>6</sup> this result shows that the rate of reaction is dependent on CO<sub>2</sub> which gets involved in the transition state.

An increase in temperature shows a retarding effect on the yield. Reactions exhibit very poor yield at a temperature of nearly 80 °C, Fig. 5. As per the literature, at high temperature the

desired product decomposes and  $\beta$ -keto acid forms.<sup>6a</sup> Therefore, the lowering yield may be attributed to the decomposition of  $\beta$ -keto acid,<sup>18</sup> which occurs at the first step of the reaction. Since RCC is stable even at 120 °C (Fig. 2), the cause of depleted product yield is not due to decomposition of RCC. In fact, by lowering the reaction temperature to 18–20 °C, we were able to isolate the  $\beta$ -keto acid of cyclohexanone which was precipitated in the reaction pot and identified characterized by spectroscopic means. Thus, the reaction consists of two steps in the same reaction pot, as described by eqn (1).

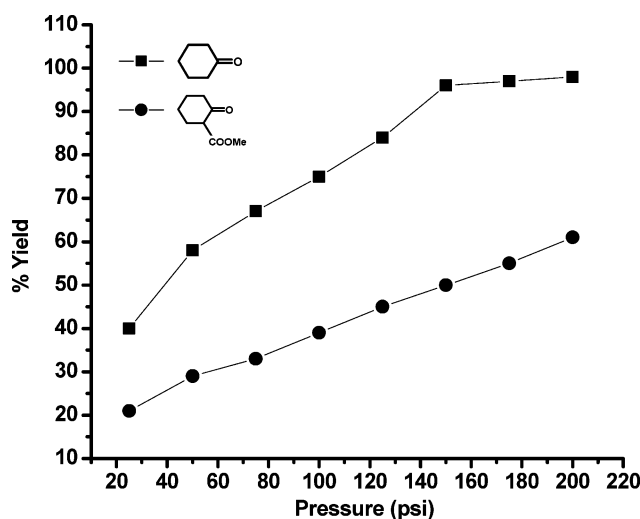


Fig. 4 Effect of pressure on yield. In methanol, cat HMS-DBU-CO<sub>2</sub> 0.25 g, room temp, 4 h.

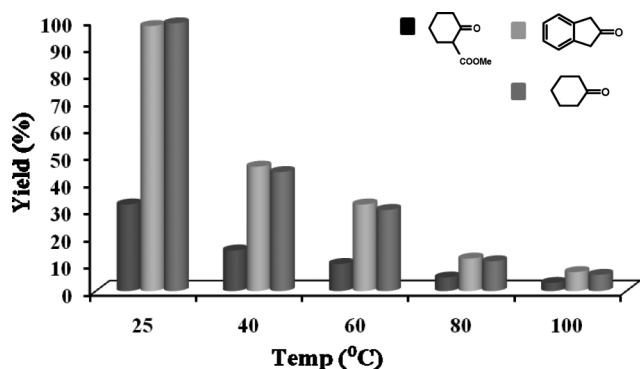
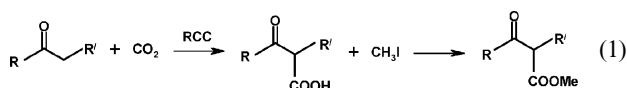


Fig. 5 Effect of temperature on yield. CO<sub>2</sub> 1 atm, in methanol, cat HMS-DBU-CO<sub>2</sub> 0.25 g, 4 h.

While comparing the activity of RCC with free DBU, we found that both free DBU and RCC showed almost identical activity (Fig. 6). This is contrary to the most supported catalyst, where unsupported catalysts are more efficient than the supported ones.<sup>19</sup> Interestingly, NaHCO<sub>3</sub> under similar conditions could not carboxylate cyclohexanone, indicating the importance of the DBU moiety and excluding the possibility of carboxylation *via* probable HCO<sub>3</sub><sup>-</sup> formation by H<sub>2</sub>O and CO<sub>2</sub>, [DBUH<sup>+</sup>HCO<sub>3</sub><sup>-</sup>].<sup>16</sup>

To broaden the application of the immobilization technique, we have demonstrated two reactions, namely the etherification of phenol<sup>20</sup> and the Baylis–Hilman reaction,<sup>21</sup> listed in Table 2; subsequently the results are compared with literature reported values. Evidently, there is a close match between reported and observed yields, showing the versatility of the immobilized catalyst.

After the reaction, catalyst could be easily separated just by filtration, unlike the reaction with free DBU where silica-gel chromatography is necessary. Recovery of the product was

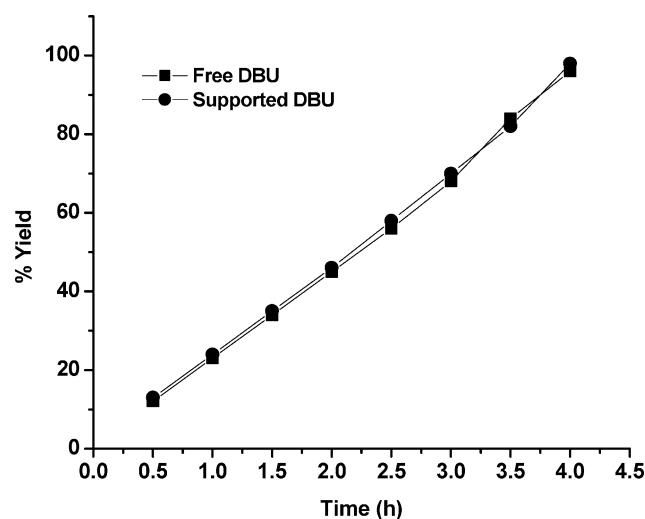


Fig. 6 Comparison of RCC and DBU (free base). Cyclohexanone 0.5 g, RCC 0.25 g, DBU 3.6 mg, MeOH 50 mL, 60 °C, CO<sub>2</sub> 1 atm.

then achieved from the reaction mixture with ether extraction followed by evaporation under reduced pressure. RCC was recovered at >96% by weight and confirmed by FTIR, TGA, %N by elemental analysis, and <sup>13</sup>C NMR, which indicated a similar identity with the original one. The recovered catalyst was then recycled 5 times. The results are shown in Table 3 and shows almost indistinguishable activity in each recycle. For large scale operation, distillation could be followed for recovering the product.

Absence of Si in the product<sup>22</sup> is indicative of no leaching of Si during the reaction. Retention of activity in each recycle and absence of Si in the product signify that RCC is a stable material which can be sustained in the reaction conditions.

## Conclusion

In conclusion, HMS-DBU-CO<sub>2</sub> has been found to be a recyclable RCC catalyst for carboxylation of the enolizable ketones at 1 atm CO<sub>2</sub>. Direct carboxylation of ketones to β-keto ester has been prepared. The extent of carboxylation may be correlated to the enol content of the substrate. Usually reactions involving CO<sub>2</sub> are carried out at a very high pressure, which may not be economically suitable. However, the present work describes a method where a low pressure of CO<sub>2</sub> may be conveniently used for chemical transformations, and is thus economic. HMS-DBU prepared by the immobilization technique presented here is shown to be applicable to the reactions where DBU is used, getting rid of the difficulty in separation.

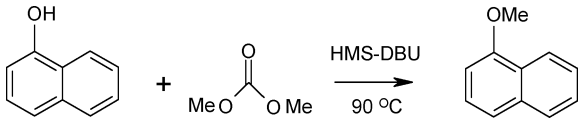
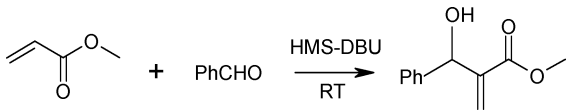
## Experimental

### General

Polyhydrosiloxane was obtained from Gelest Inc. and used as received. All other chemicals and solvents were purchased from the Aldrich Chemical Company and used without further purification unless otherwise mentioned. Reactions were carried out at 1 atmospheric pressure unless stated. Infrared spectra (IR) were recorded using a Madison Instrument, model 980602. Purity of reaction products were analyzed by HPLC using a

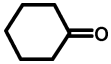
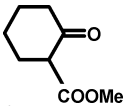


**Table 2** Reactions catalyzed by HMS-DBU

No.	Reactions	Time/h	Yield (%)	
			Obs.	Rptd.
1		16	<sup>a</sup> 98	99 (ref. 20)
2		24	<sup>b</sup> 72	74 (ref. 21)

<sup>a</sup> HMS-DBU 0.5 g. <sup>b</sup> HMS-DBU 0.05 g. Obs. = Observed. Rptd. = Literature reported.

**Table 3** Recyclability test of RCC

Cycle	RCC/g			Yield <sup>e</sup> (%)
1	0.25 <sup>a</sup>	0.51	0.70	95
2	0.24 <sup>b</sup>	0.54	0.75	96.5
3	0.25	0.53	0.74	96
4	0.248	0.55	0.76	95.8
5	0.249	0.53	0.74	96

<sup>a</sup> Used. <sup>b</sup> Recovered. <sup>c</sup> Substrate. <sup>d</sup> Product. <sup>e</sup> Yield = absolute. 60 °C, 4 h, RCC 0.25 g, CO<sub>2</sub> 1 atm.

Waters  $\mu$ -Bondapak C18 (300 mm  $\times$  3.9 mm  $\times$  10  $\mu$ m) column. <sup>1</sup>H NMR spectra were obtained in a 300 MHz Varian FT spectrometer using deuterated solvent as the lock. The spectra were collected at 25 °C and chemical shifts ( $\delta$ , ppm) were referenced to residual solvent peak (CDCl<sub>3</sub>,  $\delta$ , 1H, 7.26 ppm). Electrospray ionization mass spectra (ESI-MS) were recorded using a Micromass Q-TOF mass spectrometer. The elemental analyses (C, H and N) were carried out using a Perkin-Elmer 240 C elemental analyzer. Thermal analyses were conducted on TA Instruments TGA, model 2950. Desorption study was monitored through pre-calibrated Sartorius moisture analyzer Model MA35. Silicon (Si) was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), (Perkin Elmer, Optima 4300 DV) within the limit of 1 ppm.

#### Preparation of 6-vinyl DBU (V-DBU)

To a round bottom flask equipped with a magnetic stir bar was added 25 mL of dry tetrahydrofuran (THF). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 152 mg, 1 mmol) was added to THF and stirred for 5 min. The solution was then cooled to -78 °C. To the mixture 1.0 mL (0.95 mmol) of BuLi (1 M in hexane) was added drop-wise over a period of 30 min. The solution was then stirred for an additional 30 min. Vinyl chloride (62.5 mg, 1 mmol) was then added to the reaction mixture slowly. After the addition of vinyl chloride, the reaction mixture was brought to the room temperature and stirred for 3 h. At the end of the reaction, 2 mL of methanol was added to the

reaction mixture. Finally the reaction mixture was concentrated under reduced pressure and purified through a silica gel column with solvent eluent of ethylacetate-hexane (1 : 5) mixture. Yield, 171 mg, 96%. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.4–1.9 (m 8H), 2.4 (dd 1H), 2.8 (t, 2H), 3.4 (t, 2H), 3.8 (dd, 1H), 5.0 (dd, 1H), 3.27 (dd 1H), 4.46 (m 2H); ms:  $m/z$  179.34, 177.41 (M<sup>+</sup>); IR, 1450 cm<sup>-1</sup> (-CH=CH<sub>2</sub>). Elemental analysis: C, 74.16; H, 10.10; N, 15.74. Calculated for C<sub>11</sub>H<sub>18</sub>N<sub>2</sub>: C, 74.157; H, 10.11; N, 15.73.

#### Preparation of poly(6-ethyl-DBU) methylsiloxane (HMS-DBU)

The reaction was carried out under inert atmosphere (Argon). V-DBU (445 mg, 2 mmol) methylhydrosiloxane-dimethylsiloxane (6.6 g, 27.5 mmol Si-H) with 15–18 mole% methylhydrosiloxane dimethyl siloxane copolymer and trimethylsiloxane terminated and platinum-(vinyl tetramethyldisiloxane) (200 mg) were taken in a 100 mL round bottom flask. To this mixture were added 50 mL xylene and 30 mL of THF. The solution was stirred for 4 h at room temperature and then heated to 45 °C. The solution was stirred for another 12 h at 45 °C and from this point the solution turned brownish yellow during heating. Reaction was monitored by recording IR spectra where disappearance of the Si-H stretching frequency at 2157 cm<sup>-1</sup> followed. Completion of the reaction was also verified using <sup>1</sup>H NMR (300 MHz Bruker) by following the disappearance of the peak at 4.7 ppm (Si-H). After reaction the solvent was removed under reduced pressure to obtain a yellowish waxy material. Finally, the waxy material was washed with methanol several times to get poly(6-ethyl-DBU)methylsiloxane and dried under vacuum. Yield, 6.69 g; %N 0.22 (w/w).

#### Carboxylation of poly(1-carboxy-6-ethyl-DBU) methylsiloxane (HMS-DBU-CO<sub>2</sub> or RCC)

HMS-DBU (6.69 g) was taken in a 100 mL two necked round bottom flask and 50 mL methanol was added to it. To the mixture was added a drop of water and stirred. The mixture was then purged with CO<sub>2</sub> for 2 h while stirring. Methanol was then evaporated and the product was dried under vacuum. The final weight of the product was 6.76 g which corresponds to 98% yield, based on % N. <sup>13</sup>C NMR (DMSO d<sup>6</sup>) 161.1 ppm.

## Desorption of HMS-DBU-CO<sub>2</sub>

HMS-DBU-CO<sub>2</sub> (6.67 g) was taken on the weighing moisture analyzer pan. The sample was heated slowly at constant heating rate of 5 °C min<sup>-1</sup>, under air. Weight of the sample was recorded over a period of time and loss in weight was calculated accordingly.

## Carboxylation reaction using HMS-DBU

**Methyl 2-oxocyclohexanecarboxylate.** Cyclohexanone (0.5 g, 5 mmol) CH<sub>3</sub>I (0.35 mL, 5.6 mmol) and RCC (0.25 g) were taken in a round-bottom flask and 35 mL methanol was added into the flask while CO<sub>2</sub> was bubbled through the solution at room temperature. Progress of reaction was monitored by recording IR spectra (by following –COOMe group). After stirring the reaction for 4 h, the RCC was removed by filtration. The filtrate was then concentrated under reduced pressure. Purity of the isolated product was determined by HPLC comparing with authentic sample of cyclohexanone and 2-carboxy cyclohexanone. <sup>1</sup>H NMR, δ (ppm) 3.71 (1, 3H), 1.60 (4, 1H), 1.82 (4, 1H), 1.41 (m, 1H) 1.6 (m, 1H), 2.44 (4 1H), 2.53 (m, 1H), 1.94 (4, 1H) 1.81 (4, 1H) 3.53 (m, 1H). MS (EI) *m/z* (rel. intensity) 157.17. Elemental analysis: C, 61.34; H, 7.72. Calculated for C<sub>8</sub>H<sub>12</sub>O<sub>3</sub>: C, 61.52; H, 7.74.

**Methyl 2-acetyl-3-oxobutanoate.** <sup>1</sup>H NMR, δ (ppm) 3.74 (1, 3H), 2.21 (m, 6H), 4.87 (m, 1H). MS (EI) *m/z* (rel. intensity) 159.16 (M<sup>+</sup>, 19). Elemental analysis: C, 53.0; H, 6.34. Calculated for C<sub>7</sub>H<sub>10</sub>O<sub>4</sub>: C, 53.16; H, 6.37.

**Ethylacetoacetate-2-carboxylic acid methylester.** <sup>1</sup>H NMR, δ (ppm) <sup>1</sup>H NMR, 1.15 (1, 3H), 3.73 (2, 3H), 2.23 (3, 3H), 4.15 (m, 2H), 5.23 (m, 1H). MS (EI) *m/z* (rel. intensity) 189.18 (M<sup>+</sup>, 35). Elemental analysis: C, 51.02.; H, 6.32. Calculated for C<sub>8</sub>H<sub>12</sub>O<sub>5</sub>: C, 51.06; H, 6.38.

**1-Oxo-indan-2-carboxylic acid methyl ester.** <sup>1</sup>H NMR, δ (ppm) <sup>1</sup>H NMR (CDCl<sub>3</sub>), 3.717 (s, 3H), 7.24 (dd, 1H), 7.20 (dd, 1H), 7.27 (dd, 1H), 7.50 (m, 1H), 3.512 (m, 1H), 3.51 (m, 1H), 4.54 (m, 1H). MS (EI) *m/z* (rel. intensity) 191.19. Elemental analysis: C, 69.41; H, 5.34. Calculated for C<sub>11</sub>H<sub>10</sub>O<sub>3</sub>: C, 69.47; H, 5.30.

**Methylcyclopentanone-2-carboxylate.** <sup>1</sup>H NMR, δ (ppm), <sup>1</sup>H NMR 3.710 (1, 3H), 1.916 (m, 1H), 1.97 (4, 1H), 2.51 (m, 1H), 2.46 (m, 1H), 1.96 (m, 1H), 2.13 (m, 1H), 3.74 (m, 1H). MS (EI) *m/z* (rel. intensity) 143.15. Elemental analysis: C, 59.12; H, 7.11. Calculated for C<sub>7</sub>H<sub>10</sub>O<sub>3</sub>: C, 59.14; H, 7.09.

**Methyl 4-chlorobenzoylacetate.** <sup>1</sup>H NMR, δ (ppm), 3.69 (s, 3H), 7.523 (dd 2H), 7.847 (dd 2H), 3.86 (m 2H). MS (EI) *m/z* (rel. intensity) 213.63. C 56.49, H 4.27, Cl 16.67. Elemental analysis: C, 56.48; H, 4.28; Cl, 16.66. Calculated for C<sub>10</sub>H<sub>9</sub>O<sub>3</sub>Cl: C, 56.49; H, 4.27; Cl, 16.67.

**3-(4-Methoxyphenyl)-3-oxo-propionic acid methylester.** 3.69 (s 3H), 3.794 (s, 3H), 7.054 (dd, 2H), 7.98 (d 2H), 3.82 (s, 2H). MS (EI) *m/z* (rel. intensity) 209.21. Elemental analysis: C, 63.44; H, 5.82. Calculated for C<sub>11</sub>H<sub>12</sub>O<sub>4</sub>: C, 63.45; H, 5.81.

**Methylbenzoylacetate.** <sup>1</sup>H NMR, δ (ppm), 3.69 (s, 3H), 7.62 (t, 1H) 7.531 (dd 2H), 7.97 (dd, 2H), 3.87 (s, 2H). *m/z* 179.18.

Elemental analysis: C, 66.44; H, 5.62. Calculated for C<sub>10</sub>H<sub>10</sub>O<sub>3</sub>: C, 67.41; H, 5.66.

**2-Oxo-indan-1-carboxylic acid methyl ester.** <sup>1</sup>H NMR, δ (ppm), 3.72 (s, 3H), 7.24 (m, 2H), 7.20 (d, 1H), 7.5 (d, 1H), 3.512 (d, 2H), 4.54 (t, 1H). MS (EI) *m/z* (rel. intensity) 191.19. Elemental analysis: C, 69.43; H, 5.21. Calculated for C<sub>11</sub>H<sub>10</sub>O<sub>3</sub>: C, 69.47; H, 5.30.

**Dimethyl 2-oxocyclohexane-1,3-dicarboxylate.** <sup>1</sup>H NMR, δ (ppm), 3.71 (s, 6H), 1.58 (t, 1H), 1.41 (t, 1H), 1.93 (dd, 2H), 1.74 (t, 1H), 1.80 (dd, 1H), 3.74 (dd, 1H), 3.63 (dd, 1H). MS (EI) *m/z* (rel. intensity) 215.21. Elemental analysis: C, 56.05; H, 6.55. Calculated for C<sub>10</sub>H<sub>14</sub>O<sub>5</sub>: C, 56.07; H, 6.59.

**Ethyl 4-nitrobenzoylacetate.** <sup>1</sup>H NMR, δ (ppm), 3.69 (s, 3H), 8.134 (d, 2H) 8.15 (d, 2H), 4.02 (s, 2H). MS (EI) *m/z* (rel. intensity) 224.19. Elemental analysis: C, 53.80; H, 4.00; N, 6.30. Calculated for C<sub>10</sub>H<sub>9</sub>O<sub>5</sub>: C, 53.82; H, 4.06; N, 6.28.

## Reaction using HMS-DBU

**Preparation of 1-methoxynaphthelene.** In a round bottomed flask 0.5 g (0.039 mmol DBU) of HMS-DBU, 6.1 mg (0.042 mmol) of 1-naphthol and 10 mL dimethyl carbonate were taken along with a magnetic stir bar and placed over oil bath. The mixture was heated at 90 °C for 16 h. The yield of the product was determined after analyzing the reaction mixture by HPLC. Yield, 98%, <sup>1</sup>H NMR, δ (ppm) 1.26 (3H), 7.31 (1H), 7.6 (1H), 7.4 (1H), 7.1 (1H), 7.98 (1H), 7.5 (2H)). MS (EI) *m/z* (rel. intensity) 159.11. Elemental analysis: C, 83.24; H, 6.31. Calculated for C<sub>11</sub>H<sub>10</sub>O: C, 83.52; H, 6.37.

**Preparation of 2-hydroxyphenylmethylacrylate (Baylis-Hillman adduct of methyl acrylate and benzaldehyde).** In a round bottomed flask 0.05 g (0.0039 mmol DBU) of HMS-DBU, 3.5 mg (0.04 mmol) of methyl acrylate, 4.2 mg (0.04 mmol) benzaldehyde were taken in 10 mL dichloromethane and stirred for 24 h at room temperature under nitrogen. At end of the reaction the mixture was acidified with aqueous HCl (2 M, 20 mL) and separated the organic layer and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The mixture was concentrated using a rotary evaporator below 50 °C and analyzed by HPLC. Yield, 72%. <sup>1</sup>H NMR, δ (ppm) 5.9 (1H), 6.29 (1H), 3.71 (3H), 7.28 (1H), 7.4 (2H), 7.43 (2H), 6.01 (1H). MS (EI) *m/z* (rel. intensity) 193.15. Elemental analysis: C, 68.24; H, 6.01. Calculated for C<sub>11</sub>H<sub>12</sub>O<sub>3</sub>: C, 68.74; H, 6.29.

## Preparation of 2-oxocyclohexanecarboxylic acid

Cyclohexanone (0.5 g, 5 mmol) and RCC (0.25 g) were taken in a round-bottom flask that was placed in a cold bath maintaining temperature ~18–20 °C. 35 mL of methanol was added into the flask while CO<sub>2</sub> was bubbled through the solution under constant stirring. Progress of reaction was monitored by recording IR spectra (by following –COOH group). After stirring the reaction for 4 h, the RCC was removed by filtration. 10 mL of ice cold water was then added into the mixture. A white precipitate of the product settled at bottom which was then filtered and stored under dark and cold atmosphere. <sup>1</sup>H NMR, δ (ppm) 1.810 (1H), 1.596 (2H), 1.405 (1H), 2.529 (1H), 2.434 (1H), 1.807 (1H), 1.947 (1H), 3.509 (1H). MS (EI) *m/z*

(rel. intensity) 143.15. Elemental analysis: C, 59.10; H, 7.10. Calculated for  $C_7H_{10}O_3$ : C, 59.14; H, 7.09.

### Comparison of RCC and DBU

0.25 g of RCC and 3.6 mg of DBU were reacted separately to perform carboxylation with 0.5 g of cyclohexanone along with  $CH_3I$  (0.35 mL, 5.6 mmol) in the similar manner as described above. Plot of yield% versus time in both the cases provides comparative study of RCC and DBU.

**Estimation of Si in the product.** The cyclohexanone-2-carboxylic acid isolated from the reaction of cyclohexanone was digested with 1 mL of concentrated  $HNO_3$  (69% w/w) in a porcelain crucible for 5 h and then evaporated to dryness. The crucible was then washed with double distilled water (100 mL) and washing was collected. Care was taken to maintain pH of the solution low by adding dilute  $HNO_3$  (6.9%) and finally the solution was analyzed by ICP-OES. Results showed no trace of Si in the solution indicating no leaching of Si.

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