

## Article

# One-Pot, Metal-Free Synthesis of Dimethyl Carbonate from CO<sub>2</sub> at Room Temperature

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**Abstract:** Herein, we report on the metal-free, one-pot synthesis of industrially important dimethyl carbonate (DMC) from molecular CO<sub>2</sub> under ambient conditions. In this process, initially the CO<sub>2</sub> was chemisorbed through the formation of a switchable ionic liquid (SIL), [DBUH] [CH<sub>3</sub>CO<sub>3</sub>], by the interaction of CO<sub>2</sub> with an equivalent mixture of organic superbase 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) and methanol. The obtained SIL further reacted with methyl iodide (CH<sub>3</sub>I) to form DMC. The synthesis was carried out in both dimethyl sulfoxide (DMSO) and methanol. Methanol is preferred, as it not only served as a reagent and solvent in CO<sub>2</sub> capture and DMC synthesis, but it also assisted in controlling the side reactions between chemical species such as CH<sub>3</sub>I and [DBUH]<sup>+</sup> cation and increased the yield of DMC. Hence, the use of methanol avoided the loss of captured CO<sub>2</sub> and favored the formation of DMC with high selectivity. Under the applied reaction conditions, 89% of the captured CO<sub>2</sub> was converted to DMC. DBU was obtained, achieving 86% recovery of its salts formed during the synthesis. Most importantly, in this report we describe a simple and renewable solvent-based process for a metal-free approach to DMC synthesis under industrially feasible reaction conditions.

**Keywords:** carbon dioxide to chemicals; dimethyl carbonate; switchable ionic liquid; organic superbase; methanol

## 1. Introduction

Dimethyl carbonate (DMC) is a commercially important organic carbonate, considering its valuable and widespread industrial applications. DMC has attracted much attention from researchers at both the academic and industrial levels, as it is an important and environmentally friendly precursor for phosgene-free polycarbonate synthesis, whereas polycarbonates are extensively used in construction materials, automobiles, and certain medical devices [1,2]. Additionally, due to its high dielectric constant, DMC is also used as an electrolyte in lithium ion batteries and could emerge as a sustainable alternative to fossil fuels [3]. As a result of having a high oxygen content (53%), high octane number, high biodegradability, and low toxicity, DMC is considered to be an efficient and alternative fuel additive compared to the environmentally hazardous methyl tert-butyl ether [4]. Hence, due to DMC's various green and sustainable applications, the annual demand for this chemical has increased rapidly during the past decade. Therefore, several industrially applied processes produce enormous amounts of DMC every year.

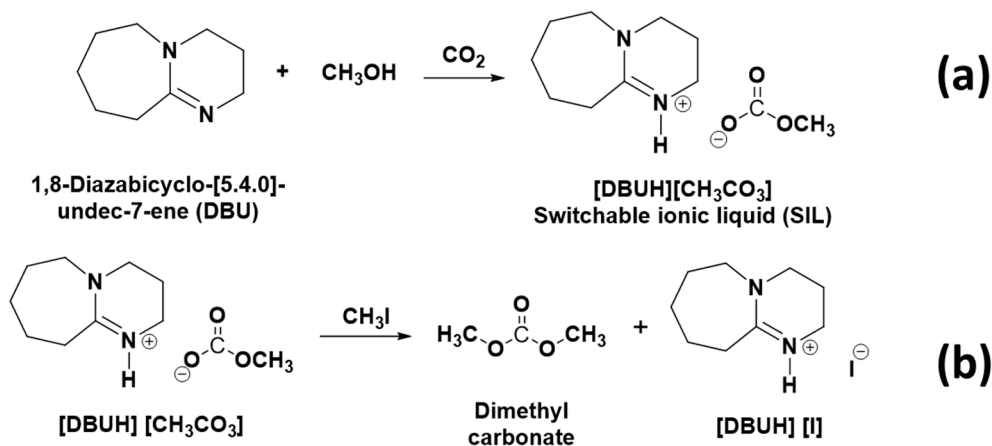
Until now, several catalytic routes have been applied in order to synthesize DMC, whereby phosgenation, transesterification, oxidative carbonylation, and urea methanolysis have been extensively studied and industrially applied [4–7]. However, these catalytic routes are accompanied by the use of

toxic raw materials or catalytic deactivation, or are less selective and reactive in nature. These are the main challenges that still remain in developing more industrially feasible processes. The conversion of CO<sub>2</sub> to alkyl carbonates such as linear and cyclic carbonates can be considered a sustainable approach, since CO<sub>2</sub> is widely known as a renewable, cheap, and safe C<sub>1</sub> source. Simultaneously, the use of CO<sub>2</sub> avoids the possible risk of explosion, since the process does not include the combination of CO and O<sub>2</sub>, as in other synthetic approaches. Apart from this, considering the negative consequences of CO<sub>2</sub> on the environment, such as global warming, the conversion of CO<sub>2</sub> into fuels and fine chemicals is an attractive solution to many challenges related to energy and the environment [8]. As such, the direct conversion of CO<sub>2</sub> to DMC has been carried out using various types of catalytic reaction approaches, despite certain thermodynamic and kinetic limitations [9]. Metal oxides such as ZrO<sub>2</sub> and CeO<sub>2</sub> were found to be active catalysts in DMC synthesis. After detailed studies, it was concluded that having both acid and base sites and the special redox properties of ZrO<sub>2</sub> and CeO<sub>2</sub> assisted the selective synthesis of DMC and diethyl carbonate (DEC) in a direct CO<sub>2</sub> conversion route [10–12]. Metal-oxide-supported organotin catalysts with dehydrating agents and metal-oxide-supported hetero-polyacids have also been successfully applied in DMC synthesis [13–15]. However, considering the chemical inertness of CO<sub>2</sub> (even after applying a high-temperature and high-pressure reaction approach), catalyst deactivation, as well as hydrolysis of DMC by co-produced water (causing low yield), these catalytic systems are still less attractive for DMC synthesis. Besides the direct conversion of CO<sub>2</sub> to DMC, a two-step synthesis approach was also invented, whereby synthesis of DMC is carried out using reagents such as olefin–ethylene oxide, methanol, and CO<sub>2</sub> [4]. As such, several catalytic routes such as epoxide, chlorohydrin, and isobutene–epoxide were applied in DMC synthesis. Even though these synthesis approaches have been industrially applied in DMC synthesis, the synthesis of epoxides from olefins and subsequent conversion to cyclic carbonates is accompanied by the use of toxic or costly reagents, and also involves potential explosion hazards and a tedious work-up process for product separation.

Methyl iodide (CH<sub>3</sub>I) and potassium metals containing base catalysts such as K<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>OK, or KOH were also successfully applied in the direct conversion of CO<sub>2</sub> to DMC, whereupon the applied reaction conditions were milder than in the case of the previously discussed catalyzed processes [16,17]. In this case, the previous studies explained that the methyl carbonate anion formed after interaction between the basic catalyst, methanol, and molecular CO<sub>2</sub>, which further interacted equivalently with CH<sub>3</sub>I upon formation of DMC. After mechanistic studies, it was confirmed that CH<sub>3</sub>I played a role as a reagent in a similar way to methanol in DMC synthesis instead of as a promotor, while the base assisted in the activation of methanol molecules [15]. Even though this base-catalyzed direct CO<sub>2</sub> conversion approach emerged as an alternative to metal-oxide- and organotin-catalyzed processes, the catalyst deactivation and loss of the methoxide anion to the dimethyl ether (DME) as a byproduct caused the low reaction yield. Catalyst deactivation occurs during the course of the reaction, where hydrogen iodide formed in situ reacts with metal carbonates and forms corresponding metal iodides. This metal-carbonate-based reaction approach was also highly pressure-dependent, whereby the optimum yield of DMC was obtained at 40–60 bar of applied CO<sub>2</sub> pressure. In this regard, a high-pressure reaction was carried out to suppress DME formation. Recently, another CH<sub>3</sub>I-promoted and CH<sub>3</sub>OK-catalyzed approach has been applied for DMC synthesis, whereby various dehydrating agents were used to improve the yield of DMC through removal of water formed in situ. However, a mere 43% yield of DMC was obtained at 80 °C and under 40 bar of CO<sub>2</sub> pressure [18].

Switchable ionic liquids (SILs) are a special class of ionic liquids, whose synthesis is usually proceeded by capture of the acid gases [19–21]. The synthesis of SILs is not only a fascinating process in terms of acid gas capture and storage at ambient conditions, but it also introduces a new and efficient solvent system for organic synthesis and biomass processing, such as wood delignification [22,23]. In SIL synthesis, an equimolar mixture of organic superbases such as phosphazenes, amidines, or guanidines as well as proton sources such as alcohols, alkanolamines, or water interacts with acid gases such as CO<sub>2</sub> or SO<sub>2</sub> [24–26]. In this study, for the first time we report the transformation of

chemisorbed  $\text{CO}_2$  in the form of SIL to DMC by mimicking the previously discussed  $\text{CH}_3\text{I}$ -involved, base-catalyzed reaction approach. In contrast to previous  $\text{CH}_3\text{I}$ -involved processes, DMC synthesis in this report was carried out at ambient reaction conditions by implementing a single-solvent system such as methanol. As shown in the reaction Scheme 1, upon the actual synthesis, an equivalent mixture of organic superbase such as DBU and methanol activates  $\text{CO}_2$  and the obtained [DBUH]  $[\text{CH}_3\text{CO}_3]$ , i.e., SIL further interacts with an equivalent amount of  $\text{CH}_3\text{I}$  to form DMC. In this report, we described the synthetic protocol for DMC in terms of type of solvent, amount of  $\text{CH}_3\text{I}$ , reaction time, recovery of DBU, etc. The progress as well as the amount of chemical species formed in the reaction mixture were monitored and explained by means of nuclear magnetic resonance (NMR) spectroscopy analysis.



**Scheme 1.** Synthesis of (a) switchable ionic liquid, [DBUH]  $[\text{CH}_3\text{CO}_3]$ , and (b) dimethyl carbonate,  $(\text{CH}_3\text{O})_2\text{CO}$ .

## 2. Materials and Methods

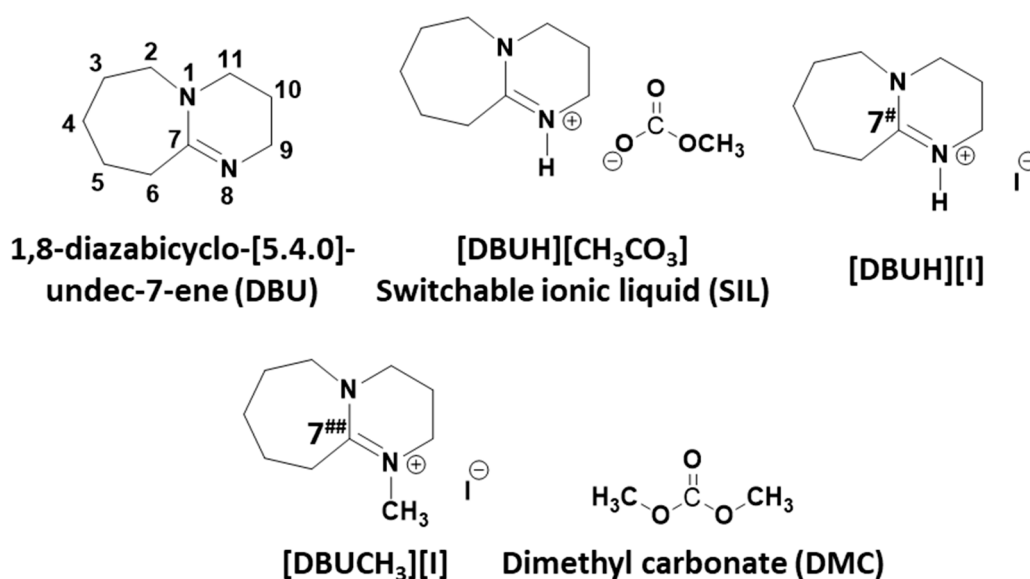
### 2.1. Chemicals and Methods

#### 2.1.1. Chemicals

Methyl iodide (99.5%), 1,8-Diazabicyclo-[5.4.0]-undec-7-ene (DBU, 99.0%),  $\text{D}_2\text{O}$  (99.9 atom% D), and  $\text{CDCl}_3$  (99.96 atom% D) were purchased from Sigma Aldrich, while methanol ( $\geq 99.0\%$ ) and dimethyl sulfoxide ( $\geq 99.0\%$ ) were purchased from VWR chemicals. All the purchased chemicals were used further without purification. A  $\text{CO}_2$  gas bottle was obtained from AGA AB (Linde Group, Sweden) and used without further purification.

#### 2.1.2. NMR Analysis

The composition of the reaction mixtures was confirmed by NMR analysis using a Bruker Avance 600 MHz spectrometer operated at  $^1\text{H}$  and  $^{13}\text{C}$  frequencies of 600.17 and 150.91 MHz, respectively. NMR analyses were carried out in different solvents such as with crude reaction mixture and glass capillary filled with  $\text{D}_2\text{O}$  or in neat  $\text{D}_2\text{O}$  or  $\text{CDCl}_3$ . NMR data were further processed with TopSpin 3.2 software. After conducting the NMR analysis, the chemical species that were identified in the reaction composition for DMC synthesis process are shown in Figure 1.



**Figure 1.** Chemical species used and formed during DMC synthesis.

## 2.2. Synthesis of DMC with and without DMSO Solvent

### 2.2.1. Synthesis of SIL [DBUH] [CH<sub>3</sub>CO<sub>3</sub>]

SIL, i.e., [DBUH] [CH<sub>3</sub>CO<sub>3</sub>], was synthesized by the interaction of CO<sub>2</sub> with DBU (0.75 mL, 4.9 mmol) and methanol (0.2 mL, 4.9 mmol) in DMSO solvent (4 mL). During the actual synthesis, CO<sub>2</sub> gas (100 mL/min) was bubbled under stirring, at room temperature, in DMSO solution containing equimolar amounts of DBU and methanol for 20 min. In the DMSO-free reaction mixture, CO<sub>2</sub> gas was bubbled in alcoholic solutions of DBU (25 or 50 vol.% of DBU in methanol, 0.5 mL or 1 mL of DBU in 1.5 or 1 mL of methanol, respectively), at room temperature for 20 min. In all cases, pale yellow colored clear solutions were obtained, and their compositions were further confirmed by NMR analyses.

### 2.2.2. Synthesis of DMC

In this synthesis, the reaction mixtures with different reaction compositions were used in order to improve the yield of DMC. In these regards, in the first approach DMC synthesis was accomplished with addition of CH<sub>3</sub>I (based on equivalents of DBU) to DMSO solution containing SIL. In another reaction approach, the DMSO solution containing SIL was diluted initially with different amounts of methanol, and then CH<sub>3</sub>I was added to initiate the formation of DMC. Finally, in the case of DMSO-free synthesis, the CH<sub>3</sub>I was added to the alcoholic solution of SIL containing different amounts of methanol. As per requirement, in all reaction approaches, the reactions were quenched after the desired period, and the progress of the reaction was monitored by NMR analysis. All experiments for DMC synthesis were carried out at room temperature. In all experiments, CH<sub>3</sub>I was added in amounts ranging from 1 to 5 equivalents based on the amount of DBU used in the reaction mixture.

### 2.2.3. Separation of DBU Salts from the Reaction Mixture

The DBU salts, namely [DBUH] [I] and [DBUCH<sub>3</sub>] [I], formed during DMC synthesis were separated from the reaction mixture in order to facilitate the recovery of DBU. Upon actual separation, these DBU salts were precipitated after addition of ethyl acetate in the reaction mixture. Prior to ethyl acetate addition, NMR analysis was carried out to ensure complete conversion of the [CH<sub>3</sub>CO<sub>3</sub>]<sup>−</sup> anion. The obtained mixture of white salts was further separated from the reaction mixture by filtration and washed 2–3 times with ethyl acetate. Next, this mixture was dried under high vacuum, at room temperature, and was further analyzed by means of NMR spectroscopy whereupon either D<sub>2</sub>O or CDCl<sub>3</sub> was used as the internal reference.

#### 2.2.4. Recovery of DBU from DBU Salts ([DBUH] [I] and [DBUCH<sub>3</sub>] [I])

DBU was recovered from [DBUH] [I] and [DBUCH<sub>3</sub>] [I] salt mixtures by using alkaline NaCl-saturated aqueous solution following a previously reported procedure [27,28]. Initially, NaCl saturated aqueous solution was prepared by mixing NaCl in water under stirring, and the required amount of solution was taken to make 4 wt% solution of NaOH in NaCl-saturated solution. The mixture of DBU salts comprising [DBUH] [I] and [DBUCH<sub>3</sub>] [I] was added to the alkaline solution of NaCl, and the reaction mixture was further stirred for 30 min at room temperature. Ethyl acetate was used further to extract DBU from the aqueous phase, whereby DBU was further obtained through the removal of ethyl acetate from the organic phase. The purity of the as-recovered DBU was confirmed by means of NMR analysis, whereas the recovery percentage (weight %) of DBU was calculated from its recovered amount and the initial amount used for CO<sub>2</sub> capture in the reaction.

#### 2.2.5. Amount of Chemical Species in the Reaction Mixture

The synthesis of DMC was accompanied with the formation of methanol in situ as well as consumption of [CH<sub>3</sub>CO<sub>3</sub>]<sup>−</sup> anions. The formation of methanol during the reaction is discussed in the following sections. Quantification (in %) of DMC, methanol, and [CH<sub>3</sub>CO<sub>3</sub>]<sup>−</sup> anions in the mixture was carried out using <sup>13</sup>C NMR analysis. Equations (1)–(3) were used to calculate the amount of DMC, methanol, and [CH<sub>3</sub>CO<sub>3</sub>]<sup>−</sup> anions in the reaction mixture, respectively. *I*<sub>(DMC)</sub>, *I*<sub>(methanol)</sub>, and *I*<sub>(CH<sub>3</sub>CO<sub>3</sub><sup>−</sup>)</sub> represent the integrated value of the carbon atom in the methyl groups of these chemical species in <sup>13</sup>C NMR spectra. The equations were applied as such for the reactions carried out in DMSO solvent. However, in the case of DMSO-free reactions, i.e., where methanol was used as the reagent as well as solvent, the alternative value for methanol was the integrated value of the methyl group in the [DBUCH<sub>3</sub>] [I] salt.

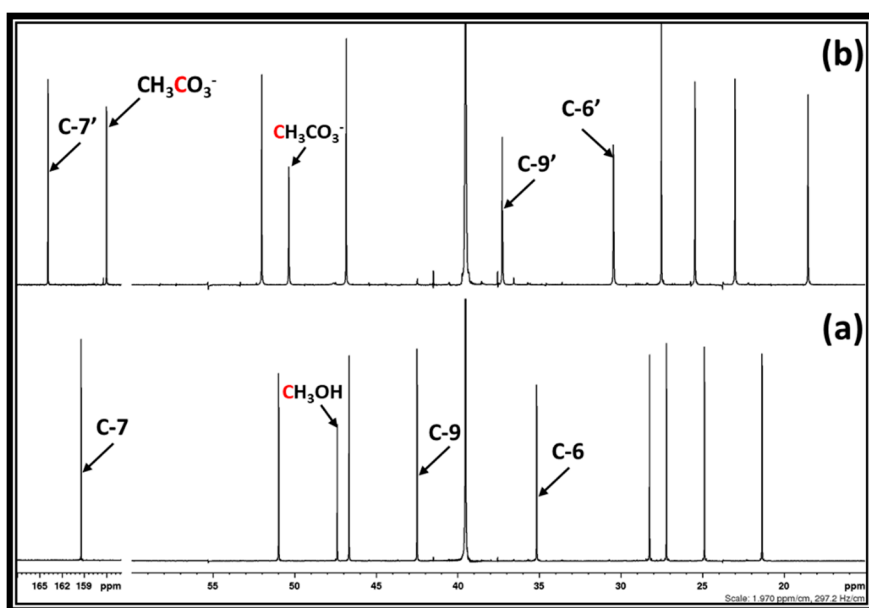
$$\% \text{DMC} = \frac{[I(\text{DMC})/2] \times 100}{I(\text{DMC})/2 + I(\text{CH}_3\text{OH}) + I(\text{CH}_3\text{CO}_3^-)} \quad (1)$$

$$\% \text{CH}_3\text{OH} = \frac{I(\text{CH}_3\text{OH}) \times 100}{I(\text{DMC})/2 + I(\text{CH}_3\text{OH}) + I(\text{CH}_3\text{CO}_3^-)} \quad (2)$$

$$\% \text{CH}_3\text{CO}_3^- = \frac{I(\text{CH}_3\text{CO}_3^-) \times 100}{I(\text{DMC})/2 + I(\text{CH}_3\text{OH}) + I(\text{CH}_3\text{CO}_3^-)} \quad (3)$$

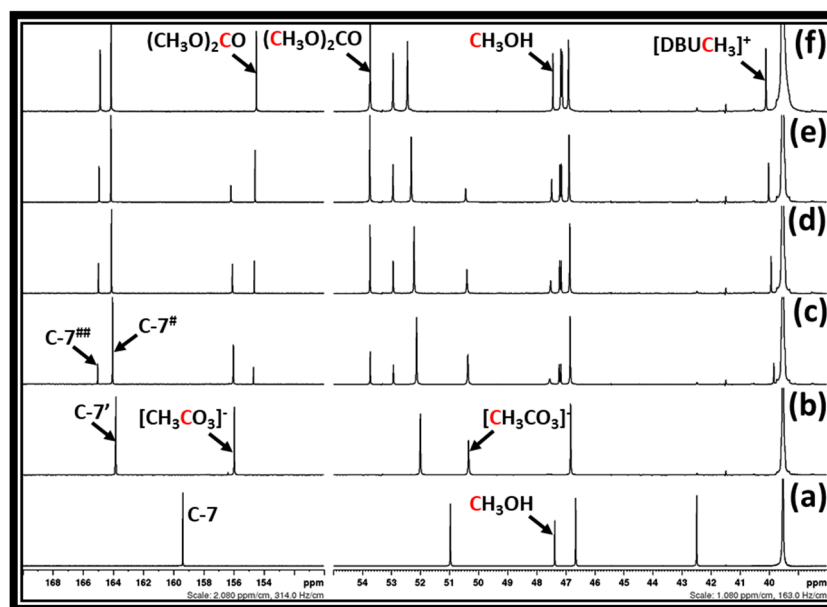
### 3. Results and Discussion

Being chemically inert, CO<sub>2</sub> was initially activated via the synthesis of SIL, which is considered as a well-practiced process for the capture of CO<sub>2</sub>. In a consecutive step, the obtained SIL further reacted with CH<sub>3</sub>I to form DMC. In order to achieve the maximum yield upon DMC synthesis, reaction parameters such as the type of solvent system, amount of CH<sub>3</sub>I, and reaction time were examined. In case of variations in the solvent system, the two-step DMC synthesis approach mentioned in the reaction Scheme 1 was carried out. Initially, this was tried in the DMSO solvent and further explored in a similar synthesis protocol in methanol. In the case of SIL, i.e., [DBUH] [CH<sub>3</sub>CO<sub>3</sub>] synthesis, after bubbling the CO<sub>2</sub> in the DMSO solution of DBU and methanol, the composition of the obtained pale-yellow solution was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR analysis. As shown in Figure 2, the carbon atoms at position 6 and 9, respectively, in DBU were shielded by 5–6 ppm, whereas the peak for carbon at position 7 was de-shielded by 5 ppm after CO<sub>2</sub> capture. In addition, the peak at chemical shift 47.44 ppm for the methyl group disappeared, corresponding to methanol, and new peaks for the methyl group and the carbonyl carbon in the [CH<sub>3</sub>CO<sub>3</sub>]<sup>−</sup> anion appeared at 50.06 and 155.97 ppm, respectively. This confirmed the formation of SIL, i.e., [DBUH] [CH<sub>3</sub>CO<sub>3</sub>], after interaction of DBU and methanol with CO<sub>2</sub>. Regarding the <sup>1</sup>H NMR spectrum, it also confirmed the formation of SIL since changes in the chemical shifts for the protons, especially at positions 6 and 9, were observed in the case DBU, and a new peak for the protons in the methyl group of [CH<sub>3</sub>CO<sub>3</sub>]<sup>−</sup> anion was also observed (Figure S1).



**Figure 2.**  $^{13}\text{C}$  NMR for the synthesis of [DBUH] [CH<sub>3</sub>CO<sub>3</sub>] from DBU, methanol, and CO<sub>2</sub> in DMSO. (a) DBU and CH<sub>3</sub>OH, and (b) [DBUH] [CH<sub>3</sub>CO<sub>3</sub>] (NMR analysis with D<sub>2</sub>O capillary).

As shown in the reaction Scheme 1, after the synthesis of SIL, CH<sub>3</sub>I was added to the DMSO solution of SIL to synthesize DMC. In this case, in order to gain insight into the progress of the reaction, CH<sub>3</sub>I was added as 0.25, 0.5, 0.75, and 1 equivalents based on the amount of DBU used previously during the SIL synthesis. After 15 min of reaction time, for each and every reaction, the reaction mixture was further analyzed by  $^{13}\text{C}$  NMR analysis, and the obtained spectra are shown in Figure S2 and Figure 3, respectively.

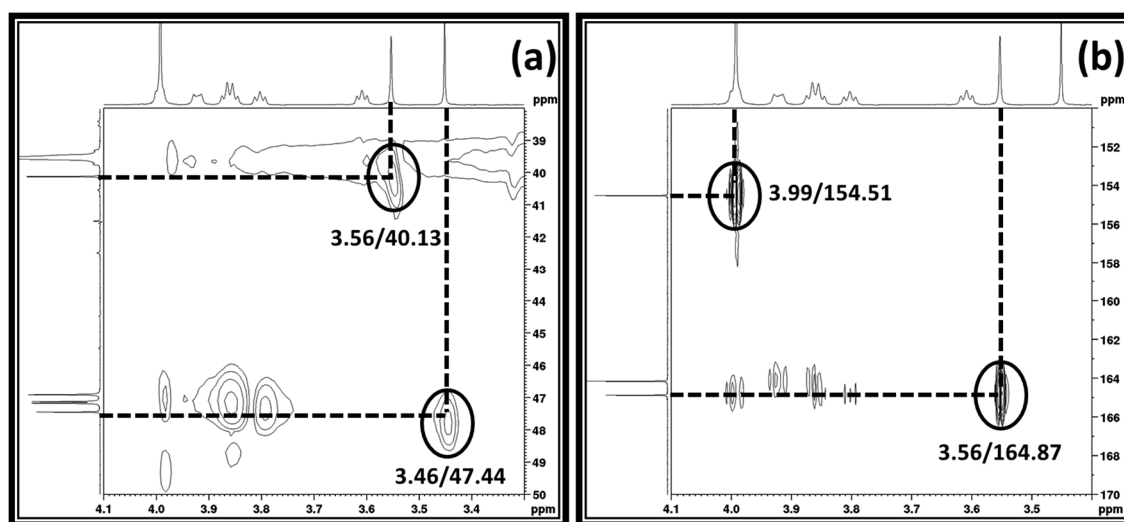


**Figure 3.**  $^{13}\text{C}$  NMR for the synthesis of DMC from [DBUH] [CH<sub>3</sub>CO<sub>3</sub>] and CH<sub>3</sub>I in DMSO. (a) DBU and methanol, (b) [DBUH] [CH<sub>3</sub>CO<sub>3</sub>], reaction mixture after addition of (c) 0.25, (d) 0.50, (e) 0.75, and (f) 1 equivalents of CH<sub>3</sub>I in DMSO solution of [DBUH] [CH<sub>3</sub>CO<sub>3</sub>] (NMR analysis with D<sub>2</sub>O capillary).



As shown in Figure 3, after addition of different equivalents of  $\text{CH}_3\text{I}$  to the reaction mixture, the peaks belonging to the methyl group and carbonyl carbon in the  $[\text{CH}_3\text{CO}_3]^-$  anion, at the chemical shifts 30.45 and 155.98 ppm, respectively, steadily decreased. On the other hand, new peaks appeared at the chemical shifts 40.09, 47.44, 53.74, 154.51, 164.15, and 164.87 ppm, respectively, whereby the intensities of these peaks increased with increasing amounts of  $\text{CH}_3\text{I}$ . As observed during the synthesis of SIL, the peak with the chemical shift 47.44 ppm is related to the methyl group of methanol. Further, after comparing the NMR spectra of both reaction mixtures (with addition of 1 eq.  $\text{CH}_3\text{I}$ ) and commercially available DMC, signals at 53.74 and 154.51 ppm, respectively, belonging to the carbon atoms in  $\text{CH}_3$ - and carbonyl group of the DMC were observed (Figure S2). Hence, as mentioned in the proposed reaction Scheme 1, it is possible to synthesize DMC after the synthesis of SIL followed by its equivalent interaction with  $\text{CH}_3\text{I}$ .  $^1\text{H}$  NMR spectra of the reaction mixture also confirmed the formation of DMC in the reaction mixture. Similar to the case of  $^{13}\text{C}$  NMR analysis, upon an increase in the amount of  $\text{CH}_3\text{I}$ , the amount of DMC steadily increased (Figures S3 and S4). Simultaneously, the peak intensity for the free protons of the methyl group in methanol, at 3.45 ppm, along with an unknown signal at 3.55 ppm, also increased in the reaction mixture upon increasing the amount of  $\text{CH}_3\text{I}$ . In order to identify the unknown peaks in both  $^1\text{H}$  and  $^{13}\text{C}$  NMR, as well as to gain insights into the formation of methanol in the reaction mixture, two-dimensional NMR (2D NMR) analysis of the reaction mixture was carried out further.

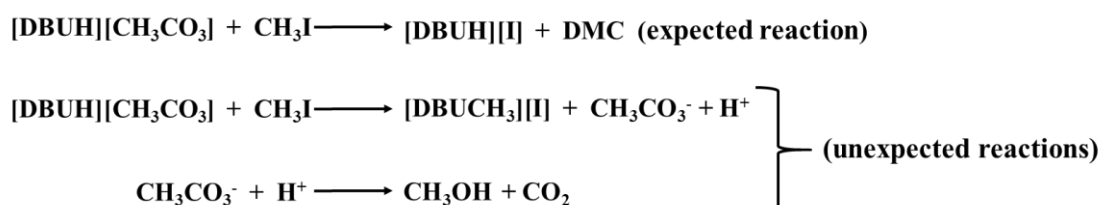
In Figure 4a, the correlation peak observed in the HSQC analysis at 3.46/47.44 ppm belongs to the methyl group of methanol; hence, as shown in  $^1\text{H}$  and  $^{13}\text{C}$  NMR previously, 2D NMR also confirmed that a free methanol molecule formed during DMC synthesis. Usually, interaction of SIL with protic acids is the pathway for the room temperature decomposition of  $[\text{CH}_3\text{CO}_3]^-$  anions upon regeneration of methanol through the release of  $\text{CO}_2$ . This was further confirmed by the equivalent interaction of para-toluene sulfonic acid and SIL in a DMSO solution. After the addition of acid in the DMSO solution of SIL,  $\text{CO}_2$  bubbles were suddenly released in the reaction mixture, and the formation of methanol was confirmed by  $^1\text{H}$  NMR analysis (Figure S5). Hence, during DMC synthesis, it seems that the acidic moieties formed in-situ in the reaction mixture, thus allowing further decomposition of the  $[\text{CH}_3\text{CO}_3]^-$  anion in the SIL composition.



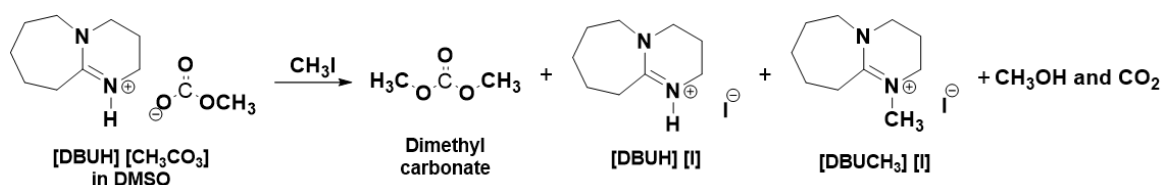
**Figure 4.** 2D NMR analysis of the reaction mixture after interaction of  $[\text{DBUH}] [\text{CH}_3\text{CO}_3]$  with  $\text{CH}_3\text{I}$  in DMSO, (a)  $^1\text{H}$ - $^{13}\text{C}$  HSQC, and (b)  $^1\text{H}$ - $^{13}\text{C}$  HMBC (NMR analysis with  $\text{D}_2\text{O}$  capillary).

The unknown peak at chemical shift 3.56 ppm appeared as a singlet and showed an integration value identical to that of the methyl group in methanol. Thus, it seems that the unknown peak at this position belongs to the methyl group. Further, it was also observed that this methyl group showed correlation peaks at 3.56/40.13 and 3.56/164.87 ppm in HSQC and HMBC analyses, respectively

(Figure 4). As shown in both  $^1\text{H}$  and  $^{13}\text{C}$  NMR analyses, two types of DBU salts formed in the reaction mixture after addition of 1 eq. of  $\text{CH}_3\text{I}$  in the reaction mixture (Supplementary Materials S2 and S4). The peaks for the carbon atoms at position 7 (i.e., C-7) in these two salts appeared at 164.15 and 164.87 ppm, respectively, in the  $^{13}\text{C}$  NMR spectra. One of the two DBU salts is protonated (i.e.,  $[\text{DBUH}]^+[\text{I}]^-$ ) since DMC formed in the reaction mixture as shown in the reaction Scheme 1b. Further, since the newly appearing methyl group at the chemical shift 3.56 ppm has a long range coupled with the carbon atom C-7 at chemical shift 164.87 ppm in HMBC spectra, the peak appearing at 164.17 ppm belongs to the C-7 atom in the  $[\text{DBUH}]^+[\text{I}]^-$ . In other words, apart from the formation of  $[\text{DBUH}]^+[\text{I}]^-$ , the methylated salt of DBU (i.e.,  $[\text{DBUCH}_3]^+[\text{I}]^-$ ) also formed in the reaction mixture during DMC synthesis, whereby the  $\text{CH}_3^-$  group (3.56 ppm) was attached to the  $sp^2$ -hybridized N atom of DBU. The peaks for the C-7 atoms obtained at chemical shifts 164.15 and 164.87 ppm in the protonated and methylated DBU, respectively, are shown as C-7 $^\#$  and C-7 $^\#\#$  in  $^{13}\text{C}$  NMR spectra (Figure 3). Hence, during the synthesis of DMC, a part of  $\text{CH}_3\text{I}$  reacted with the  $[\text{DBUH}]^+[\text{I}]^-$  cation of the SIL through an interaction between the  $\text{CH}_3$  group and  $sp^2$ -hybridized N atom to form  $[\text{DBUCH}_3]^+[\text{I}]^-$  (reaction Scheme 2). In this case, an equivalent number of protons was released in the reaction mixture, which subsequently decarboxylated  $[\text{CH}_3\text{CO}_3]^-$  anions of the SIL to facilitate the formation of methanol and  $\text{CO}_2$ . Hence, under the used reaction compositions and applied reaction conditions, as shown in the reaction Schemes 2 and 3, the  $[\text{CH}_3\text{CO}_3]^-$  anion is distributed to DMC and methanol.



Scheme 2. Main and possible side reactions during DMC synthesis.

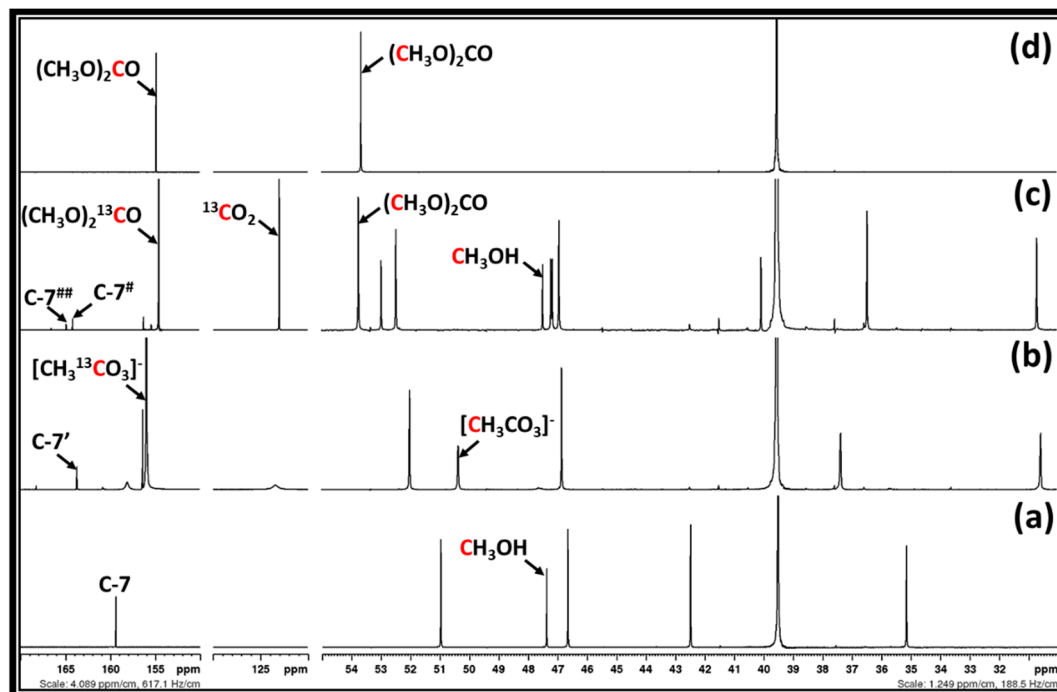


Scheme 3. Synthesis of DMC in DMSO along with formation of  $[\text{DBUH}]^+[\text{I}]^-$ ,  $[\text{DBUCH}_3]^+[\text{I}]^-$ ,  $\text{CH}_3\text{OH}$ , and  $\text{CO}_2$ .

Further, in order to confirm that the captured  $\text{CO}_2$  during SIL synthesis became a part of DMC, labeled  $\text{CO}_2$  (i.e.,  $^{13}\text{C}$ -enriched  $\text{CO}_2$  (tracer technique)) was used during the two-step DMC synthesis process. The existence of  $^{13}\text{C}$ -enriched  $\text{CO}_2$  in SIL as well as DMC was further confirmed by  $^{13}\text{C}$  NMR and HMBC analyses, respectively. As shown in Figure 5b, SIL formed after the reaction of DBU and methanol with  $^{13}\text{C}$ -enriched  $\text{CO}_2$ , and the high-intensity peak for the carbonyl carbon in  $[\text{CH}_3\text{CO}_3]^-$  anion was observed at the chemical shift of 154.56 ppm. After an addition of  $\text{CH}_3\text{I}$  in the DMSO solution of SIL, the high-intensity peak for the carbonyl carbon atom in DMC was observed, and this was further confirmed with the help of  $^{13}\text{C}$  NMR of the commercially available DMC (Figure 5c,d). Being  $^{13}\text{C}$ -enriched, the intensities of the peaks for the carbonyl carbon atoms in both  $[\text{CH}_3\text{CO}_3]^-$  and DMC were found significantly higher than the corresponding intensities of the C-7', C-7 $^\#$ , and C-7 $^\#\#$  in DBU cations formed in the reaction mixture. On the other hand, as shown in Figure 3, the intensity of the peak for the carbonyl carbon was comparable with the intensities of these  $sp^2$ -hybridized carbons in the DBU cation when no  $^{13}\text{C}$ -enriched  $\text{CO}_2$  was used. Further, HMBC analysis also revealed that a correlation peak was observed for the protons of the methyl group and  $^{13}\text{C}$ -enriched carbonyl carbon atom in DMC (Figure S6a). In addition, due to having a  $^{13}\text{C}$ -enriched carbon atom, the doublet peak was observed for the protons for the methyl group in DMC, whereas when no  $^{13}\text{C}$ -enriched  $\text{CO}_2$  was



used, a singlet peak was observed for these protons (Figure S6b) [29]. Therefore, these above-mentioned NMR analysis studies revealed that the  $^{13}\text{C}$ -enriched  $\text{CO}_2$  became a part of DMC formed after the reaction of  $^{13}\text{CO}_2$  enriched SIL with  $\text{CH}_3\text{I}$ . Hence, it can be concluded that DMC can be synthesized from  $\text{CO}_2$  following a two-step synthetic approach, mentioned in the reaction Scheme 1.



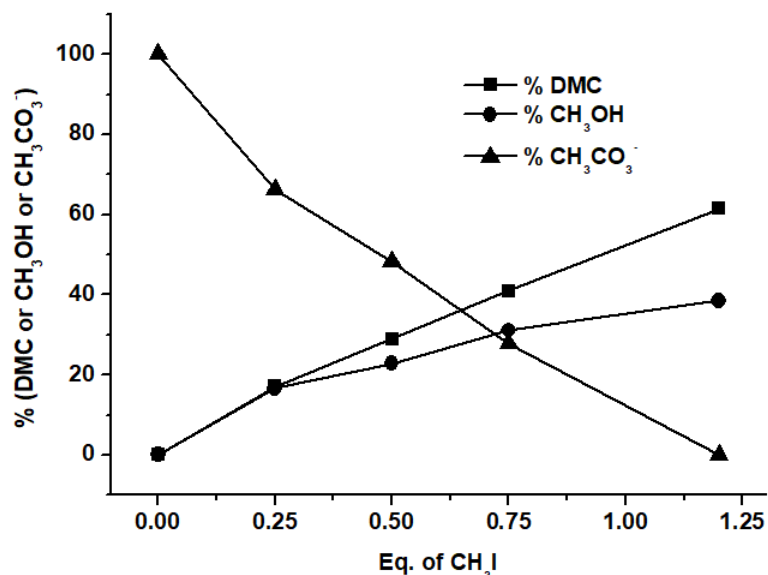
**Figure 5.**  $^{13}\text{C}$  NMR for the synthesis of DMC from [DBUH]  $[\text{MeCO}_3]$  and MeI in DMSO. (a) DBU and methanol, (b) SIL, [DBUH]  $[\text{CH}_3^{13}\text{CO}_3]$ , (c) reaction mixture after addition of 1 eq. of  $\text{CH}_3\text{I}$  in DMSO solution of [DBUH]  $[\text{CH}_3^{13}\text{CO}_3]$ , and (d) commercially available DMC (NMR analysis with  $\text{D}_2\text{O}$  capillary).

Besides confirming the origin of carbonyl carbon in DMC, in the  $^{13}\text{C}$  NMR spectra of the reaction mixture, the peak for molecular  $\text{CO}_2$  at 123.01 ppm was also observed (Figure 5c) [30]. Hence, as shown in the reaction Scheme 3, this control experiment further proved that  $\text{CO}_2$  was released in the reaction mixture through the decomposition of  $[\text{CH}_3\text{CO}_3]^-$  anions upon DMC synthesis.

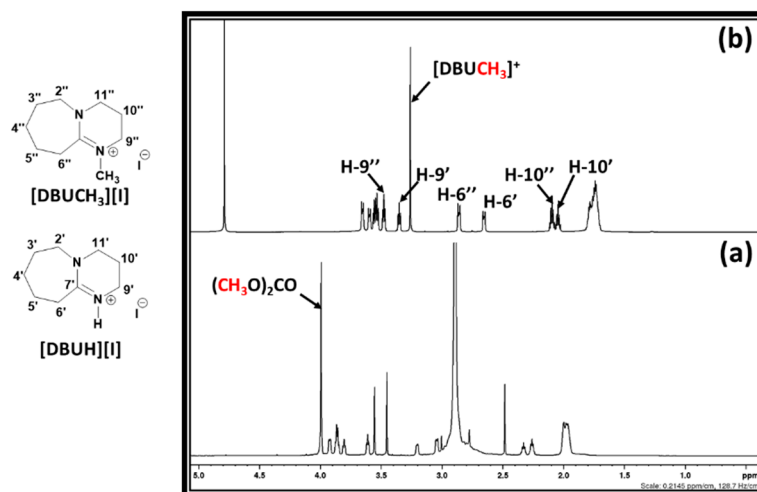
The amounts (%) of DMC, methanol, and  $[\text{CH}_3\text{CO}_3]^-$  anions in the reaction mixture after each addition of  $\text{CH}_3\text{I}$  were calculated using Equations (1)–(3), respectively. As described in the experimental section, the equations correspond to the integrated peak area of the carbon atom in the methyl group of these chemical species obtained from the  $^{13}\text{C}$  NMR spectra. The number of  $[\text{CH}_3\text{CO}_3]^-$  anions was also taken into consideration because both DMC and methanol formed upon consumption of the  $[\text{CH}_3\text{CO}_3]^-$  anion (reaction Scheme 2). Representative integrations of the required signals in  $^{13}\text{C}$  NMR spectra are shown in Figure S7. The obtained values for the amounts of DMC, methanol, and  $[\text{CH}_3\text{CO}_3]^-$  anions after calculation are shown in Figure 6.

After sequential addition of  $\text{CH}_3\text{I}$  in DMSO solution of SIL, the number of  $[\text{CH}_3\text{CO}_3]^-$  anions steadily decreased and were completely consumed after addition of 1 eq. of  $\text{CH}_3\text{I}$ . At the same time, the amounts of both DMC and methanol increased and reached values corresponding to 62 and 38% in the reaction mixture, respectively. In this case, it seems that as a result of the direct interaction between  $\text{CH}_3\text{CO}_3^-$  anions and  $\text{CH}_3\text{I}$ , a higher amount of DMC can be obtained. On the other hand, methanol synthesis possibly proceeds through a three-step process, namely interaction of  $\text{CH}_3\text{I}$  with  $\text{DBUH}^+$ , intermolecular proton transfer, and decarboxylation of  $[\text{CH}_3\text{CO}_3]^-$  anions to methanol. These intermediate steps might have slowed down the formation of methanol compared to DMC. Further, after addition of 1 eq. of  $\text{CH}_3\text{I}$  and complete conversion of  $[\text{CH}_3\text{CO}_3]^-$  anions, the reaction mixture was

added to the ethyl acetate, and the thus-obtained white solid was analyzed by  $^1\text{H}$  NMR analysis after separation from the reaction mixture. As shown in Figure 7, the NMR spectra confirm that the obtained white solid is a physical mixture of iodide salts of protonated and methylated DBU, i.e.,  $[\text{DBUH}]^+ [\text{I}]^-$  and  $[\text{DBUCH}_3]^+ [\text{I}]^-$ . The occurrence of  $[\text{DBUCH}_3]^+ [\text{I}]^-$  in the mixture of salts was also confirmed by HMBC analysis (Figure S8).



**Figure 6.** Amounts (%) of DMC,  $\text{CH}_3\text{OH}$ , and  $\text{CH}_3\text{CO}_3^-$  anions in the reaction mixture after addition of different amounts of  $\text{CH}_3\text{I}$ .

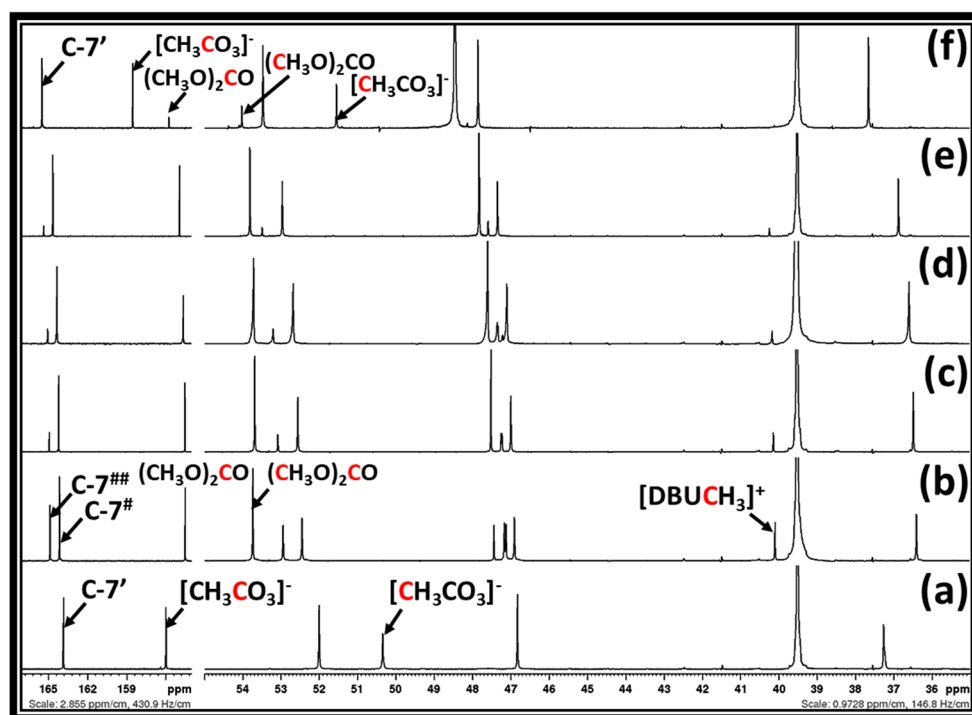


**Figure 7.**  $^1\text{H}$  NMR spectra (a) reaction mixture with 1 eq.  $\text{CH}_3\text{I}$  added (NMR analysis with capillary filled with  $\text{D}_2\text{O}$ ), and (b) mixture of DBU salts, i.e.,  $[\text{DBUH}]^+ [\text{I}]^-$  and  $[\text{DBHCH}_3]^+ [\text{I}]^-$  (NMR analysis with  $\text{D}_2\text{O}$ ).

Hence, as shown in the reaction Scheme 1, DMC formed after equivalent interaction between SIL and  $\text{CH}_3\text{I}$ . In this case, even though  $\text{CO}_2$  is a chemically inert species, the highly basic (Brønsted base) characteristics of DBU further facilitated the activation of  $\text{CO}_2$  under ambient reaction conditions. Further,  $\text{CH}_3\text{I}$  has negligible steric hindrance, and since  $\text{I}^-$  is a good leaving group, its interaction with the  $[\text{DBUH}]^+$  cation and  $[\text{CH}_3\text{CO}_3]^-$  anion of the SIL was further promoted. Hence, as a result of having the reagents with these special chemical characteristics, the overall synthesis proceeded with lower energy consumption in terms of temperature and pressure. However, as described previously, the reaction is not atom efficient, as simultaneous formation of methanol and  $\text{CO}_2$  also proceeds

after decomposition of  $[\text{CH}_3\text{CO}_3]^-$  anions (reaction Schemes 2 and 3). This side-reaction not only involves the loss of  $\text{CH}_3\text{I}$  reagent, but it also releases equally important  $\text{CO}_2$ , which is needed upon DMC synthesis. Since this side-reaction occurred due to the interaction between the  $[\text{DBUH}]^+$  cation and  $\text{CH}_3\text{I}$ , it is necessary to avoid their interaction in order to increase the yield of DMC in this synthetic approach.

Considering these aspects, prior to the addition of  $\text{CH}_3\text{I}$ , the DMSO solution of SIL was initially diluted with methanol, whereby the total reaction mixture volume of methanol was maintained as 6, 12, 25, or 50 vol.%. In these diluted reaction mixtures, three equivalents of  $\text{CH}_3\text{I}$  (based on DBU in the composition) were added, and after 1 h the reaction mixture was analyzed by NMR analysis. As shown in Figure 8, peaks related to the methylated DBU cation steadily decreased as the amount of methanol in the reaction mixture increased from 6 to 50 vol.%. The amounts of DMC, methanol, and  $[\text{CH}_3\text{CO}_3]^-$  anions in the reaction mixture were calculated using Equations (1)–(3), respectively. As the reaction mixture comprised an excess quantity of methanol, the integrated value of the peak belonging to  $\text{CH}_3$ -group in  $[\text{DBUCH}_3]^+$  cation was used for methanol. This was decided based on the fact that equal integrated values were observed for the methyl group in both methanol and  $[\text{DBUCH}_3]^+$  cations when the reaction was previously carried with only DMSO as a solvent (Figure S7). The calculated amounts of DMC, methanol, and  $[\text{CH}_3\text{CO}_3]^-$  anions observed in the reaction mixture are shown in Figure S9.



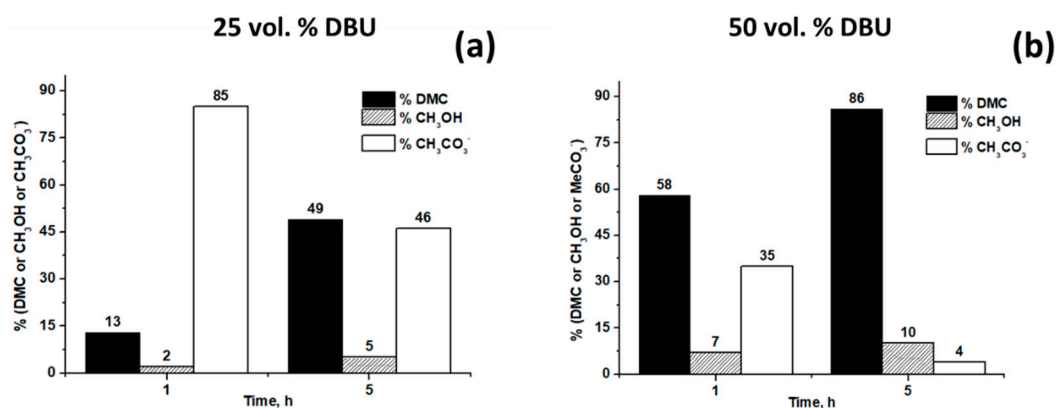
**Figure 8.**  $^{13}\text{C}$  NMR spectra of (a) SIL, [DBUH]  $[\text{CH}_3\text{CO}_3]^-$  in DMSO, (b) SIL in DMSO and 1 eq. of  $\text{CH}_3\text{I}$  (15 min of reaction time). The reaction mixture containing SIL in DMSO and various amounts of methanol such as (c) 6 vol.%, (d) 12 vol.%, (e) 25 vol.%, and (f) 50 vol.%.  $\text{CH}_3\text{I}$  (3 equivalents of  $\text{CH}_3\text{I}$  were added according to the amount of DBU in the reaction mixture, reaction time 1h) (NMR analysis with  $\text{D}_2\text{O}$  capillary).

Figure S9 depicts that dilution imparts a positive effect on the DMC formation, where the amount of DMC increased from 62% (reaction proceeded with no dilution with methanol) to 81 and 86% with 12 and 25 vol.% of methanol used in the reaction composition, respectively. However, further dilution with 50 vol.% methanol did not improve the DMC yield, and only 16% yield was obtained and 76% of  $[\text{CH}_3\text{CO}_3]^-$  anions remained unreacted. In this case, having 50 vol.% of methanol in the reaction mixture could not allow efficient interaction between the  $[\text{CH}_3\text{CO}_3]^-$  anion and  $\text{CH}_3\text{I}$ .

Most importantly, upon an increase in the amount of methanol, the intensity of the peaks for the carbon atoms in DBU and the methyl group in [DBUCH<sub>3</sub>] [I] salt steadily decreased. In other words, instead of using neat DMSO solution of SIL, its diluted solution using methanol allowed more selective interaction between CH<sub>3</sub>I and [CH<sub>3</sub>CO<sub>3</sub>]<sup>−</sup> anions, whereas it seems that the side-reaction for the interaction between [DBUH]<sup>+</sup> and CH<sub>3</sub>I was significantly hampered.

The influence of the amount of CH<sub>3</sub>I on the formation of DMC in the reaction mixture was further examined in a diluted reaction mixture, whereupon excess methanol was used with SIL and DMSO. In the actual study, the different equivalents of CH<sub>3</sub>I (on the basis of DBU in the composition) such as 1, 3, or 5 were added to the reaction mixture in which 88 vol.% of DMSO solution of SIL and 12 vol.% of methanol were present in the reaction composition. As shown in Figure S10, with increasing amounts of CH<sub>3</sub>I from 1 to 3 equivalents, the amount of DMC also increased from 62 to 83% in the reaction mixture. This could be observed since it resulted in a shift in the equilibrium towards DMC with more equivalents of CH<sub>3</sub>I compared to SIL amount. However, further increase in the CH<sub>3</sub>I to 5 equivalents did not improve the amount of DMC in the reaction mixture.

As it was observed that dilution with methanol resulted in an increase in the amount of DMC, this synthesis approach was further upgraded by replacing DMSO with methanol. During the actual experimental process, 25 or 50 vol.% solutions of DBU in methanol were prepared and used for CO<sub>2</sub> capture through SIL formation. Further, DMC was synthesized after addition of CH<sub>3</sub>I (3 equivalents based on amount of DBU) in the resultant alcoholic solution of SILs, and the obtained <sup>13</sup>C NMR spectra are shown in S11. Here, along with the influence of the amount of DBU in its alcoholic solution (25 and 50 Vol.%), the influence of the reaction time was also examined in terms of the formation of DMC. As shown in Figure 9a,b in 1 h of reaction time, 13 and 58% of DMC formed when 25 and 50 vol.% of DBU were used, respectively. As observed previously, the use of excessive amounts of methanol resulted in lower amounts of DMC in the reaction mixture. On the other hand, in a comparatively concentrated system, i.e., with 50 vol.% of DBU, a higher amount of DMC was obtained as a result of effective interaction between [CH<sub>3</sub>CO<sub>3</sub>]<sup>−</sup> anions and CH<sub>3</sub>I. In addition, a similar trend was also observed in the case of methanol formation, whereby higher amounts of methanol were found (7%) with 50 vol.% DBU compared to 25 vol.% DBU-containing reaction mixture. Further, for 5 h reaction period, with 25 vol.% DBU-containing reaction mixture, merely 54% of the [CH<sub>3</sub>CO<sub>3</sub>]<sup>−</sup> anion reacted and 49% of DMC was formed. On the other hand, in the reaction mixture in which 50 vol.% of DBU was used, 96% of [CH<sub>3</sub>CO<sub>3</sub>]<sup>−</sup> anion was consumed, whereas 10 and 86% of methanol and DMC were formed, respectively. DBU is a well-known organocatalyst, and various organic transformations have been performed where it acts either as a strong Brønsted base or good nucleophile. In non-protic solvents the [DBUH]<sup>+</sup> cation is usually involved in a proton exchange with DBU, and there DBU can perform both as a nucleophile as well as a base in the reaction. Since DMSO is a non-protic solvent (not acting as a proton source), during this proton exchange it further allows the interaction between DBU formed in situ with CH<sub>3</sub>I. On the other hand, in protic solvents, good nucleophilic characteristics of DBU can be diminished, and it transforms to a weak base as the nucleophilic nitrogen becomes engaged in hydrogen bonding with protic solvents [31]. Since methanol is a protic solvent, there is a lower probability of DBU forming from its protonated form, and nucleophilic interaction of DBU (and hence [DBUH]<sup>+</sup> cation) with CH<sub>3</sub>I is kept under control. Hence, instead of DMSO, the use of methanol as a solvent efficiently controlled the side-reactions and further improved the yield of DMC in the reaction mixture.



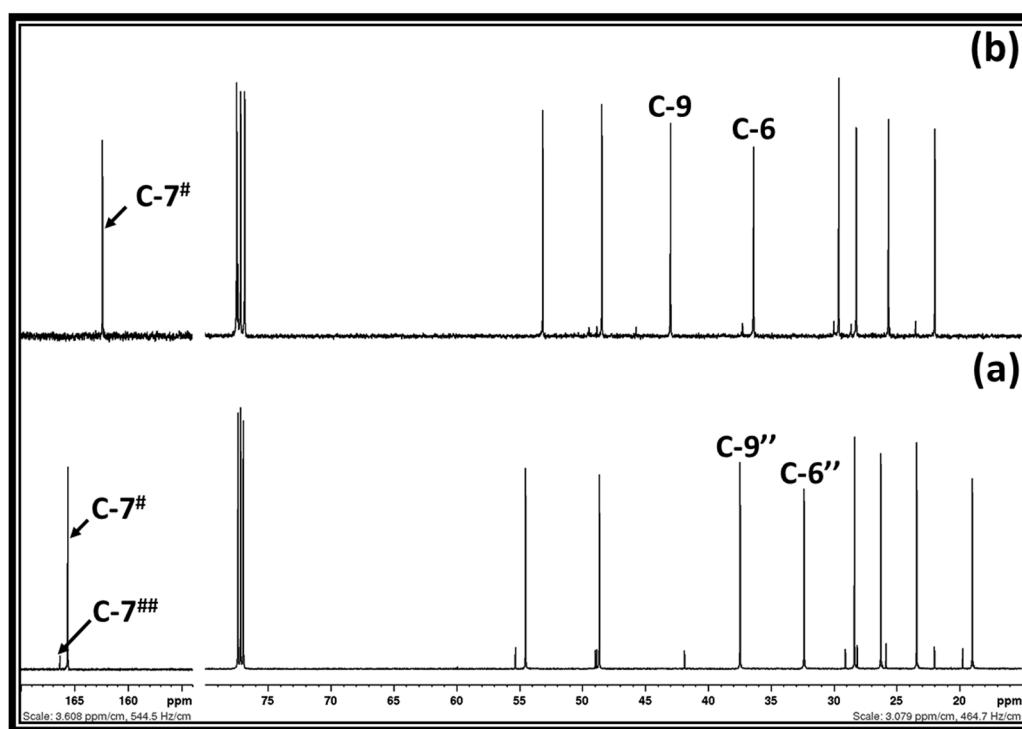
**Figure 9.** Amounts of DMC, methanol, and  $\text{CH}_3\text{CO}_3^-$  anions formed in the reaction mixture with (a) 25 vol.% of DBU and (b) 50 vol.% of DBU in alcoholic solution; 3 eq. of  $\text{CH}_3\text{I}$  were added.

In order to complete conversion of  $[\text{CH}_3\text{CO}_3]^-$  anions in the reaction mixture with 50 vol.% of DBU, the reaction time was further increased from 5 h to 7 and 10 h. The corresponding  $^{13}\text{C}$  NMR spectra for this study are shown in Figure S12. As shown in Figure S13, the  $[\text{CH}_3\text{CO}_3]^-$  anion was completely consumed in the reaction mixture, whereas the amount of DMC increased from 86 to 89% in 10 h of reaction time. Simultaneously, the amount of methanol did not significantly increase, and 11% was found in the reaction mixture. Since no formation of other methylated products (such as dimethyl ether) except methanol was observed, DMC formation reached 89% selectivity in 10 h. Hence, in this reaction approach, as mentioned previously, methanol not only became a part of the  $\text{CO}_2$  capture process, but it also assisted in the synthesis of DMC with high selectivity. In this regard, excess methanol in the reaction composition significantly influenced the interactions between the chemical species and favored the formation of more DMC.

The reaction mixture in which 50 vol.% of DBU was used was further added to ethyl acetate after 10 h reaction to separate the salts of DBU forming during the reaction. The composition of these salts was confirmed by  $^{13}\text{C}$  NMR analysis. As shown in Figure 10a,b, both DBU salts, i.e.,  $[\text{DBUH}] [\text{I}]$  and  $[\text{DBUCH}_3] [\text{I}]$ , were selectively separated from the reaction mixture. Based on the intensity of the peaks belonging to both salts, a major part of the salt mixture was  $[\text{DBUH}] [\text{I}]$ , whereas its methylated analogue was present in much lower quantities. In order to recover the DBU from the mixture of salts, 4 wt.% NaOH in saturated solution of NaCl was used. The purity and recovery of the DBU was controlled by  $^1\text{H}$  NMR analysis and gravimetric measurements, respectively. As shown in Figure S14, a pure form of DBU was recovered following alkaline solvent treatment. Besides that, 86% recovery of DBU was achieved from the recovered DBU salts.

Hence, as a part of capture and storage,  $\text{CO}_2$  is stored chemically through the formation of DMC, where initially the SIL was prepared to activate chemically inactive  $\text{CO}_2$ ; subsequently, it reacted with  $\text{CH}_3\text{I}$  to form DMC. In this reaction approach, a reaction yield >85% was obtained under mild reaction conditions. Even though the use of alcoholic solution further led to slow reaction kinetics, it simultaneously improved the yield of DMC through control over loss of chemisorbed  $\text{CO}_2$  through side-reactions. Previous reports based on metal carbonates and oxides were accompanied with the use of high reaction temperature and pressure to reach the optimized DMC yield. In addition, in these cases, the catalyst and product decomposition (due to formation of water during the reaction) and formation of by-products (e.g., dimethyl ether in metal carbonate based process) significantly influenced DMC yield. Simultaneously, the regeneration of catalysts or promoters was not carried out in these metal carbonate and oxide-based processes. On the other hand, in this report, the industrially feasible, single-solvent-based and metal-free synthetic approach was established to obtain DMC with high yields and selectivity, at room temperature and under atmospheric pressure. This synthetic approach also demonstrated the recovery of organic superbase, which was considered as an important moiety in the synthesis. The current organic superbase-induced DMC synthesis approach is also accompanied

with the use of equivalent amounts of  $\text{CH}_3\text{I}$  as the methylating reagent. This substrate is unfortunately considered as a toxic chemical moiety to the ecosystem as well as human beings. However,  $\text{CH}_3\text{I}$  is considered as a more active reagent and a more powerful methylating agent compared to others such as DMC, methanol, and dimethyl sulphate [32]. Additionally, the reaction with  $\text{CH}_3\text{I}$  usually proceeds under mild reaction conditions and is frequently active without any catalyst, whereas in the case of other methylating agents, the reaction proceeds under harsh reaction conditions and also requires catalysts and sometimes results in low yields. If  $\text{CH}_3\text{I}$  is handled safely during its use by considering all the necessary safety precautions, then it can be explored in bulk implementation for DMC synthesis, at industrial scale. Further, this reaction approach involving an organic superbase was carried out with easily available reagents as well as a solvent system, and this fundamental study for DMC synthesis can be extended to synthesize a wide range of industrially important alkyl carbonates. In this case, several alcoholic moieties as well as alkyl halides ranging from lower to high molecular weight can be applied.



**Figure 10.**  $^{13}\text{C}$  NMR spectra for (a) reaction mixture obtained where 50 vol.% of DBU and 3 equivalents of  $\text{CH}_3\text{I}$  were used for DMC synthesis in 10 h reaction period (NMR analysis with  $\text{D}_2\text{O}$  capillary). (b) DBU salts separated from reaction mixtures with the use of ethyl acetate (NMR analysis with  $\text{D}_2\text{O}$ ).

#### 4. Conclusions

The industrially important dimethyl carbonate (DMC) was synthesized from  $\text{CO}_2$  following switchable ionic liquid (SIL) involved in a one-pot and metal-free reaction approach under ambient conditions.  $\text{CO}_2$  was activated through its equivalent interaction with organic superbase DBU and methanol, and the resultant SIL reacted with  $\text{CH}_3\text{I}$  and formed DMC. Initially, this synthetic approach was proven in DMSO solvent, where 62% of chemisorbed  $\text{CO}_2$  was converted to DMC. The yield of DMC was further increased to 89% with the DMSO-free reaction approach where synthesis was carried out with methanol as a solvent. Based on NMR analysis, it was observed that with DMSO as a solvent, along with DMC synthesis, as a side reaction, the  $\text{CH}_3\text{I}$  also simultaneously reacted with protonated DBU in SIL and formed methylated DBU cations. Hence, released protons further decarboxylated  $[\text{CH}_3\text{CO}_3^-]$  anions in unreacted SIL to form methanol and released  $\text{CO}_2$  in the reaction mixture. However, the use of methanol as a solvent further improved the yield of DMC where the



loss of CO<sub>2</sub> was avoided by control over the side reactions. Therefore, in this regard, methanol not only performed as a reagent in CO<sub>2</sub> capture and DMC synthesis processes, but it also simultaneously assisted in the efficient conversion of chemisorbed CO<sub>2</sub> to DMC. DBU salts such as [DBUH][I] and [DBUCH<sub>3</sub>][I] were also converted to pure DBU, where 86% recovery was achieved. Hence, metal-free, single-solvent-based, and one-pot synthesis of DMC was performed under ambient conditions. As a main achievement, in this fundamental study anthropogenic CO<sub>2</sub> was not only captured but also converted to a valuable chemical.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2673-4079/1/3/20/s1>, Figure S1. <sup>1</sup>H NMR spectra of (a) DBU and methanol and (b) [DBUH][CH<sub>3</sub>CO<sub>3</sub>] (NMR analysis with D<sub>2</sub>O capillary); Figure S2: <sup>13</sup>C NMR spectra of the (a) reaction mixture after addition of 1 equivalents of CH<sub>3</sub>I in DMSO solution of [DBUH][CH<sub>3</sub>CO<sub>3</sub>] and (b) commercially available DMC (NMR analysis with D<sub>2</sub>O capillary); Figure S3. <sup>1</sup>H NMR spectra for the synthesis of DMC from [DBUH][MeCO<sub>3</sub>] and CH<sub>3</sub>I in DMSO. (a) DBU and methanol, (b) [DBUH][CH<sub>3</sub>CO<sub>3</sub>], reaction mixture after addition of (c) 0.25, (d) 0.50, (e) 0.75, and (f) 1 equivalents of CH<sub>3</sub>I in DMSO solution of [DBUH][CH<sub>3</sub>CO<sub>3</sub>] (NMR analysis with D<sub>2</sub>O capillary); Figure S4. <sup>1</sup>H NMR of the (a) reaction mixture after addition of 1 equivalent of CH<sub>3</sub>I in DMSO solution of [DBUH][CH<sub>3</sub>CO<sub>3</sub>] and (b) commercially available DMC (NMR analysis with D<sub>2</sub>O capillary); Figure S5. <sup>1</sup>H NMR spectra of the reaction mixture (a) containing [DBUH][CH<sub>3</sub>CO<sub>3</sub>] in DMSO and (b) after addition of *p*-toluene sulfonic acid in DMSO solution of [DBUH][CH<sub>3</sub>CO<sub>3</sub>] (NMR analysis with D<sub>2</sub>O capillary), and (c) methanol in DMSO (NMR analysis with D<sub>2</sub>O capillary); Figure S6. (a) 1H-13C HMBC spectra of the reaction mixture after addition of 1 eq. of CH<sub>3</sub>I in DMSO solution of [DBUH][CH<sub>3</sub>CO<sub>3</sub>] and (b) 1H NMR spectra of the reaction mixtures where ‘normal’ and 13C-enriched CO<sub>2</sub> were used (NMR analysis with D<sub>2</sub>O capillary); Figure S7. Integration of characteristic peaks in the 13C NMR spectra of the reaction mixture after addition of different equivalents of CH<sub>3</sub>I in DMSO solution of [DBUH][CH<sub>3</sub>CO<sub>3</sub>] (a) 0.25, (b) 0.50, (c) 0.75, and 1 eq. of CH<sub>3</sub>I (NMR analysis with D<sub>2</sub>O capillary); Figure S8. <sup>1</sup>H-<sup>13</sup>C HMBC spectra of recovered DBU salts, [DBUH][I] and [DBUCH<sub>3</sub>][I] (NMR analysis with D<sub>2</sub>O. As the neat D<sub>2</sub>O used for analysis, the mentioned chemical shifts values are different compared to the values obtained when D<sub>2</sub>O capillary used during analysis.); Figure S9. Amounts (%) of DMC, CH<sub>3</sub>OH, and CH<sub>3</sub>CO<sub>3</sub><sup>−</sup> anions in the reaction mixture containing different amounts of methanol or DMSO solution of SIL; 3 eq. of CH<sub>3</sub>I was added (based on the amounts of DBU), 1h of reaction time; Figure S10. Amounts (%) of DMC, CH<sub>3</sub>OH, and [CH<sub>3</sub>CO<sub>3</sub>]<sup>−</sup> anions in the reaction mixture after addition of different amounts of CH<sub>3</sub>I (1, 2, and 5 eq. based on amount of DBU). The reaction performed with 12 vol.% of methanol with 88 vol.% of SIL in DMSO for 1h; Figure S11. <sup>13</sup>C NMR spectra of the reaction mixture for the different reaction times after addition of 3 eq. of CH<sub>3</sub>I (based on amount of DBU) in the solution of SIL ([DBUH][CH<sub>3</sub>CO<sub>3</sub>]) in methanol. The 25 or 50 vol.% of DBU in methanol was taken during SIL synthesis, (a) 0 h (only SIL in methanol), (b) 1h, and (c) 5h (NMR analysis with D<sub>2</sub>O capillary); Figure S12. <sup>13</sup>C NMR spectra for the synthesis of DMC in reaction mixtures with 50 vol.% of DBU in alcoholic solution with different reaction times: (a) 0 h (only SIL in methanol), (b) 1h, (c) 5h, (d) 7h, and (e) 10h; 3 eq. of CH<sub>3</sub>I was added (NMR analysis with D<sub>2</sub>O capillary); Figure S13. Amounts of DMC, methanol, and [CH<sub>3</sub>CO<sub>3</sub>]<sup>−</sup> anions formed in the reaction mixture with different reaction times with reaction composition having 50 vol.% of DBU in alcoholic solution; 3 eq. of CH<sub>3</sub>I was added; Figure S14. <sup>13</sup>C NMR spectra of the (a) recovered DBU salts, [DBUH][I] and [DBUCH<sub>3</sub>][I], and (b) recovered DBU (NMR analysis with CDCl<sub>3</sub>).

**Author Contributions:** S.G.K.: conceptualization, investigation, resources, visualization, validation, writing—original draft, writing—reviewing and editing; T.Q.B.: resources, validation and writing—reviewing and editing; J.-P.M.: supervision, writing—reviewing and editing, project administration and funding acquisition. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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