RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2015, **5**, 81515

Cycling of waste fusel alcohols from sugar cane industries using supercritical carbon dioxide†

F. S. Pereira, L. J. Pereira, D. F. A. Crédito, L. H. V. Girão, A. H. S. Idehara and E. R. P. González*

Received 13th August 2015
Accepted 8th September 2015

DOI: 10.1039/c5ra16346c

www.rsc.org/advances

The present study describes the clean synthesis of non-phosgene organic carbonates (NPOCs) from a selective multicomponent reaction with two important by-products from sugar and alcohol industries, namely, fusel alcohols and carbon dioxide, in the presence of 1,8-diazabicycloundecene (DBU), 1,5-diazabicyclo[4.3.0]-non-5-ene (DBN) or 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]-pyrimidine (TBD) and an alkylating agent. The bases were used for the nucleophilic activation of the alcohols. The synthesis of carbonates was carried out without solvent and confirmed by GC-MS with EI ionization mode, ^{1}H- and ^{13}C-NMR and FT-IR analysis. The carbonates were obtained in excellent yields. Crude fusel alcohol can be converted to alkylcarbonates. The proposed methodology can also be employed to convert other hydroxylated compounds into carbonates.

Introduction

Fusel alcohol is one of the by-products of sugar and alcohol industries; however, these industries generate large amounts of by-products and waste, which cause impact on the environment.[1,2] 2.5 litres of fusel alcohol is obtained per 1000 litres of ethanol produced. Brazil stands out for having a great number of sugar and alcohol industries; it produced 23.6 billion litres of ethanol in the 2012 harvest.[3] Therefore, the production of fusel alcohol was approximately 59 million gallons. Fusel alcohol is basically composed of approximately 15% isobutyl and 45% isopentyl alcohols, among other compounds such as acids, esters and aldehydes.[1] The perspective for the growth of ethanol production is large and, consequently, the generation of fusel alcohols will also increase.

Over the last few years, the concentration of greenhouse gases has increased because of the increase in industrial activities, agriculture and transport, mainly due to the use of fossil fuels. The greenhouse gas emissions from sugarcane harvest systems are an issue of national concern.[4]

Thus, to minimize the environmental impacts caused by the by-products (fusel alcohols and CO_2) and for recycling them, the development of synthetic methods for the formation of organic carbonates from fusel alcohols by the capture and fixation of carbon dioxide has become of great importance, seeking an efficient, clean and low-cost synthesis.

Due to the high content of alcohols, several studies have been reported that use them as sustainable materials. The synthesis of lauric, stearic, benzoic and phthalic esters was performed by the direct esterification of fusel alcohol with carboxylic acids, using a free-solvent microwave activation method and *p*-TsOH or $H_3PW_{12}O_{40}$ (HPW) as catalyst.[5] Fusel alcohol and coconut cream were used as starting materials for the biosynthesis of ethyl-, butyl-, isobutyl- and isoamyl- octanoates (flavor-active octanoic acid esters) using lipase palatase as the biocatalyst.[6]

The potential of reactive distillation for the valorization of fusel alcohols and increase their reaction with acetic acid has been reported, which separates the esters in their pure form. The experiment was performed on a laboratory-scale reactive distillation column, and a simulation model was validated.[7] Other studies presented some data regarding the uncatalyzed esterification of fusel alcohols with acetic, propionic and butyric acids. The formation rates of the butyric acid esters were found to be higher than those of acetic acid and propionic acid esters.[8]

Among the methods used for the preparation of carbonates, the reaction of phosgene with diols[9] involves highly toxic and corrosive products such as carbon monoxide and hydrochloric acid. New methods for the synthesis of carbonates that consider the utilization of carbon dioxide as raw material[10,11] can be an alternative to replace phosgene and its related compounds.[12–14] Organic carbonates can be used as solvents[15,16] or reagents[17] in the chemical industry[18] and medicinal chemistry.[19] They can also be used as fuel additives.[20,21]

Universidade Estadual Paulista – Faculdade de Ciências e Tecnologia, Departamento de Física, Química e Biologia – Laboratório de Química Orgânica Fina C.P. 467, Presidente Prudente, 19060-900, SP, Brazil. E-mail: eperez@fct.unesp.br

† Electronic supplementary information (ESI) available: Mass spectra of isopentyl alcohol, isobutyl alcohol, crude fusel alcohol, DBU, carbonates from DBN, carbonates from TBD, 2,4-dichlorobenzyl isopentyl carbonate, 2,4-dichlorobenzyl isobutyl carbonate, isononyl alcohol, butyl-isononyl carbonate and cholesterol-butyl carbonate; ^{1}H and ^{13}C NMR spectra of the carbonates; FTIR spectra of crude fusel oil and the corresponding NPOCs. See DOI: 10.1039/c5ra16346c

Fang and Fujimoto[22] reported the synthesis of dimethyl carbonate from carbon dioxide and methanol using base catalysis in the presence of the promoter CH_3I, which is considered a toxic reagent. The synthesis was carried out at high temperatures of 80–100 °C for 2 h. The results showed that at 100 °C, dimethyl ether was detected as a by-product but when the temperature was decreased to 80 °C, the formation of the by-product decreased drastically, while the yield of DMC remained at a constant level. The synthesis of carbonates was also reported by Yamazaki *et al.*[23] The synthetic procedure for dialkyl carbonates occurred under 1 atm pressure of CO_2 using an alcohol, Cs_2CO_3 and CH_2Cl_2 as the solvent. The syntheses were performed at 100 °C with 12 h of reaction time. However, high temperatures, long reaction times, toxic solvents and an expensive catalyst were employed in this study.

Amidine and guanidine bases have been used as catalysts in reactions involving the use of carbon dioxide as proton transfer reagents.[24–29] These bases have been used as nucleophiles for CO_2 fixation to afford bicarbonate or zwitterionic adducts.[28–30]

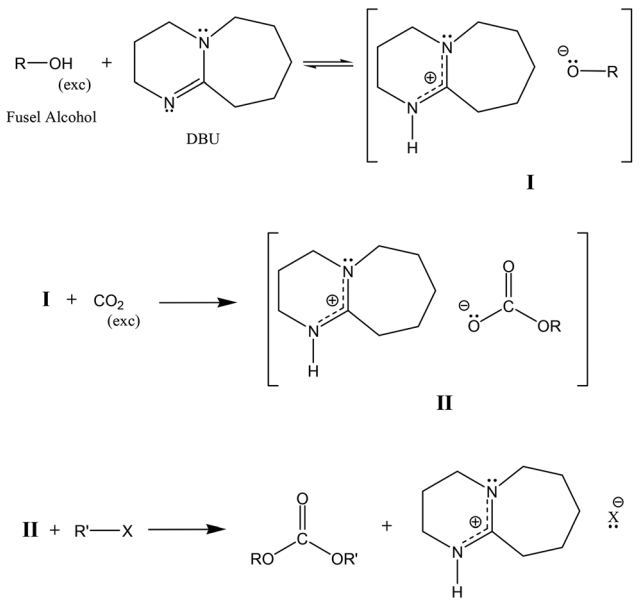
The amidine DBU has been investigated to activate and transfer the carbon dioxide molecule to amines[28,29] due to its basicity and nucleophilicity.[31] DBU has also been used as a nucleophile in its reaction with phosphorochloridates to form DBU–phosphorus intermediates *via* N–P bond formation.[32]

Copolymers bearing DBU and DBN and copolymers derived from 4-chloromethylstyrene were able to fix carbon dioxide under atmospheric pressure.[33]

The catalyst can be later recovered as a free base. It has been reported that a recovery of about 75% of DBU was achieved and it was reutilized once again for the synthesis of *N*-cyclohexyl ethyl carbamate with reproducible yield and purity.[12]

The present study describes an efficient and eco-friendly procedure for the conversion of fusel alcohols and CO_2, the by-products from sugarcane and ethanol industries, to non-phosgene organic carbonates. The multi-component selective reaction utilized two important by-products from sugar and alcohol industries, the pre-activated alcohols from fusel oil and pressurized CO_2, as starting materials, with an alkylating agent. 1,8-Diazabicycloundecene (DBU), 1,5-diazabicyclo[4.3.0]-non-5-ene (DBN) or 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]-pyrimidine (TBD) were used as agents for the initial nucleophilic activation of starting alcohols. The protocol was also investigated for other hydroxylated compounds. The formation of alkyl carbonates was performed at low temperatures in short reaction times and confirmed by GC-MS, ^{1}H and ^{13}C-NMR and FT-IR techniques.

Scheme 1 shows the proposed mechanism for the formation of alkyl carbonates *via* the capture and fixation of CO_2 with alcohols using the amidine base DBU as promoter and the alkylating agent butyl bromide (BuBr).



Scheme 1 Capture and fixation of CO_2 with isolated fusel alcohols promoted by DBU using an alkylating agent.

Experimental

Materials and reagents

Fusel oil was obtained from a sugar and alcohol industry of São Paulo State. All the reagents were of analytical grade and used without further purification.

Procedure for obtaining isobutyl and isopentyl alcohols from fusel oil

The fusel oil is composed of a number of main alcohols such as ethyl, propyl, butyl, isobutyl, and isopentyl alcohols. Other compounds identified were hexyl acetate, methyl benzoate as well as the octanoic, decanoic, dodecanoic and pentadecanoic acids.

For the separation of alcohols from fusel oil, a conventional fractional distillation system was used. 100 mL of fusel oil was distilled and each sample was collected in the following temperature ranges: first fraction at 80–85 °C, second fraction at 87–90 °C, and third at 106–129 °C.

Procedure for the synthesis of alkyl carbonates from isobutyl, isopentyl and isononyl alcohols

The general procedure for the synthesis of alkyl carbonates involves adding 10 mmol (1.5 g) of the nucleophilic activator DBU, DBN or TBD to a solution containing 10 mmol of alcohol under stirring for 30 minutes at 25 °C for partial deprotonation of the alcohol. Subsequently, the reaction mixture was transferred to a Parr Autoclave reactor fitted with a stainless steel vessel with a 50 mL capacity. 10 mL of acetonitrile (CH_3CN) and 20 mmol (2.74 g) of the alkylating agent (butyl bromide) or (3.91 g) 2,4-dichlorobenzyl chloride were added for the formation of an alkyl carbonate. The reaction time was 1 h under pressurized CO_2 (68 mmol) at 80 bar and 40 °C. This pressure value was maintained during the entire reaction time. The remaining starting products and solvent were evaporated under reduced pressure and the product was washed with chloroform and distilled water (3 × 10 mL) to remove the base that was in the form of an unstable white salt. This salt was

solubilized in a solution of K_2CO_3 and the base was recovered by extraction with EtOAc.[12]

To investigate the role of the solvent, the synthesis was also studied without the use of either CH_3CN or any common organic solvent; instead, 10 mL of the starting alcohol was used in excess. In both cases, the product was obtained as a brown oil.

General procedure for the synthesis of alkyl carbonates from fusel alcohols

For the reaction with crude fusel alcohol, 10 mmol (1.5 g) of DBU was added to a round-bottom flask containing 3 g of fusel alcohol and stirred for 30 min at 25 °C. Then, the reaction mixture was transferred to a Parr Autoclave reactor fitted with a stainless steel vessel of 50 mL capacity. 20 mmol (2.74 g) of alkylating agent (butyl bromide) was added for the formation of the alkyl carbonates. The reaction time was 1 h under pressurized CO_2 (68 mmol) at 80 bar and 40 °C. The reaction was studied without the use of an organic solvent. The product was obtained as a light yellow oil.

Procedure for the synthesis of alkyl carbonate from cholesterol

For the synthesis of cholesteryl-butyl carbonate, 5 mmol of cholesterol was solubilized in 10 mL of dichloromethane, and 10 mmol (1.5 g) of DBU with 0.5 mmol of tetraethylammonium bromide (TEAB) was added to this solution with stirring for 30 min at 25 °C for the partial deprotonation of the alcohol. The reagent TEAB was used in this procedure to enhance the catalytic activity for an efficient deprotonation of hydroxyl group. Subsequently, the reaction mixture was transferred to a Parr Autoclave reactor fitted with a stainless steel vessel of 50 mL capacity. 20 mmol (2.74 g) of alkylating agent (butyl bromide) was added for the formation of the alkyl carbonate. The reaction time was 6 h under pressurized CO_2 (68 mmol) at 80 bar and 40 °C. The product was obtained as a light yellow oil.

Characterization

GC-MS analyses were performed using a gas chromatograph equipped with an Rtx-Wax column (30 m length, 0.25 mm diameter and 0.25 mm thick). Operational conditions for the analysis of butyl-isopentyl and butyl-isobutyl carbonates: detector temperature 250 °C, injector temperature 250 °C, injection mode 1 : 15, injection volume 1 μL, flow of carrier gas (He) 0.80 mL min^{-1}. The heating ramp was initiated at 50 °C, held at this temperature for 5 min, then increased at 4 °C min^{-1} up to 100 °C for 3 min, 2 °C min^{-1} to 110 °C for 5 minutes and 10 °C min^{-1} to 230 °C until the end of the analysis. The operational conditions for the analysis of fusel alcohols and the NPOCs from fusel alcohols: detector temperature 250 °C, injector temperature 250 °C, injection mode 1 : 15, injection volume 1 μL, flow of carrier gas (He) 1.00 mL min^{-1}. The heating ramp was initiated at 50 °C, held at this temperature for 5 min, then increased at 2 °C min^{-1} up to 100 °C for 3 min, 5 °C min^{-1} to 190 °C for 30 minutes and 5 °C min^{-1} to 220 °C until the end of the analysis.

GC-FID analysis was carried out on a Shimadzu apparatus, GC-2010 model, equipped with a flame ionization detector. A capillary Rtx-Wax column (30 m length, 0.25 mm diameter and 0.25 mm thick) was used. The operational parameters used were as follows: column temperature of 50 °C was maintained for 5 min, then increased at 2 °C min^{-1} up to 100 °C for 3 min, 5 °C min^{-1} to 190 °C for 30 minutes and 5 °C min^{-1} to 220 °C until the end of the analysis at 69.4 kPa. The injector and detector were kept at 250 °C and 250 °C, respectively. The carrier gas flow (N_2) was 0.87 mL min^{-1} with a linear velocity of 23.4 cm s^{-1}. The injection mode was 1 : 15 and injection volume was 1 μL.

The remaining alkylating agent 2,4-dichlorobenzyl chloride was quantified by a calibration curve using the GC-FID with Restek Rtx-WAX column. The calibration curve was obtained by dilutions of a stock solution of the analyte in methanol (5.0 mol L^{-1}). The curve was constructed using five points of concentrations in the range of 0.2–1.0 mol L^{-1}. The calibration curve for the remaining alkylating agent was obtained using linear regression, plotting the area of the analyte *versus* analyte concentration.

The analysis was carried out on a Shimadzu apparatus, model GC-2010, equipped with a flame ionization detector. The operation parameters used were as follows: column temperature of 50 °C for 8 min, then 2 °C min^{-1} up to 100 °C for 3 min, 5 °C min^{-1} to 190 °C for 30 minutes and 5 °C min^{-1} to 230 °C until the end of analysis at 79.9 kPa. The injector and detector were kept at 250 °C and 250 °C, respectively. The carrier gas flow (N_2) was 0.87 mL min^{-1} with a linear velocity of 23.4 cm s^{-1}. The injection mode was 1 : 15 and injection volume was 1 μL.

^1H and ^{13}C NMR analyses were recorded on a Bruker DRX400 Ultra Shield NMR spectrometer, 400 MHz, at 25 °C. The solvent used in the experiments was $CDCl_3$.

FT-IR analyses were performed on a Bruker spectrophotometer, Model Vector 22, KBr pellets. Spectra were recorded at 23 °C in the 4000–400 cm^{-1} range at a resolution of 4 cm^{-1} and 120 scans.

Butyl-isopentyl and butyl-isobutyl carbonates. ^1H-NMR (500 MHz, $CDCl_3$): δ 4.13 (2H), 3.90 (2H), 1.98 (1H), 1.66 (2H), 1.42 (2H), 0.94 (9H). ^{13}C-NMR (500 MHz, $CDCl_3$): δ 155.4, 73.9, 67.7, 30.6, 27.7, 18.9, 13.6. IR ν_{max} 2959, 2872, 1750, 1059 cm^{-1}. GC-MS: $[C_5H_{10}O_3 + H]^+$ of *m/z* 118, $[C_4H_9 + H]^+$ of *m/z* 57, $[C_3H_6 + H]^+$ of *m/z* 41.

2,4-Dichlorobenzyl-isopentyl and 2,4-dichlorobenzyl-isobutyl carbonates. ^1H-NMR (500 MHz, $CDCl_3$): δ 7.40 (2H), 7.25 (2H), 5.22 (2H), 4.20 (2H), 1.72 (1H), 1.58 (2H), 0.94 (6H). ^{13}C-NMR (500 MHz, $CDCl_3$): δ 154.9, 134.9, 131.8, 130.6, 129.4, 127.2, 67.1, 65.9, 37.2, 24.7, 22.4. IR ν_{max} 3458, 2999, 2872, 1750, 1650, 1255 cm^{-1}. GC-MS: $[C_8H_6Cl_2O_3 + H]^+$ of *m/z* 220, $[C_7H_5Cl_2 + H]^+$ of *m/z* 159, $[C_3H_7 + H]^+$ of *m/z* 43.

Butyl-isononyl carbonate. IR ν_{max} 3436, 2925, 2858, 1750, 1644, 1257, 1054 cm^{-1}. GC-MS: $[C_{10}H_{19}O_3 + H]^+$ of *m/z* 187, $[C_8H_{15}O_3 + H]^+$ of *m/z* 159, $[C_4H_9 + H]^+$ of *m/z* 57.

Cholesteryl-butyl carbonate. IR ν_{max} 3440, 2940, 2868, 1745, 1634, 1250 cm^{-1}. GC-MS: $[C_{27}H_{45} + H]^+$ of *m/z* 368, $[C_{11}H_{15} + H]^+$ of *m/z* 147, $[C_4H_9 + H]^+$ of *m/z* 57.

Results and discussion

The initial experiments were carried out to study the synthesis of alkyl carbonates using butyl bromide as the alkylating agent and DBU as the nucleophilic activator. An excess of alcohol was used for substitution of any common organic solvent, and the synthesis was performed for the first time in 1, 2, 3 and 6 h. The temperature was fixed at 40 °C and CO_2 was pressurized at 80 bar (both the temperature and pressure are close to CO_2 supercritical conditions).[18] Table 1 shows the chromatographic conversion obtained for the synthesized alkyl carbonates. The chromatographic yield was calculated by area integration of the alcohols and carbonates peaks from the chromatograms. The yield of carbonates after 1 h of reaction time at 40 °C was quite quantitative; therefore, this value was used for the subsequent experiments. Further increase in the reaction time did not improve the yields significantly. In addition, at reaction times lesser than 1 h, no carbonate was formed.

Having established the optimal reaction time, the next step was to investigate the influence of the variation of reaction temperature on the yield of the carbonates. Thus, the syntheses were carried out at four different temperature values ranging from 25 to 80 °C. For butyl-isopentyl and butyl-isobutyl carbonates, 40 °C was found to be the optimal temperature for the reaction (Table 2). In the chromatograms of the carbonates, no by-products were observed at higher temperatures. The decrease in yield with temperatures higher than 40 °C could be associated to the presence of adventitious water in the reaction media, which could partially hydrolyze the carbonate intermediates.

The effect of some other experimental conditions was also examined. Reactions were performed without the nucleophilic activator or promoter (DBU) and the alkylating agent (butyl bromide). Non-supercritical pressure (10 bar) and constant CO_2 flow at normal pressure were also investigated. All the experiments were carried out without the use of a solvent. The results of this study are reported in Table 3. Both carbonates were obtained in low yield when the reaction was carried out at 10 bar, in which the pressure is directly related to the rate of reaction, expressed by the activation volume in the system.[34] Furthermore, the molecularity number decreases when staring materials are converted to products (condensation reaction), enhancing the rate with increasing pressure as expected.[35]

The amount of promoter DBU amidine and the presence of an alkylating agent were found to be of great importance for carbonates conversion, supporting the proposed mechanism (Scheme 1). In addition, the results show that the successful syntheses of carbonates (NPOCs) can be performed from a one-pot capture of CO_2 with fusel alcohols under clean conditions using an excess of fusel alcohols without solvents, which is a relevant advance to a green chemistry procedure.

Fig. 1a displays the chromatogram obtained from the synthesis of butyl-isopentyl carbonate under the determined optimal experimental conditions, 25 °C and 80 bar of CO_2 for 1 h of reaction time, under clean conditions. Peak 1 (~11 min) is associated to the remaining isopentyl alcohol and peak 2 (~23 min) corresponds to the formation of butyl-isopentyl carbonate (2), which can be confirmed by its MS spectra, as shown in Fig. 1b.

Fig. 2a shows the chromatogram of butyl-isobutyl carbonate synthesized under the optimal reaction conditions. The presence of remaining isobutyl alcohol represented by peak 3 (~7 min) can be seen. Fig. 2b corresponds to the mass spectra of peak 4 (~18 min) associated to the formation of butyl-isobutyl carbonate.

Butyl-isopentyl and butyl-isobutyl carbonates synthesized under the optimal experimental conditions, 40 °C and 80 bar of CO_2 for 1 h of reaction time were quantified using a calibration curve. The results showed that from 10 mmol of alcohols, used in both reactions, 7 mmol of butyl-isopentyl carbonate (70%) and 7.3 mmols of butyl-isobutyl carbonate (73%) were obtained. Table 4 shows the linear regression coefficient (R) of the curve, the values obtained for the converted quantities (mmol) of carbonates and the standard deviation (S) calculated considering the average concentration as the results were obtained in triplicate. The retention indexes for the compound were 23 min for butyl-isopentyl carbonate and 18 min for butyl-isobutyl carbonate.

Table 1 Chromatographic yields (%) of butyl-isopentyl and butyl-isobutyl carbonates at different reaction times (40 °C, 80 bar)

Reaction time (h)	Butyl-isopentyl carbonate	Butyl-isobutyl carbonate
1	**93%**	**94%**
2	94%	96%
3	97%	96%
6	96%	95%

Table 2 Chromatographic conversion (%) of butyl-isopentyl and butyl-isobutyl carbonates from preliminary experiments (1 h, 80 bar)

T (°C)	Butyl-isopentyl carbonate	Butyl-isobutyl carbonate
25	92%	80%
40	**94%**	**96%**
60[a]	85%	61%
80[a]	65%	75%

[a] Remaining percentage to reach 100% was starting alcohol.

Table 3 Chromatographic yield (%) of butyl-isopentyl and butyl-isobutyl obtained under different experimental conditions (alcohols = 10 mmol, 1 h, 40 °C were fixed in all the experiments)

mmol of DBU	mmol of BuBr	P (bar)	Butyl-isopentyl carbonate	Butyl-isobutyl carbonate
—	15	80	—	—
1	15	80	—	—
5	15	80	80	74
10	—	80	—	—
10	15	10	~6	~2
10	15	—	—	—
10	**15**	**80**	**94**	**96**

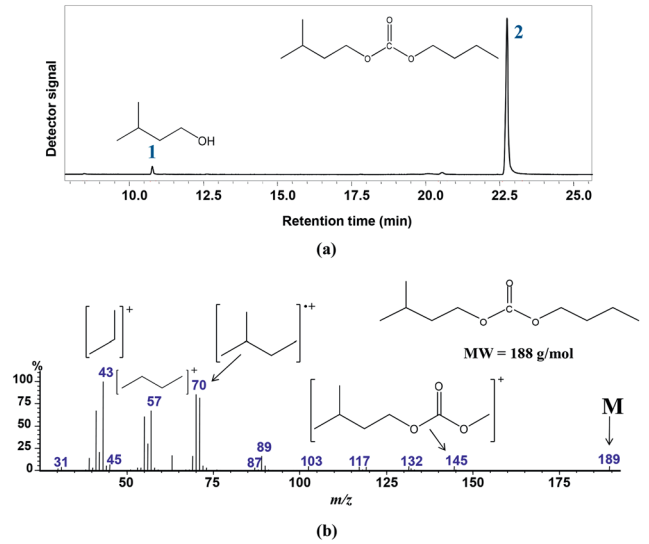


Fig. 1 (a) The chromatogram obtained from the synthesis of butyl-isopentyl carbonate at 40 °C and 80 bar for 1 h and (b) the mass spectrum of the carbonate eluted at ~23 min (peak 2).

In an exploratory experiment, a crude fusel alcohol sample was used as the raw material for the synthesis of NPOCs by direct reaction with CO_2. The reaction was carried out without any solvent and the temperature was 40 °C. The corresponding chromatogram is shown in Fig. 3. The remaining isopentyl alcohol (1-residual) can be observed; however, no isobutyl alcohol is seen. Peaks 4 and 2 correspond to butyl-isobutyl carbonate (7%) and butyl-isopentyl carbonate (71%), respectively. Peaks 6 and 7 are attributed to butyl-ethyl (12%) and butyl–butyl (9%) carbonates, respectively. These carbonates are also formed due to the presence of the corresponding alcohols in the crude fusel alcohol. The chromatographic conversion (%)

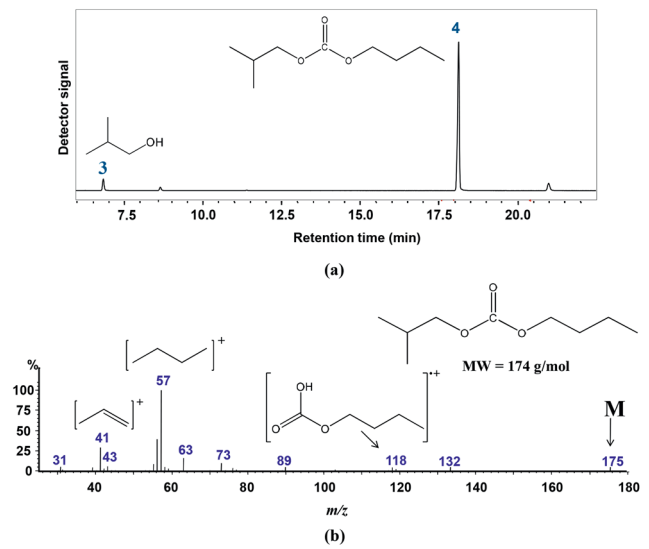


Fig. 2 (a) The chromatogram obtained from the synthesis of butyl-isobutyl carbonate at 40 °C and 80 bar for 1 h and (b) the mass spectrum of the carbonate eluted at ~18 min (peak 4).

Table 4 The data obtained from the calibration curves of butyl-isopentyl and butyl-isobutyl carbonates (0.2, 0.4, 0.6 and 1.0 mol L^{-1}). *R*: linear coefficient and *S*: standard deviation

Quantified reaction	*R*	Converted carbonates (mmol)	*S*
Butyl-isopentyl carbonate	0.9992	9.97	0.69%
Butyl-isobutyl carbonate	0.9993	9.86	0.44%

is relative to the carbonates formed in the reaction. For comparison, the chromatogram of crude fusel alcohols has been shown, which shows the presence of ethyl alcohol (3%), propyl alcohol (1%), butyl alcohol (2%), isobutyl alcohol (5%) and isopentyl alcohol (89%). The chromatogram of crude fusel alcohol can be found in the ESI.†

The syntheses of both carbonates were also carried out using the strong bases DBN and TBD as nucleophilic activators of the starting alcohols. The results showed that butyl-isopentyl and butyl-isobutyl carbonates were obtained in 86% and 89% of chromatographic conversion, respectively, when DBN was used in the reaction. This might be due to the lower Brönsted base character of the amidine DBN (when compared with DBU),[32] and consequently its lower deprotonating activity. In addition, when the reactions were performed with TBD, butyl-isopentyl and butyl-isobutyl carbonates were obtained in 49% and 45% of chromatographic conversion, respectively. The resulting low yield of carbonates might be due to the fact that DBN[28] and TBD[29,36] can also form a carbamic adduct with CO_2 and this could compete with the formation of the ionic carbonate intermediate. The chromatograms and the mass spectra of the carbonates are shown in the ESI (S7 to S17†).

2,4-Dichlorobenzyl chloride, an intermediate of Diclorbutrazol and Miconazole fungicides, was also studied as an alkylating agent. 2,4-Dichlorobenzyl chloride is the precursor for potential fungicides with resistance to sun irradiation or high temperatures and does not injure the host plant when applied to destroy fungi. However, its synthesis requires long reaction times, high temperatures and the products are obtained in low yields.[37] Thus, other materials can be prepared using this precursor and their fungicidal properties can be further investigated. The syntheses were performed using fusel isopentyl and isobutyl alcohols and the promoter base DBU, because it shows better effectiveness in the reactions. The corresponding carbonates were obtained in excellent yields of 99% and 97%,

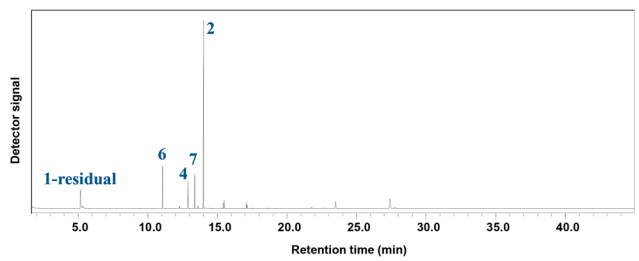


Fig. 3 Chromatogram obtained from the synthesis of NPOCs from fusel oil at 40 °C and 80 bar for 1 h.

respectively. The chromatogram and the mass spectra of both carbonates are shown in the electronic ESI (S-18 to S-21†).

The unreacted 2,4-dichlorobenzyl chloride obtained from the synthesis of 2,4-dichlorobenzyl-isopentyl and 2,4-dichlorobenzyl-isobutyl carbonates was quantified using a calibration curve. The results showed that from 10 mmol of alkylating agent, used in both reactions, only 0.028 and 0.14 mmol remained unreacted. For the reactions carried out with butyl bromide, we did not built a calibration curve because it was all consumed in the reactions. Table 5 shows the linear regression coefficient (R) of the curve, the values obtained of unreacted and converted quantities (mmol) of alkylating agent and the standard deviation (S) calculated considering the average concentration as the results were obtained in triplicates. The retention index for this compound was 16 min.

In the ^{1}H-NMR spectra of the butyl-isobutyl and butyl-isopentyl carbonates, due to the withdrawing nature of oxygen, the H3 and H4 signals are observed in the deshielding region at 3.90 and 4.18 ppm. H1, H2, H5 and H6 resonate from 0.94 to 1.98 ppm. In the ^{13}C-NMR spectra of such compounds, the chemical shift of carbon (OCOO) from the carbonyl group is centered at 155 ppm, which is in agreement with the literature[38] and confirms the formation of the expected products.

In the ^{1}H-NMR spectra of 2,4-dichlorobenzyl-isopentyl and 2,4-dichlorobenzyl-isobutyl carbonates, the hydrogen signals of the aliphatic region are observed in the range between 0.94 and 5.22 ppm. The formation of these carbonates can also be confirmed by the presence of aromatic hydrogens in the region between 7.24 and 7.40 ppm. For these compounds, a new signal appears at ~4.65 ppm in both spectra. This is attributed to the methylene hydrogen of the remaining alkylating agent that could not be removed during the purification process. The ^{13}C-NMR spectra show the chemical shifts of the aromatic ring carbons in the range of 127–134 ppm, and the carbonate carbon resonates at ~155 ppm. In addition, the methylene carbon signal of the remaining alkylating agent is observed at 42 ppm. All the ^{1}H-NMR and ^{13}C-NMR spectra can be found in the ESI.†

Fig. 4 shows the FT-IR spectra of isopentyl alcohol (A), butyl-isopentyl carbonate (B), isobutyl alcohol (C) and butyl-isobutyl carbonate (D). The formation of both carbonates is confirmed by the presence of the characteristic bands at 1256 ν(C–O) and 1750 cm^{-1} ν(C=O). Other absorption bands that are present in the alcohols spectra are also observed for both carbonates such as at 1459, 2870 and 2956 cm^{-1} ν(C–H). The bands associated to the presence of –CH_2– groups at 2870 and 2956 cm^{-1} were higher for carbonates than for alcohols, supporting the alkyl carbonate formation. The band at 1638 cm^{-1} ν(C=O) observed in the spectra is due to the esters (methyl benzoate and methyl acetate) and aldehydes (acetaldehyde), which are low boiling point compounds present in the crude fusel oil and might co-distillate with the isobutyl and isopentyl alcohols. The formation of the carbonates from fusel oil is confirmed by the presence of the band at 1750 cm^{-1} ν(C=O), which is not observed in the fusel oil spectra. The main bands and attributions observed in Fig. 4 are summarized in Table 6. The FT-IR spectra of the crude fusel alcohol and its corresponding NPOCs, 2,4-dichlorobenzyl-isopentyl and 2,4-dichlorobenzyl-isobutyl carbonates are shown in the ESI (S35 and S36†).

Butyl-isononyl carbonate was synthesized in this study to investigate if the methodology is also suitable for long-chain alcohols. Long-chain alcohols have been used for the synthesis of urethane upon their reaction with urea using metal salts such as zinc acetate and lead acetate as catalysts. The addition of triphenylphosphine as a co-catalyst yielded carbonates.[39] Isononyl alcohol is used to produce plasticizers of low cost with several applications.[40] It is also used as a fragrance ingredient in cosmetics, shampoos, household cleaners, among others.[41] Therefore, the formation of carbonates from isononyl

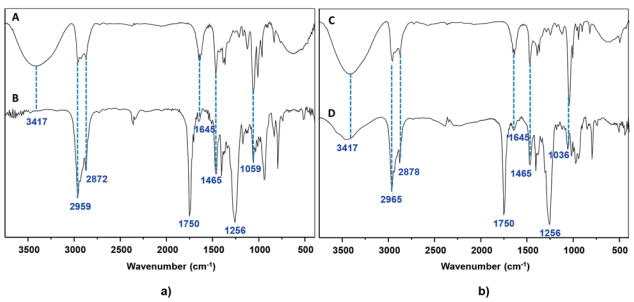


Fig. 4 The FT-IR spectra of (a) isopentyl alcohol (A) and butyl-isopentyl carbonate (B) and (b) butyl alcohol (C) and butyl-isobutyl carbonate (D).

Table 5 The data obtained from the calibration curve of 2,4-dichlorobenzyl chloride (0.2, 0.4, 0.6 and 1.0 mol L^{-1}). 2,4-DCBC: 2,4-dichlorobenzyl chloride; R: linear coefficient; and S: standard deviation

Quantified reaction	R	Unreacted 2,4-CDBC (mmol)	Converted 2,4-CDBC (mmol)	S
2,4-DCB-isopentyl carbonate	0.9992	0.028	9.97	0.69%
2,4-DCB-isobutyl carbonate	0.9992	0.14	9.86	0.44%

Table 6 Main bands (cm^{-1}) observed in the FT-IR spectra of butyl-isopentyl and butyl-isobutyl carbonates

Compounds	ν(O–H)	ν(C–H)	ν(C=O)	ν(C–O) primary alcohols
Isopentyl alcohol	3417	2959 2872	—	1059
Butyl-isopentyl carbonate	—	2959 2872	1750	1059[a]
Isobutyl alcohol	3417	2965 2878	—	1036
Butyl-isobutyl carbonate	3417[a]	2965 2878	1750	1036[a]
Fusel alcohols	3441	2956 2870	—	1054
NPOCs from fusel alcohols	3441	2870	1750	1054[a]

[a] Comparatively lower intensity.

alcohol might be of great interest for their use as materials for industrial applications.

The synthesis of butyl-isononyl carbonate was carried out using the nucleophilic activator DBU and BuBr under the same previously determined experimental conditions. The reaction was also carried out without any solvent. The results show that the carbonate was obtained in 93% of chromatographic conversion, which confirms that the proposed methodology can be employed to convert long chain alcohols to carbonates. The chromatograms and the mass spectra of isononyl alcohol and the corresponding carbonate can be found in the ESI (S30 to S33†).

Cholesteryl group can be considered a promising functional group present in molecules, which could be applied to optical filters for high-power laser systems,[42] rewritable memories and also recording media.[43] Thus, the crystal structures of cholesteryl-butyl carbonate and cholesteryl-oleyl carbonate are being investigated for liquid crystals applications. Furthermore, a series of esters and carbonates of cholesterol have been studied to understand these substances in biological systems.[44]

Moreover, cholesteryl carbonates are generally prepared using cholesteryl chloroformate as a precursor.[45,46] However, the synthesis of this precursor is limited to using toxic phosgene as a raw material.[47] Therefore, in our study, we also explored an efficient and non-phosgene route to cholesteryl carbonate synthesis using the nucleophilic activators DBU and TEAB, BuBr and pressurized CO_2 under the previously described experimental conditions. The results showed that cholesteryl-butyl carbonate was successfully obtained using the proposed methodology. The mass spectrum of the carbonate can be found in the ESI (S34†).

The FT-IR spectra of isononyl alcohol and butyl-isononyl carbonate, cholesterol and cholesteryl-butyl carbonate can be found in the ESI (S37 and S38†).

The present study describes an eco-friendly and non-expensive proposal of methodology for recycling fusel alcohols and carbon dioxide, from ethanol production, in an unique process for the synthesis of chemical products with added value and in a productive cycle with zero% of undesirable residuals. This procedure can be further studied for scaling up the production of organic carbonates with several applications. This technology could be relevant to decrease the environmental impact of high emissions of CO_2 and fusel alcohols from sugar and ethanol industries. This goal is of great interest for countries such as Brazil and the United States.[48] Our procedure can be considered as novel because to the best of our knowledge, no other study has reported the same advantages.

Conclusions

In summary, the syntheses of alkyl carbonates *via* the capture and fixation of CO_2 with isopentyl and isobutyl alcohols isolated from crude fusel alcohol were confirmed by GC-MS, NMR and FTIR analyses. The protocol is even applicable for other hydroxylated compounds and alkylating agents for the formation of materials with biological and industrial interests. In general, it has been found that it is possible to obtain the carbonates in excellent yields under clean conditions, without the use of solvents, at low temperatures and with short reaction time. Exploratory experiments show the conversion of crude fusel alcohol to NPOCs. DBU amidine used as the nucleophilic activator or promoter showed higher effectiveness in the reactions.

Acknowledgements

The authors are thankful to Fundação de Apoio a Pesquisa do Estado de São Paulo (FAPESP) for research funds (2013/21668-0 and 2013/24487-6), a PhD fellowship (2012/13901-3), undergraduation research fellowships (2011/23438-6, 2012/24330-7, 2012/24661-3 and 2014/00289-3) and to Programa de Pós-graduação em Ciência e Tecnologia de Materiais (POSMAT). Authors are also grateful to Professor Dr Gil Valdo José da Silva e Dr Vinicius Palaretti from Universidade de São Paulo (USP) for the NMR measurements. This work is a special dedicatory from Eduardo R. Pérez González addressed to Prof. Douglas Wagner Franco by introducing me in the study of the Chemistry of Carbon Dioxide and Fusel Alcohols.

Notes and references

1 E. R. Pérez, D. Cardos and D. W. Franco, *Quim. Nova*, 2001, **24**, 10–12.
2 A. G. Patil, S. M. Koolwal and H. D. Butala, *Int. Sugar J.*, 2002, **104**, 51–58.
3 União da indústria de cana-de-açúcar (UNICA), available in: http://www.unica.com.br/noticias, Last accessed, December, 2013.
4 E. B. Figueiredo, A. R. Panosso, R. Romão and N. J. La Scala, *Carbon Balance Manage.*, 2010, **5**, 3.
5 E. R. Pérez, N. C. Carnevali, P. J. Cordeiro, U. P. F. Rodrigues and D. W. Franco, *Org. Prep. Proced. Int.*, 2001, **33**, 395–400.
6 J. Sun, B. Yu, P. Curran and S. Liu, *Food Chem.*, 2012, **135**, 2714–2720.
7 P. Patidar and S. Mahajani, *Ind. Eng. Chem. Res.*, 2013, **52**, 16637–16647.
8 Z. Kuçuk and K. Ceylan, *Turk. J. Chem.*, 1998, **22**, 289–300.
9 M. Aresta, *Carbon Dioxide as Chemical Feedstock*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2010.
10 T. Sakakura, J. C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365–2387.
11 T. Sakakura and K. Kohno, *Chem. Commun.*, 2009, 1312–1330.
12 E. R. Pérez, M. O. da Silva, V. C. Costa, U. P. Rodrigues-Filho and D. W. Franco, *Tetrahedron Lett.*, 2002, **43**, 4091–4093.
13 P. Alessio, D. M. Ferreira, A. E. Job, R. F. Aroca, A. Riul, C. J. L. Constantino and E. R. P. González, *Langmuir*, 2008, **24**, 4729–4737.
14 C. R. Gomes, D. M. Ferreira, C. J. L. Constantino and E. R. P. Gonzalez, *Tetrahedron Lett.*, 2008, **49**, 6879–6881.
15 B. Schaffner, J. Holz, S. P. Verevkin and A. Borner, *ChemSusChem*, 2008, **1**, 249–253.

16 J. Bayardon, J. Holz, B. Schaffner, V. Andrushko, S. Verevkin, A. Preetz and A. Borner, *Angew. Chem., Int. Ed.*, 2007, **46**, 5971–5974.
17 P. Tundo and M. Selva, *Acc. Chem. Res.*, 2002, **35**, 706–716.
18 C. Vollmer, R. Thomann and C. Janiak, *Dalton Trans.*, 2012, **41**, 9722–9727.
19 A. K. Ghosh, T. T. Duong, S. P. Mckee and W. J. Thompson, *Tetrahedron Lett.*, 1992, **32**, 2781–2784.
20 M. Aresta, *Carbon Dioxide Recovery and Utilization*, Kluwer Academic Publishers, London, 2003.
21 M. A. Pacheco and C. L. Marshall, *Energy Fuels*, 1997, **11**, 2–29.
22 S. Fang and K. Fujimoto, *Appl. Catal., A*, 1996, **142**, L1–L3.
23 Y. Yamazaki, K. Kakuma, Y. Du and S. Saito, *Tetrahedron*, 2010, **66**, 9675–9680.
24 T. E. Waldman and W. McGhee, *J. Chem. Soc., Chem. Commun.*, 1994, **8**, 957–958.
25 W. McGhee, Y. Pan and D. P. Riley, *J. Chem. Soc., Chem. Commun.*, 1994, **6**, 699–700.
26 W. McGhee and D. Riley, *J. Org. Chem.*, 1995, **60**, 6205–6207.
27 T. Mizuno, N. Okamoto, T. Ito and T. Miyata, *Tetrahedron Lett.*, 2000, **41**, 1051–1053.
28 E. R. Pérez, R. H. A. Santos, M. T. P. Gambardella, L. G. M. Macedo, U. P. Rodrigues-Filho, J. Launay and D. W. Franco, *J. Org. Chem.*, 2004, **69**, 8005–8011.
29 F. S. Pereira, E. R. DeAzevedo, E. F. Silva, T. J. Bonagamba, D. Agostini, A. Magalhães, A. Job and E. R. Pérez, *Tetrahedron*, 2008, **64**, 10097–10106.
30 F. S. Pereira, D. Agostini, R. D. E. Santo, E. R. deAzevedo, T. J. Bonagamba, A. Job and E. R. Pérez, *Green Chem.*, 2011, **13**, 2146–2153.
31 M. Baidya and H. Mayr, *Chem. Commun.*, 2008, 1792–1794.
32 A. Kers, I. Kers and J. Stawinski, *J. Chem. Soc., Perkin Trans. 2*, 1999, **10**, 2071–2075.
33 B. Ochiai, K. Yokota, A. Fuji, D. Nagai and T. Endo, *Macromolecules*, 2008, **41**, 1229–1236.
34 N. S. Isaacs, *Liquid phase high pressure chemistry*, John Wiley & Sons, Michigan, 1981.
35 K. Matsumoto and A. Sera, *Synthesis*, 1985, **11**, 999–1027.
36 C. Villiers, J. Dognon, R. Pollet, P. Thuéry and M. Ephritikhine, *Angew. Chem., Int. Ed.*, 2010, **49**, 3465–3468.
37 M. M. Thomas, Tributyl-2, 4-dichlorobenzylammonium chloride, *US Pat.*, 3 218 356, 1962.
38 C. Copeland, R. J. Conway, J. J. Patroni and R. V. Stick, *Aust. J. Chem.*, 1981, **34**, 555–557.
39 A. Paquin, *Z. Naturforsch.*, 1946, **1**, 518–523.
40 A. Boy and R. Thiel, *Evonik Commissions Plant for Production of the Plasticizer Alcohol 2-PH*, Evonik Industries, Press release, 2009, pp. 1–3.
41 D. McGinty, J. Scognamiglio, C. S. Letizia and A. M. Api, *Food Chem. Toxicol.*, 2010, **48**, 79–81.
42 M. Mitsuyama and K. Kondo, *Macromol. Chem. Phys.*, 2000, **201**, 1613.
43 N. Tamaoki, A. V. Parfenov, A. Masaki and H. Matsuda, *Adv. Mater.*, 1997, **9**, 1102.
44 S. Abrahamsson, B. Dahlen, H. Lofgren, I. Pascher and S. Sundell, in *Structure of Biological Membranes*, ed. S. Abrahamsson and I. Pascher, Plenum Press, New York, London, 1977, p. 1.
45 R. Chuealee, P. Aramwit and T. Srichana, *Proceedings of the 2nd IEEE International Conference on Nano/Micro Engineered and Molecular Systems*, 2007, pp. 1098–1103.
46 J. Qu, Y. Suzuki, M. Shiotsuki, F. Sanda and T. Masuda, *Macromol. Chem. Phys.*, 2007, **208**, 1992–1999.
47 R. A. Mosey and P. E. Floreancing, *Org. Biomol. Chem.*, 2012, **10**, 7980.
48 United States Department of Agriculture, available in: http://www.usda.gov/wps/portal/usda/usdahome, Last accessed, May, 2015.

