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PAPER

Investigating the formation of dialkyl carbonates using high speed ball milling

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We investigated the synthesis of dialkyl carbonates under solvent-free high speed ball milling conditions. We converted various metal carbonates with the assistance of metal complexing reagents into a variety of dialkyl carbonates. We also observed the increased reactivity of urea under similar reaction conditions.

Organic chemistry has a history of using hazardous chemicals and solvents in order to perform chemical reactions. Increasing environmental concerns about solvent-based chemistry has led to a renewed interest in solvent-free reactions.[1–3] Toda helped pioneer the field of solvent-free reactions using a mortar and pestle, but the mechanical method of high speed ball milling (HSBM) has since shown to be more reproducible and efficient. In the HSBM approach, the chemical reactants are placed inside a custom made $\frac{1}{2}'' \times 2''$ screw-capped stainless steel vial along with a stainless steel ball bearing. Shaking this vial in the ball mill causes collisions and creates good mixing of the reactants so that a chemical reaction can occur.[4–6] The use of commercial ball mills have allowed these reactions to be scaled up to industrial levels, therefore understanding organic reactions using this methodology can significantly reduce solvent waste.[7–16]

Our group studies different reactions using a SPEX Certiprep Mixer/Mill 8000 in order to better understand this solvent-free process.[17–23] In addition to our work, others have also been studying mechanochemistry as a novel alternative to solvent-based chemistry.[24–34] Here, we report our investigation of the formation of dialkyl carbonates under high speed ball milling conditions.

Dialkyl carbonates have been used for a variety of purposes, such as fuel additives, dyes, agrochemicals, and drugs for the treatment of lipidemia and depression. However, the current methods available to make dialkyl carbonates either perform inadequately or use unsafe reaction conditions and create large amounts of harmful solvent waste.[35–37] The most common methods of synthesizing dialkyl carbonates involve starting with a carbonyl source (*e.g.*, phosgene,[38–40] carbon dioxide,[36,41] tetraethyl ammonium carbonate,[42] or metal carbonates[43,44]) and then attaching the alkyl portion of the molecule in the reaction. Although effective, phosgene is a deadly compound that was the most lethal of the World War I war gases.[45] Carbon dioxide is an excellent environmentally benign alternative, but reactions of carbon dioxide often use specialized equipment. Metal carbonates are also environmentally benign but solubility and reactivity issues cause sluggish reactions and low yields. We chose to study the creation of dialkyl carbonates using metal carbonates because HSBM is a solvent-free and high energy method. Therefore, reactant solubility is not an issue and the high energy of the system will alleviate sluggish reactions.

Our initial study focused on creating a baseline for studying how effective HSBM could be in creating dialkyl carbonates from metal carbonates. We analyzed four different metal carbonates, as shown in Table 1. These results are not of great interest by themselves, but some important insights can be taken from this study. The metal cations that are known to be more tightly bound to oxygen (Li^+ and Na^+) showed no reactivity while less tightly bound cations (K^+ and Cs^+)[46] allowed for a reaction to occur.[47] This shows that hard–soft acid–base theory plays a significant role in chemical reactions under ball milling conditions. As expected, the availability of the oxygen to act as a nucleophile is critical to the formation of the dialkyl carbonate product. With this knowledge, we chose to investigate different methods of increasing the oxygen's nucleophilicity using HSBM.

18-crown-6 was first used in ball milling synthesis in 2008 by Dong *et al.*[26] Also, studying 18-crown-6 in our previous work on enolate chemistry,[18] we observed that adding 18-crown-6 to potassium carbonate increased its basicity but also acts to increase nucleophilicity and create dialkyl carbonates. The reaction between potassium carbonate and 4-bromobenzyl bromide increases from a 2% conversion in 17 h without 18-crown-6 to a 74% conversion in 17 h with two equivalents of 18-crown-6; one molecule of 18-crown-6 for every potassium cation. From this, we were interested in investigating if a catalytic amount of 18-crown-6 could be used instead of a full two equivalents. This would cut down on waste generated and

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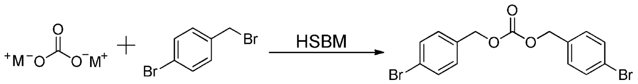
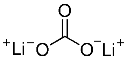
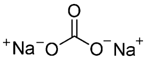
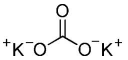
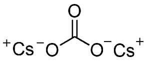
Table 1 Dialkyl carbonate synthesis using various metal carbonates



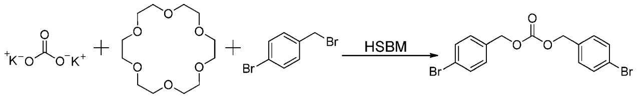
Metal carbonate	Time	% Conversion to product
	17 Hours	0%
	17 Hours	0%
	17 Hours	2%
	17 Hours	18%[a]

[a] Also 13% side products

increase the safety of the reaction. Interestingly, the reaction did not proceed as effectively without two full equivalents of 18-crown-6 for every one equivalent of potassium carbonate. After the 18-crown-6 complexes a potassium ion, the complex cannot dissociate as easily as it might in solution. Therefore, if a catalytic amount of 18-crown-6 is used, it would become less available to react further in the solid state and thus hinder the reaction. These results are summarized in Table 2.

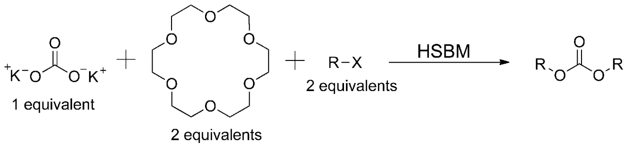
Another interesting observation is that the reaction gives similar percent conversions to product in 2 h with the addition of 18-crown-6. With these results, we sought to further study the scope of this reaction while using two full equivalents of 18-crown-6 and running the reaction for 2 h (Table 3). Regardless of the substituent on the aromatic ring, benzyl bromides react relatively the same. However, benzyl chloride is much more sluggish and proceeds in less than 1% conversion to product in 2 h. The Cl leaving group appears to slow down the reaction. We attribute this to the carbon–chlorine bond having a higher bond dissociation energy.[48] Also, in 1968, Radhakrishnamurti and Panigrahi showed that benzyl bromides react faster than benzyl chlorides in an S_N2 type, solution based reaction.[49] Similarly, given more time and energy in the high speed ball mill, benzyl chloride reacts to give a 62% yield in 17 h. Although much less reactive, Cl can be used as a leaving group in S_N2 type reactions using high speed ball milling. Also less reactive, (2-bromoethyl)benzene gives only a 5% conversion to the dialkyl carbonate product in 2 h but jumps to 58% conversion after 17 h. We attribute this to less cationic character in the carbon next to the bromine in (2-bromoethyl)benzene when compared to the carbon next to the bromine in benzyl bromide. Further, we wanted to study the reactivity of straight chain alkyl bromides under our conditions. We looked at 1-bromopentane and 1-bromododecane as starting materials to form their respective dialkyl carbonates. As expected, both straight chain alkyl bromides reacted but more slowly than the benzyl bromides. In 17 h, 1-bromopentane formed its dialkyl carbonate in similar conversions to the benzyl bromides. However, even after 17 h, the 1-bromododecane still had a low conversion (<20%) to its dialkyl carbonate. 1-bromododecane can fold in on itself making the S_N2 reactions more sluggish.

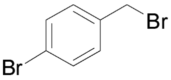
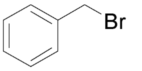
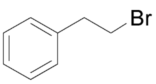
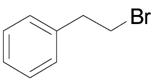
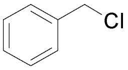
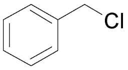
Table 2 Using 18-crown-6 to enhance the reaction



Equivalents of potassium carbonate	Equivalents of 18-crown-6	Equivalents of 4-bromobenzyl bromide	% Conversion to Product
1	1/2	2	48%
1	1	2	66%
1	2	2	74%

Table 3 Studying the scope of the dialkyl carbonate synthesis



Electrophile R–X	Time	% Conversion of product
	2 Hours	74%
	2 Hours	67%
	2 Hours	5%
	17 Hours	58%
	2 Hours	< 1%
	17 Hours	62%

One principle of green chemistry is to use safer chemicals whenever possible. With this in mind, we sought a safer alternative to 18-crown-6 to complex the metal ion. In previous literature, polysorbate 80, or Tween® 80 (Fig. 1), has been

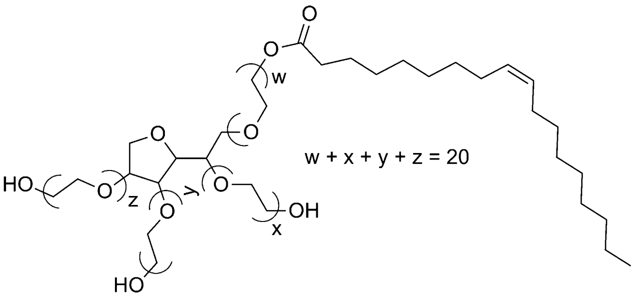


Fig. 1 Polysorbate 80 (Tween® 80).

shown to act as a phase transfer catalyst by complexing with the potassium ion of potassium cyanide.[50] Tween® 80 is often used as a surfactant and has been used as an emulsifier in food, such as ice cream, and medicine.[51] Therefore, this substance is generally much safer to use than 18-crown-6. Although not as effective as 18-crown-6, Tween® 80 proved to be an adequate substitute. Reacting 4 equivalents of potassium carbonate, 1 equivalent of 4-bromobenzyl bromide, and ~4 mol% Tween® 80 gives a 22% conversion to the dialkyl carbonate product, but there is a 53% combined conversion to 4-bromobenzyl alcohol and di-(4-bromobenzyl)ether. These side products, as discussed in previous literature,[43] arise from the loss of carbon dioxide from an intermediate of the reaction (Fig. 2). Utilizing Le Chatelier's principle, we decided to add carbon dioxide into the reaction mixture to quench this side reaction. Because our system uses a sealed vial to run the reaction, we are able to use dry ice as our carbon dioxide source. We simply added dry ice to our vial before sealing it shut and the carbon dioxide became part of the reaction without the need for additional, specialized equipment. This procedure served its purpose because the reaction proceeded in a 41% conversion to the dialkyl product in 17 h while giving less than 1% conversion to side products after the addition of carbon dioxide (Fig. 3). We decided to vary the amount of Tween® 80, potassium carbonate, and carbon dioxide in the reaction to determine the optimal conditions for this reaction under HSBM conditions.

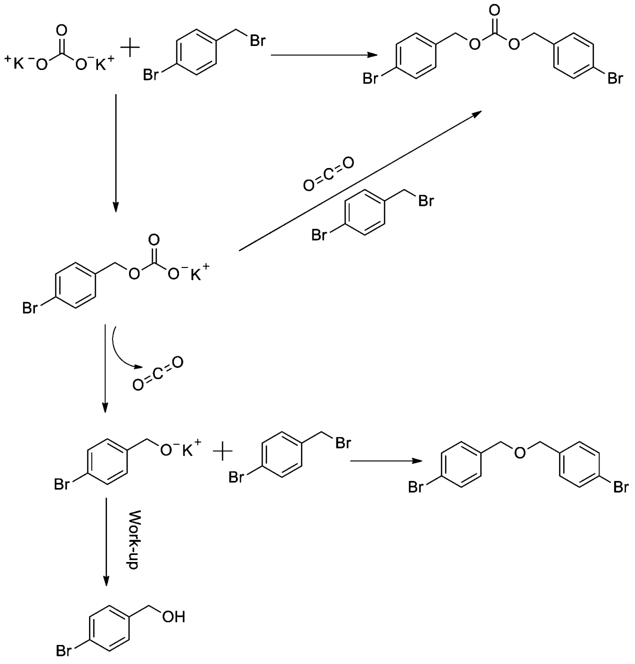


Fig. 2 The addition of CO_2 quenches side product formation.

The first trial we attempted was varying the amount of Tween® 80 added to the reaction while keeping the amount of CO_2, potassium carbonate, 4-bromobenzyl bromide, and time (17 h) constant. Adding too much Tween® 80 to the reaction proved to be detrimental to the percent conversion to product (Fig. 4). Tween® 80 is a large molecule (Fig. 1) and very viscous, so the reactants get trapped and cannot react with each other if too much Tween® 80 is present in the reaction. Four to five mole percent of Tween® 80 proved to catalyze the reaction most effectively without dampening the reaction due to its size and viscosity.

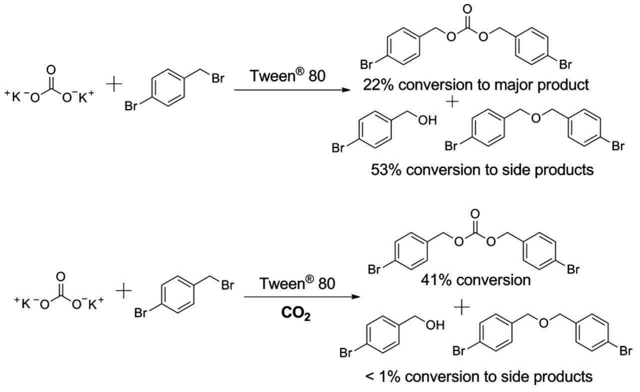
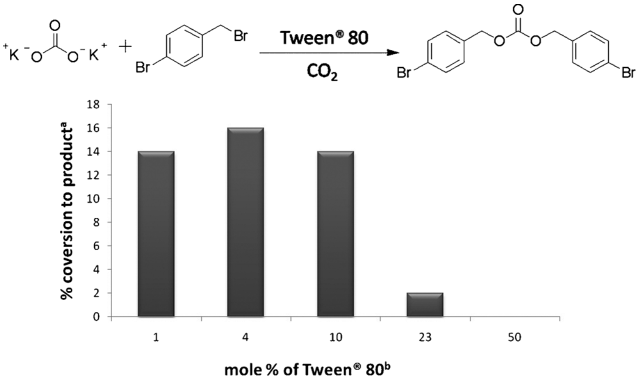


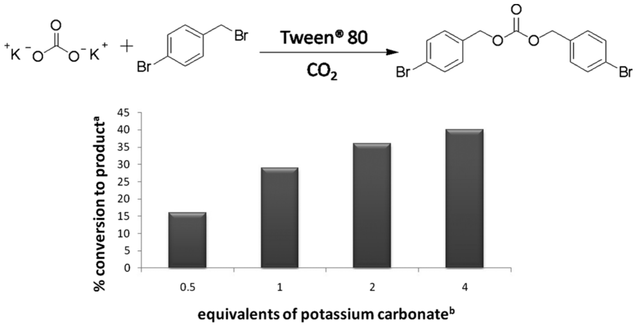
Fig. 3 Tween® 80 as a substitute for 18-crown-6.



a) % conversion from ^{1}HNMR
b) along with 1 equivalent of 4-bromobenzyl bromide, vial filled with dry ice, and 1/2 equivalent of potassium carbonate

Fig. 4 Varying the amount of Tween® 80.

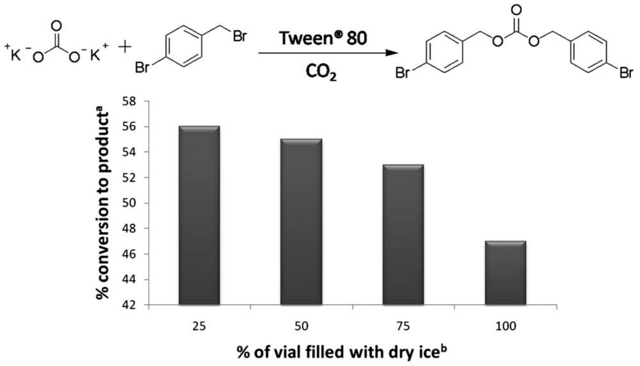
Next, using 4 mole% of Tween® 80 and a full vial of dry ice,[52] we varied the amount of potassium carbonate added into the reaction while keeping the reaction time at 17 h. Using four equivalents of potassium carbonate allowed the reactants to find each other more readily in our system and increase the percent conversion to product (Fig. 5). As discussed earlier, the size and viscosity of Tween® 80 can trap reactants so excess potassium carbonate allowed more interactions between potassium carbonate and 4-bromobenzyl bromide.



a) % conversion from ^{1}HNMR
b) along with 1 equivalent of 4-bromobenzyl bromide, vial filled with dry ice, and 4 mole % Tween® 80

Fig. 5 Varying the amount of potassium carbonate.

Finally, we wanted to determine how varying the amount of CO_2 while keeping all other variables constant affects the reaction. The easiest way to vary the CO_2 amount was to simply change how full we filled the reaction vial with dry ice.[52] Filling the vial too full with dry ice partially hinders the reaction's progress towards the product side of the reaction. While the difference is not substantial, the over-abundance of CO_2 causes less efficient mixing and the rate of the reaction decreases. Filling the reaction vial a quarter full of dry ice allowed the reaction to proceed in the highest percent conversion while still quenching side product formation (Fig. 6).[53]



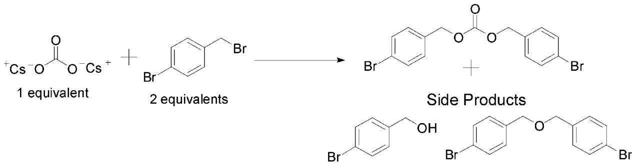
a) % conversion from ¹HNMR
b) along with 1 equivalent of 4-bromobenzyl bromide, 4 equivalents of potassium carbonate and 5 mole % Tween® 80

Fig. 6 Varying the amount of dry ice.

Overall, our best results occurred in 17 h using 5 mole% Tween® 80, 4 equivalents of potassium carbonate, and $\frac{1}{4}$ vial full of dry ice where we observed a 56% conversion to product. We have shown that we can mimic the success of 18-crown-6 as a complexing reagent in our system with a catalytic amount of a safer reagent (Tween® 80) under HSBM conditions. However, solely considering reaction time and percent conversion to product, 18-crown-6 outperforms Tween® 80.

Using cesium as the countercation of the metal carbonate is another method we implemented in order to increase the nucleophilicity of the metal carbonate's oxygen. As discussed earlier, cesium carbonate reacts with 4-bromobenzyl bromide in 17 h to show an 18% conversion to the dialkyl product, but there is also a 13% combined conversion to 4-bromobenzyl alcohol and di-(4-bromobenzyl) ether. If the reaction is run for 92 h, the dialkyl product is found in a 26% conversion, but there is also a 36% combined conversion to 4-bromobenzyl alcohol and di-(4-bromobenzyl) ether. As with the Tween® 80 situation, we attempted to minimize side product formation by the addition of carbon dioxide. After addition of the carbon dioxide, the conversion to side products went down to less than 2% while the conversion to the dialkyl carbonate remained similar at 16% after 17 h. The dialkyl product is formed in 37% yield while less than 2% is converted to side product when 4 equivalents of cesium carbonate are added to 1 equivalent of 4-bromobenzyl bromide and a full vial of carbon dioxide (Table 4). Again, we used Le Chatelier's principle to push the reaction towards completion and we showed that simply changing the cation of the metal carbonate can have a profound effect on the outcome of the reaction under HSBM conditions.

Table 4 Cesium carbonate study



Reaction time	Modification	% Conversion to dialkyl carbonate	% Conversion to side products
17 Hours	NONE	18%	13%
92 Hours	NONE	26%	35%
17 Hours	add CO_2^{a}	16%	< 2%
17 Hours	add CO_2^{a} plus excess cesium carbonate	37%	< 2%

[a] The addition of CO_2 was ~3.2 g (a full vial)

After studying the formation of dialkyl carbonates from metal carbonates, we decided to look into the formation of dialkyl ureas from urea. Traditionally, urea is considered very unreactive. However, under HSBM conditions we were able to increase the reactivity of this generally inert compound (Fig. 7). The use of sodium hydroxide proved crucial to the success of this reaction. Without NaOH, there was a negligible conversion to a dialkyl urea product. We believe that the hydroxide deprotonates the urea, increasing the nucleophilicity of the nitrogen. To run the reaction, two equivalents of NaOH were milled with one equivalent of urea for 17 h followed by addition of 2 equivalents of 4-bromobenzyl bromide and an additional 17 h of milling. The resulting solids were washed with ethyl acetate to eliminate any remaining 4-bromobenzyl bromide. This resulted in a 41% conversion to di-(4-bromobenzyl) urea with the rest being unreacted urea. Di-(4-bromobenzyl) urea can be further purified by recrystallization from ethanol. This reaction proves that we can manipulate chemical reactions under high speed ball milling conditions in order to increase the nucleophilicity of an otherwise weakly-nucleophilic substance.

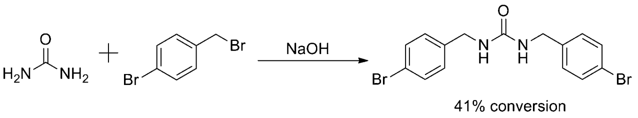


Fig. 7 Urea study.

In conclusion, the synthesis of dialkyl carbonates can be improved by increasing the nucleophilicity of the oxygens of metal carbonates. This can be accomplished using a traditional cation complexing reagent (18-crown-6), a more novel complexing reagent (Tween® 80), or a loosely bound countercation (Cs^+). We also found that adding CO_2 as dry ice can diminish side product formation in the sealed vial of the high speed ball milling method. Along with these findings, the nucleophilicity of urea can be increased using HSBM. These studies, along with our previous work, lead us to believe that both the basicity and nucleophilicty of reactants can be increased under HSBM conditions. As we increase our knowledge about the solvent-free method of HSBM, we are creating a unique and environmentally friendly toolbox for organic chemists, which will cause a paradigm shift in the way we conduct organic reactions.

Experimental

All NMR spectra were recorded on a Bruker Avance 400 spectrometer. Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories, Inc., Andover MA, and used without further purification. All products were confirmed by comparison to literature ^{1}H NMR (di-(4-bromobenzyl) carbonate,[18] dibenzyl carbonate,[54] di-phenethylcarbonate,[44] di-dodecyl carbonate,[55] di-pentyl carbonate,[44] di-(4-bromobenzyl) urea[56]). 4-bromobenzyl bromide, 18-crown-6, benzyl chloride, benzyl bromide, 1-bromododecane, 1-bromopentane and (2-bromoethyl)benzene were purchased from Acros Organics and used without further purification. Sodium hydroxide and potassium carbonate were purchased from Fisher Chemical and used without further purification. Ball milling was carried out in an 8000 M SpexCertiprep Mixer/Mill. Ball bearings were purchased from Small Parts incorporated. Custom made vials were made by the machine shop at the University of Cincinnati with metal rods purchased from ESPICorp Inc.

Typical procedure

Dialkyl carbonate

Potassium carbonate (0.69 g, 0.5 mmol), 18-crown-6 (0.264 g, 1 mmol), and 4-bromobenzyl bromide (0.250 g, 1 mmol) were added to a custom-made 2″ by $\frac{1}{2}$″ screw capped stainless steel vial along with a 3/16″ inch stainless steel ball bearing. The vial was placed in an 8000 M Spex Certiprep mixer/mill and the contents were ball milled for 2 h. The resulting mixture was dissolved in ethyl acetate (15 mL) and washed with H_2O (3 × 15 mL). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. This afforded di-(4-bromobenzyl) carbonate in a 74% conversion.

Acknowledgements

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