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## Microwave assisted synthesis of cyclic carbonates from olefins with sodium bicarbonates as the C1 source<sup>†</sup>

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An effective transformation of alkenes into cyclic carbonates has been achieved using  $NaHCO_3$  as the C1 source in acetone-water under microwave heating, with selectivities and yields significantly surpassing those obtained using conventional heating.

Since the 1986 discovery by the Gedye and Giguere-Majetich groups<sup>1</sup> that microwave irradiation leads to significant rate enhancements in organic chemical transformations, microwave heating has been exploited extensively in the synthesis community.<sup>2</sup> Spectacular rate accelerations, high yields, and good selectivity (chemo-, regio- and stereoselectivity) under nominally milder conditions than used in heating by conventional means have often been reported when microwave heating was used.<sup>3</sup> The effect of microwave irradiation is due to a combination of thermal effects, arising from direct volumetric heating, superheating and selective heating, taking advantage of microwave dielectric heating phenomena via mechanisms such as dipolar polarization and ionic conduction.<sup>4</sup> Early claims of non-thermal effects are no longer deemed credible, but the relative impacts of microwave-specific thermal effects like selective heating or superheating remain controversial.<sup>5,6</sup> It has been found that hot spots, thermal runaway and explosions are often produced during microwave assisted chemical reactions.<sup>7</sup> These issues, coupled with high pressures that can be generated on heating gases, make it difficult to conduct gas-liquid reactions in microwave-heated systems in practice.

The transformation of  $CO_2$  into useful organic chemicals is becoming an increasingly popular research topic, as  $CO_2$  is an easily available, non-toxic and economical carbon resource.<sup>8</sup> There is, however, a general reluctance to use  $CO_2$  in conventional batch

reactors in research laboratories, largely owing to potential problems with the containment of pressurized CO<sub>2</sub>, the associated safety factors, and high capital costs, although our recent studies on using continuous flow systems have solved some of these problems.9 These complications in process design and control inherent in using CO<sub>2</sub> as a feedstock become even more difficult when microwaves are used as a heating source.<sup>10</sup> In this work, we show that these complications can be overcome when bicarbonate salts, especially NaHCO<sub>3</sub>, are utilized as a convenient, inexpensive, and clean substitute for CO<sub>2</sub> as a C1 source, thus avoiding the need for pressurized autoclaves and recycling of excess, unused  $CO_2$ . Our preliminary results on the efficient microwave-assisted synthesis of cyclic carbonates from olefins and bicarbonate salts reported here show superior performance compared to the conversions and yields of desired products obtained with conventional heating (Fig. 1).<sup>11</sup> Such cyclic carbonate products have important applications as fuel additives, polar aprotic solvents, electrolytes in lithium-ion batteries, important intermediates for pharmaceutical/fine chemicals, and raw materials for the production of polycarbonates and polyurethanes.<sup>12</sup>

Our study was initiated with a solvent screening under both conventional oil bath and microwave heating conditions (Table 1). Styrene and sodium bicarbonate were selected from an economical standpoint as the model reaction for optimization of the reaction conditions. A poor but encouraging yield (25%) of carbonate **2a** was



Fig. 1 Syntheses of cyclic carbonates using NaHCO<sub>3</sub> and olefins.

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I able 1         Evaluation of solvents with different loss factor	loss factor <sup>14</sup>
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$\frac{Ph}{1a} \xrightarrow{\text{NBS (1.2 equiv), NaHCO_3 (1.1 equiv)}}_{\text{solvent, 60 °C}} \xrightarrow{Ph}_{2a}$							
				Microwave <sup>a</sup>		Oil bath <sup><i>a</i></sup>	
Entry	Solvent	Loss factor <sup><math>b</math></sup>	Time (h)	Yield (%)	Conversion (%)	Yield (%)	Conversion (%)
1-2	$H_2O$	0.122	3	25	76	10	78
3-4	Acetone-H <sub>2</sub> O	0.09	18	86	100	55	100
5-6	DMF-H <sub>2</sub> O	0.142	3	88	100	80	100
7	MeCN-H <sub>2</sub> O	0.092	3	56	100	_	_
8	Dioxane-H <sub>2</sub> O	0.079	3	23	100	_	_
9	THF-H <sub>2</sub> O	0.085	3	15	70	_	_
10	DMSO-H <sub>2</sub> O	0.467	3	37	100	_	_
11	Hexanes-H <sub>2</sub> O	0.071	3	0	0	_	_

<sup>a</sup> Conversion and yield based on crude <sup>1</sup>H NMR using trichloroethylene as the external standard. <sup>b</sup> The measurement of microwave vector network analyzer of Agilent E8362B combined with the calculation by Genetic algorithms was used to obtain loss factors of different solvent mixtures.

obtained with water alone as the solvent under microwave heating (Table 1, entry 1), but, more satisfyingly, polar solvents such as acetone, MeCN and DMF mixed with water exhibited remarkable enhancement of reactivity and selectivity of the desired transformation (entries 3, 5 and 7). Other solvents such as dioxane, THF, and DMSO resulted in strikingly decreased yields (entries 8-10). No reaction was observed with the nonpolar solvent and water mixture (entry 11). Notably, the results of comparative tests between microwave and oil bath heating clearly demonstrated the superiority of microwave heating (entries 1-6). Generally, the oil bath reactions generated significant diol and epoxide by-products even with an 18 hour reaction period, and resulted in lower yields of cyclic carbonates compared with reactions conducted under microwave heating conditions, despite the same nominal overall reaction temperatures in the two cases.13 Based on economic considerations and easier removal of acetone from the reaction product solution than of DMF and MeCN, the acetone-water mixture was chosen as the solvent system for our further studies. While epoxide by-products were detected at the end of a 3 hour reaction period, this by-product was totally depressed by allowing a prolonged reaction time (18 hours, entry 3).

To evaluate the effect of bicarbonate salts, a quick screening of various bicarbonates was carried out, which indicated most bicarbonate salts were effective in providing good conversion and yield (Table 2). For reasons of cost, availability, and practicality, we selected NaHCO<sub>3</sub> for further development. Thus, the optimal condition was: 1 equiv. olefin, 1.2 equiv. NBS, 1.1 equiv.

Table 2	Base evaluation					
	NBS (1.2 ed	quiv), Base (1.1 equiv) Ph				
	1a microwave,	acetone/H <sub>2</sub> O, 60 °C, 3 h	2a 0			
Entry	Base	Conversion <sup><i>a</i></sup> (%)	Yield <sup>a</sup> (%)			
1	NaHCO <sub>3</sub>	100	62			
2	CsHCO <sub>3</sub>	100	60			
3	$K_2CO_3$	65	24			
4	KHCO3	83	48			
5	NH <sub>4</sub> HCO <sub>3</sub>	58	0			

 $^a$  Conversion and yield based on crude  $^1{\rm H}$  NMR using trichloroethylene as the external standard.



Fig. 2 Product distribution as a function of time under microwave heating.



Fig. 3 Time-dependent product distribution when reaction mixture is heated in an oil bath.

NaHCO<sub>3</sub>, acetone (1 M), and  $H_2O$  (1 M) stirred at 60 °C for 18 hours in the microwave reactor.

In order to understand the reaction process, we investigated the product distribution evolution with time in systems heated both by microwaves (Fig. 2) and oil bath (Fig. 3). Under the



<sup>e</sup>Conversion based on <sup>1</sup>H NMR using trichloroethylene as the internal standard, isolated yield. <sup>b</sup>H<sub>2</sub>O was reduced to 2 M concentration. <sup>c</sup>Reactions conducted in DMF/H<sub>2</sub>O instead of acetone/H<sub>2</sub>O.

Scheme 1 Substrate scope.

optimized conditions, the starting olefins were converted completely into bromohydrins within 10 minutes. As the reaction proceeded further, these bromohydrins were converted to epoxides and cyclic carbonates, and epoxides themselves were transformed to cyclic carbonates at the same time. Under microwave irradiation, the maximum epoxide yield was obtained after approximately 1 hour, and the concentration decreased thereafter. Eventually, all epoxide intermediates were converted to cyclic carbonate products in the microwave reactor. Evidently, microwave irradiation accelerated the transformation of epoxides to carbonates, probably due to "hot spots" generated by enhanced microwave absorption at the surfaces of the insoluble NaHCO<sub>3</sub> particles.<sup>6b,7</sup>

Using the optimal conditions in the microwave apparatus, we investigated olefins bearing different functional groups (Scheme 1). All electron-rich aromatic olefins (2c, 2d, 2i), electron-deficient aromatic olefins (2e–2h) and terminal aliphatic olefins (2j–2p) were converted to the corresponding cyclic carbonates in moderate to good yields. The microwave-assisted conditions not only tolerate functionalities such as halide, trifluoromethyl, ether, nitrile, and ester, but also allowed for conversion of even more challenging substrates such as aldehyde, ketone, and alcohol that had potential to undergo cyclization under basic conditions (2h, 2m–2o).



Scheme 2 Plausible mechanism for production of cyclic carbonates from olefins and NaHCO $_3$ .

Notably, disubstituted olefins were also amenable substrates for this transformation with good product yield (2q, 2r). In some cases, it was necessary to use DMF-H<sub>2</sub>O as the solvent instead of acetone-H<sub>2</sub>O to improve the reaction efficiency (2f, 2p). All the products were converted into the corresponding carbonates with no or little epoxide formation, indicating the high versatility of the microwave-assisted transformation utilizing sodium bicarbonate as the C1 source.

A plausible mechanism was proposed based on the product distribution study (Scheme 2). Bromohydrin **3a** was generated first with stoichiometric NBS and olefins followed by deprotonation of the hydroxyl group to deliver anion **5a** and the *in situ* generation of CO<sub>2</sub>. The subsequent intramolecular cyclization of **5a** (path b) is more favoured than the intermolecular cycloaddition with CO<sub>2</sub> (path a), which resulted in the formation of a significant amount of epoxide **4a** within a relatively short reaction period. Two reaction pathways may contribute to the conversion of epoxide **4a** to cyclic carbonate **2a** including regeneration of intermediate **5a** (path c) and direct transformation to achieve cyclic product **2a** (path d).<sup>9a</sup>

An efficient microwave-assisted one-pot synthesis of cyclic carbonates starting from olefins has been achieved with a wide substrate scope. Compared to conventional heating methods, microwave heating provides remarkably better selectivities and yields of desired products. NaHCO<sub>3</sub> proved to be an excellent substitute for  $CO_2$  gas, thus avoiding the need for use of compressed  $CO_2$ . This is convenient for lab scale experiments and provides a potentially viable approach for exploiting microwave heating at the industrial scale.<sup>15</sup> This method is also well poised toward green processing due to the use of environmentally friendly solvents such as the acetone–water mixtures.

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## Notes and references

- 1 (*a*) R. N. Gedye, F. Smith and K. Westaway, *Tetrahedron Lett.*, 1986, 27, 279; (*b*) R. J. Giguere, T. L. Bray, S. M. Duncan and G. Majetich, *Tetrahedron Lett.*, 1986, 27, 4945.
- 2 (a) V. Polshettiwar and R. S. Varma, Chem. Soc. Rev., 2008, 37, 1546;
   (b) C. O. Kappe, Chem. Soc. Rev., 2008, 37, 1127; (c) J. J. Kiddle, J. Am. Chem. Soc., 2006, 128, 1771; (d) A. David, Nature, 2003, 421, 571.
- 3 (a) Microwave Assisted Organic Synthesis, ed. D. M. P. Mingos, Blackwell Publishing, Oxford, 2005; (b) Microwaves in Organic Synthesis, ed. A. Loupy, Wiley-VCH Verlag GmbH, Weinheim, 2nd edn., 2006; (c) Microwaves in Organic and Medicinal Chemistry, ed. C. O. Kappe and A. Stadler, Wiley-VCH Verlag GmbH, Weinheim, 2005.

- 4 (a) D. R. Baghurst and D. M. P. Mingos, *Chem. Soc. Rev.*, 1991, 20, 1;
   (b) C. Gabriel, S. Gabriel, E. H. Grant, B. S. Halstead and D. M. P. Mingos, *Chem. Soc. Rev.*, 1998, 27, 213.
- 5 Some recent studies by Kappe suggest that direct volumetric heating may be solely responsible for observed reactivity in homogeneous systems: (a) C. O. Kappe, B. Pieber and D. Dallinger, *Angew. Chem., Int. Ed.*, 2013, 52, 1088. However, this point is still under debate: (b) G. B. Dudley, A. E. Stiegman and M. R. Rosana, *Angew. Chem., Int. Ed.*, 2013, 52, 7918.
- 6 (a) Foundations of Electroheat, ed. A. C. Metaxas, John Wiley & Sons, Inc., New York, 1996; (b) A. de La Hoz, A. Díaz-Ortiz and A. Moreno, *Chem. Soc. Rev.*, 2005, 34, 164; (c) R. B. N. Baig and R. S. Varma, *Chem. Soc. Rev.*, 2012, 41, 1559.
- 7 (a) S. Horikoshi, A. Osawa, M. Abe and N. Serpone, J. Phys. Chem. C, 2011, 115, 23030; (b) C. O. Kappe, Angew. Chem., Int. Ed., 2004, 43, 6250.
- 8 (a) T. Sakakura, J. Choi and H. Yasuda, *Chem. Rev.*, 2007, 107, 2365;
  (b) L. N. He, J. Q. Wang and J. L. Wang, *Pure Appl. Chem.*, 2009, 81, 2069; (c) I. Omae, *Coord. Chem. Rev.*, 2012, 256, 1384.
- 9 (a) J. A. Kozak, J. Wu, X. Su, F. Simeon, T. A. Hatton and T. F. Jamison, J. Am. Chem. Soc., 2013, 135, 18497; (b) J. Wu,

J. A. Kozak, F. Simeon, T. A. Hatton and T. F. Jamison, *Chem. Sci.*, 2014, 5, 1227-1231.

- 10 (a) Y. H. Jin, B. A. Voss, R. McCaffrey, C. T. Baggett, R. D. Noble and W. Zhang, *Chem. Sci.*, 2012, **3**, 874; (b) H. Y. Cho, D. A. Yang, J. Kim, S. Y. Jeong and W. S. Ahn, *Catal. Today*, 2012, **185**, 35.
- 11 Previous reported syntheses of cyclic carbonates from olefins and CO<sub>2</sub> suffered from disadvantages such as the need for high temperatures and long reaction times, and from low yields, see:
  (a) N. Eghbali and C.-J. Li, *Green Chem.*, 2007, 9, 213–215;
  (b) J. Wang, J. Wang, L. He, X. Dou and F. Wu, *Green Chem.*, 2008, 10, 1218–1223;
  (c) D. Bai and H. Jing, *Green Chem.*, 2010, 12, 39–41;
  (d) F. Chen, T. Dong, T. Xu, X. Li and C. Hu, *Green Chem.*, 2011, 13, 2518–2524.
- 12 A. G. Shaikh and S. Sivaram, Chem. Rev., 1996, 96, 951.
- 13 Reaction temperatures during the microwave experiments were measured with a fiber optic sensor throughout our study.
- 14 (a) K. M. Huang, X. J. Cao, C. J. Liu and X. B. Xu, *IEEE Trans. Microwave Theory Tech.*, 2003, 51, 2106; (b) J. F. Lou, T. A. Hatton and P. E. Laibinis, *J. Phys. Chem. A*, 1997, 101, 5262.
- 15 J. M. Osepchuk, IEEE Trans. Microwave Theory Tech., 2002, 50, 975.