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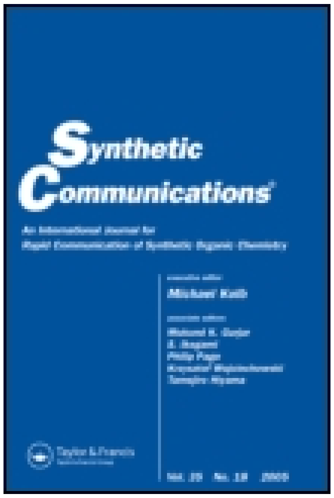

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A SAFE SYNTHESIS OF SYMMETRICAL CARBONATES FROM ALKYL HALIDES AND TETRAETHYLAMMONIUM CARBONATE

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A SAFE SYNTHESIS OF SYMMETRICAL CARBONATES FROM ALKYL HALIDES AND TETRAETHYLAMMONIUM CARBONATE

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ABSTRACT

A safe and mild procedure for the synthesis of organic carbonates from alkyl halides and tetraethylammonium carbonate (TEAC) is described. This method avoids the use of classical toxic and harmful chemicals like phosgene and carbon monoxide and works under very mild reaction conditions. An electrochemically-generated derivative of carbon dioxide

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(a cheap and abundant carbon source) was used as the main reagent (TEAC).

INTRODUCTION

Dialkyl carbonates are useful substrates for a variety of industrial and synthetic applications. They found wide use as solvents and intermediates for the synthesis of several pharmaceuticals, plastics, lubricants, herbicides and pesticides. The traditional syntheses of these compounds require toxic and harmful chemicals like phosgene, pyridine and carbon monoxide, so the development of new methodologies employing safe and clean reagents has been extensively studied in the last decade.[1,2]

Recently we found that unsymmetrical organic carbonates can be obtained, in quite good yields, by reaction of primary and secondary alcohols with tetraethylammonium carbonate (TEAC)[3] or tetraethylammonium peroxodicarbonates (TEAPC).[4] Both methods avoid hazardous reagents and are based on the electrochemical conversion of a cheap, abundant and harmless compound like carbon dioxide in derivatives showing carboxylating properties.

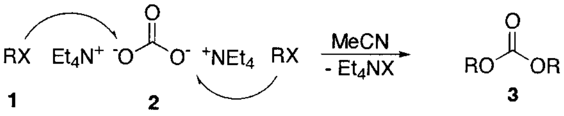
In this communication we report a safe and mild method for the synthesis of symmetrical dialkyl carbonates by reaction of alkyl halides with TEAC at room temperature in acetonitrile.

RESULTS AND DISCUSSION

The use of alkyl halides as starting materials for the synthesis of carbonates was first reported by Dehmlow[5] and Cella.[6] Both methods consist of an alkylation of alkali-metal carbonates and hydrogen carbonates performed by alkyl halides under phase transfer catalysis (PTC) conditions at high temperature (100–150°C).

Starting from these considerations we performed the reaction of different alkyl halides **1** in the presence of electrochemically generated TEAC **2** so as to obtain symmetric carbonates **3**, avoiding PTC and working under very mild reaction conditions (Scheme 1).

In order to optimise the reaction conditions, 3-phenylpropyl bromide (scheme 1 $R=Ph(CH_2)_3$ and $X=Br$) was used as a model compound and different molar ratios RX : TEAC were tested. A complete report of the results obtained is shown in Table 1. A side reaction encountered in the preparation of carbonates through this process is the formation of alcohols.



Scheme 1.

Table 1. Reaction of 3-Phenylpropyl Bromide (1.0 mmol) and TEAC via Scheme 1 Under Different Reaction Conditions

Entry	TEAC (mmol)	Reaction Products (mmol)		RX^a (mmol)	Temperature (°C)	$Yield^b$ (%)
		$ROCO_2R$	ROH			
1	0.25	0.15	0.14	0.46	r.t.	30
2	0.40	0.17	0.27	0.37	r.t.	34
3	0.50	0.20	0.28	0.21	r.t.	40
4	0.60	0.20	0.29	0.05	r.t.	40
5	0.68	0.20	0.39	0.11	r.t.	40
6	0.75	0.22	0.49	–	r.t.	44
7	1.00	0.22	0.53	–	r.t.	44
8	1.25	0.20	0.51	–	r.t.	40
9	0.60	0.20	0.34	–	80	40
10	0.60	–	–	1.00	−20	–
11[c]	0.60	0.20	0.29	0.29	r.t.	40
12[d]	0.60	0.27	0.36	0.05	r.t.	54

[a]Unreacted halide recovered at the end of the reaction; [b]Yield calculated considering the amount of alkyl halide **1** converted in carbonate; [c]DMF was used as solvent; [d]Reaction time of seven days.

These products appear to be the result of decarboxylation of the intermediate monoalkylated carbonate salt.

As shown in the table, symmetrical carbonate and alcohol yields are strongly dependent upon the amount of tetraethylammonium carbonate used. An increase of TEAC causes a direct increase in the formation of carbonate; on the other hand, the quantity of alcohol obtained at the end of the reaction also increases to the detriment of the alkyl halides potentially recoverable from the reaction mixture. It is obvious that we need to reach a compromise among the amounts of carbonate and alcohol (undesirable) obtained in the reaction. We chose a ratio alkyl halide/TEAC of 1 : 0.6 so as to get better yields without obtaining large quantity of alcohol and with the possibility of recovering the unreacted alkyl halides for further reactions. In addition, reaction times show a remarkable influence on the reaction yield;

Table 2. Reaction of Different Alkyl Halides with TEAC Under Optimised Reaction Conditions.[a] Carbonates Produced via Scheme 1

			Reaction Products (mmol)			
Entry	R	X	$ROCO_2R$	ROH	RX^b (mmol)	$Yield^c$ (%)
1	$Ph(CH_2)_3$	I	0.21	0.13	0.40	42
2	$Ph(CH_2)_3$	Cl	–	0.11	0.74	–
3	$Ph(CH_2)_3$	OTs	0.21	0.29	0.05	42
4	$Ph(CH_2)_2$	I	0.19	0.10	0.48	38
5	$PhCH_2$	Br	0.22	0.21	0.12	44
6	$Ph(CH_3)CH$	Br	0.27	0.35	0.10	54
7	$Ph_2CH(CH_2)_2$	Br	0.13	0.38	0.36	26
8	$PhCH{=}CHCH_2$	Br	0.20	0.35	0.12	40
9	CH_2CH_2	Br	0.10	–	–	20

[a]Molar ratio halide/TEAC 1 : 0.6, r.t. CN_3CN; [b]Unreacted halide recovered at the end of the reaction; [c]Yield calculated considering the amount of alkyl halide **1** converted in carbonate; [d]Reaction carried out with 1,2-dibromoethane; a molar ratio halide/TEAC of 1 : 1.2 was used.

extending the reaction time up to seven days increase the amount of carbonate obtained from 40 to 54% (Entry 12). Considering the temperature, no reaction was observed at −20°C (Entry 10), while raising the temperature to 80°C did not produce relevant improvements in the reaction yield (Entry 9).

Using the optimized reaction conditions (Entry 4), the reaction was tested on different alkyl halides in order to evaluate potential differences in reactivity. Results are reported in Table 2. 3-Phenylpropyl iodide and tosylate did not show substantial differences when compared to the corresponding bromide (Entries 1 and 3), but the chloride did not react at all (Entry 2). When an α,ω-dibromide was used, the corresponding cyclic carbonate was obtained but only in 20% of yield (Entry 11).

CONCLUSION

In conclusion this simple and safe method represents a valuable alternative to the methods up to now reported. Although reaction yields are only moderate, the procedure utilizes a safe and clean derivative of carbon dioxide and works in very mild medium, avoiding both toxic and harmful reagents and harsh reaction conditions.

EXPERIMENTAL

General

TLC analyses were performed on Merck kiesegel 60 F254 plates. Flash chromatography was carried out on Merck silica gel (230–400 mesh). ^{1}H and ^{13}C NMR were determined at 200 and 50.3 MHz respectively with a Bruker AC200 instrument using $CDCl_3$ as an internal standard. Dry acetonitrile (Lab-scan, anhydroscan) was used as received. Alkyl halides **1** are commercially available and were used as received.

Reaction of Alkyl Halides with TEAC: General Procedure (3)

A solution (20 ml) of MeCN–Et_4NClO_4 (0.1 mol dm^{-3}), with continuous CO_2 bubbling, was electrolysed (divided cell, Pt anode, 0°C) over a Cu cathode at a potential of -2.1 V (vs. SCE). At the end of electrolysis (1.2 F mol^{-1}) the halide was added and the reaction was stirred overnight. After removal of the solvent, flash chromatography afforded the desired carbonate.

Carbonates in Table 2 Entries 1–6, 9 are commercial or well-known compounds; product assignment was determinated by ^{1}H-NMR, ^{13}C-NMR and elemental analysis compared to authentic materials or literature assignments.

Carbonic acid *bis*-(3,3-diphenyl-propyl) ester: ^{1}H NMR ($CDCl_3$, 200 MHz) d; 7.34–7.15 (m, 20H, Ar); 4.14–4.04 (m, 6H, OCH_2, $CHPh_2$); 2.43 (q, 4H, $J = 6.0$ Hz, CH_2CH). ^{13}C NMR ($CDCl_3$, 50.3 MHz) d: 160.8, 155.0, 128.3, 127.8, 126.4, 66.2, 47.2, 34.3. Anal. calcd for $C_{31}H_{30}O_3$: C, 82.64; H, 6.71. Found: C, 82.52; H, 6.78.

Carbonic acid *bis*-(3-phenyl-allyl) ester: ^{1}H NMR ($CDCl_3$, 200 MHz) d; 7.41–7.23 (m, 10H, Ar); 6.68 (d, 2H, $J = 15.9$ Hz, PhCH=); 6.29 (dt, 2H, $J = 6.3$, 15.9 Hz, CH_2CH=); 4.80 (dd, 4H, $J = 1.0$, 6.3 Hz, OCH_2). ^{13}C NMR ($CDCl_3$, 50.3 MHz) d: 154.9, 136.0 134.8, 128.5, 128.1, 126.6, 122.4, 68.4. Anal. calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.41; H, 6.12.

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