# Facile stereoselective conversion of 1,2-diols into alkane-1,2-diyl carbonates

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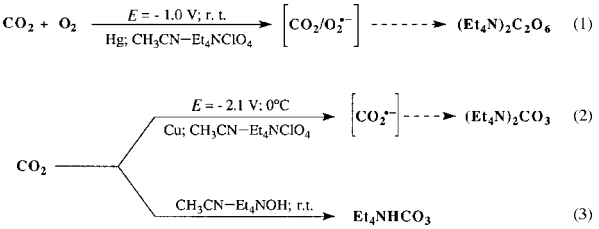
The stereoselective conversion of 1,2-diols into alkane-1,2-diyl carbonates has been carried out at room temperature without employing catalysts or toxic and/or polluting reactants, by addition of 1,2-diols and afterwards of an alkylating agent to acetonitrile solutions containing $C_2O_6^{2-}$, $CO_3^{2-}$ or $HCO_3^-$ anions in the presence of tetraalkylammonium cations. These solutions can be easily prepared by simple electrochemical or chemical routes.

The chemistry of organic carbonates was extensively reviewed in a recent article.[1] The synthetic methodologies, both for linear and cyclic carbonates, were discussed. Particular emphasis was given to those methods that avoid using toxic, dangerous, or polluting reactants. Five-membered cyclic carbonates have found important applications as solvents [*e.g.*, for poly(acrylonitrile), or as key components of superior cleaning solvents], as accelerators for curing (of phenol-formaldehyde or epoxy resins, or silicate systems used as foundry sand binders), as electrolytes (for high-energy density batteries), *etc.* Other remarkable fields of application for five-membered cyclic carbonates are in urethane chemistry, in cosmetics, in extractive techniques for metals, in photosensitive compositions for preparing lithographic plates, *etc.* Consequently, a great deal of attention has been paid to those investigations aimed at evaluating the possibility of turning cheap and abundant substrates into cyclic carbonates using safe methods.

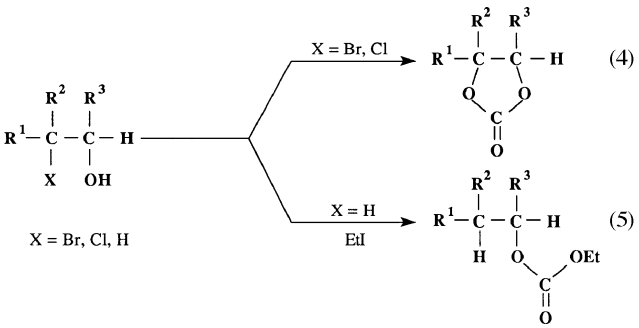
Recently, it has been shown by us and others that, in the presence of tetraalkylammonium cations, solutions containing $C_2O_6^{2-}$ (solution a) $CO_3^{2-}$ (solution b) or $HCO_3^-$ (solution c) anions show a strong carboxylating power towards alcohols[2,3] and nitrogen-containing compounds (amines, amides, or carbamates).[4] These solutions can be easily prepared by simple electrochemical or chemical processes:

(*i*) solution a by cathodic reduction of $O_2$ to $O_2^{\cdot-}$ from 0.1 M solutions of $Et_4NClO_4$ in $CH_3CN$ saturated with an $O_2$–$CO_2$ gaseous mixture[4d,5] (Scheme 1, eqn. 1); (*ii*) solution b by cathodic reduction of $CO_2$ to $CO_2^{\cdot-}$ from 0.1 M solutions of $Et_4NClO_4$ in $CH_3CN$, saturated with $CO_2$[2b,4b] (Scheme 1, eqn. 2); (*iii*) solution c by bubbling $CO_2$ in a 0.1 M solution of $Et_4NOH$ in $CH_3CN$[3,4c] (Scheme 1, eqn. 3).




**Scheme 1**

If halohydrins or alcohols (followed by an alkylating agent) are added to these solutions, cyclic or linear carbonates, respectively, can be obtained in good to high yields (Scheme 2, eqn. 4 or 5). Therefore, the formation of cyclic carbonates requires the presence of a suitable leaving group in an α position with respect to the alcoholic hydroxy group (*e.g.*, halohydrins). Consequently, according to this method, the transformation of an alcohol into a cyclic carbonate necessarily implies an initial step that allows the carbon α to the alcoholic group to be suitably functionalized. In addition, although examples of conversion of halohydrins into 1,3-dioxolan-2-ones in very high yields have been reported, there are cases for which the yields are extremely low.[3] With regards to this last point, it appears to be significant that *erythro*-2-bromo-1,2-diphenylethanol is turned into *trans*-4,5-diphenyl-1,3-dioxolan-2-one in 80% yield, while from *threo*-2-bromo-1,2-diphenylethanol, only minimal amounts of *cis*-4,5-diphenyl-1,3-dioxolan-2-one are obtained, *cis*-2,3-diphenyloxirane being the main product.[3] Since the solutions a–c (described in *i*–*iii*) are easy-to-obtain, non-toxic, non-polluting reactants potentially able to convert suitable substrates into cyclic carbonates, we thought that studying their




**Scheme 2**

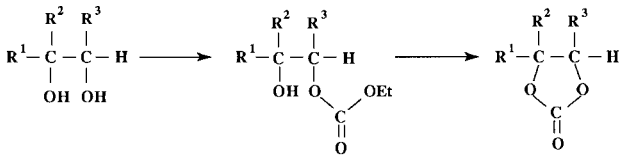
reactivity towards 1,2-diols (*i.e.*, low-cost, easily available substrates) could be of interest. Diol **1a** was taken as reference compound.

## Results and discussion

When *meso*-**1a** and subsequently EtI were added to each of the solutions a–c, cyclic carbonate *cis*-**3a** could be isolated. In the absence of the alkylating agent, the cyclic carbonate does not form at all, and the diol can be quantitatively recovered. The percentage of *meso*-**1a** turned into *cis*-**3a** increases with the molar ratio of carboxylating agent : diol, and attains a maximum value (≈20%) at a ratio of 0.5 when using solutions a,b and at 1.0 in the case of solution c. The formation of *trans*-**3a** can be always excluded. The diol not transformed into carbonate can be almost completely recovered from the reaction mixture. This suggested that repeating the process could allow a better conversion from diols into carbonates to be obtained. The reaction mixture was evaporated under reduced pressure and the same amount of the carboxylating agent, followed by EtI, was added to the residue. After the last procedure was repeated once again, the carbonates were formed with yields up to 45%. These results are largely independent of the carboxylating agent (Table 1, entries 1–3).

To see if this method for turning 1,2-diols into alkane-1,2-diyl carbonates could be generalized, the investigation was extended to diols (±)-**1a**, *meso*-**1b**, (−)-**1b**, **1c–e** (Scheme 3).

From diols (±)-**1a**, *meso*-**1b** and (−)-**1b**, we obtained cyclic carbonates *trans*-**3a**, *cis*-**3b** and *trans*-**3b**, respectively, while none of the corresponding isomers *cis*-**3a**, *trans*-**3b** or *cis*-**3b** were present in the reaction mixture (Table 1, entries 4–10). Once again the course of the reaction appears independent of the carboxylating reagent. These results suggest that in all cases the reaction occurs with total retention of the absolute configuration, in agreement with a mechanism that does not involve cleavage of the C—O bond of the chiral carbon atom.



**1** **2** **3**

| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| a | Ph | H | Ph |
| b | $CH_3$ | H | $CH_3$ |
| c | H | H | H |
| d | Ph | $CH_3$ | H |
| e | Ph | H | H |

**Scheme 3**

It may be of some interest to compare our results with those obtained by using halohydrins as substrates. It has been reported[3] that cyclic carbonates *trans*-**3b**, *cis*-**3b** and *trans*-**3a** have been isolated after addition of halohydrins *erythro*-, *threo*-3-bromobutan-2-ol and *erythro*-2-bromo-1,2-diphenylethanol, respectively, to solutions of tetraethylammonium hydrogencarbonate in acetonitrile (solution c). It follows that, unlike 1,2-diols, the cyclization of halohydrins to give 1,3-dioxolan-2-ones involves inversion of the absolute configuration. Consequently, we decided to reconsider the behaviour of halohydrins when added to solutions a and b. We verified that, from solutions containing *erythro*-2-bromo-1,2-diphenylethanol (**5a**) *trans*-**3a** together with *trans*-2,3-diphenyloxirane could be isolated. In contrast, from solutions containing *threo*-**5a** a mixture of *trans*-**3a** and *cis*-**3a** together with *trans*- and *cis*-2,3-diphenyloxirane could be isolated (see Experimental). Therefore, the conversion of halohydrins into cyclic carbonates may also involve retention of the absolute configuration, depending on the characteristics of the substrate. Consequently, this conversion is not stereoselective in all the cases examined, unlike the cyclization of 1,2-diols.

Lastly, the investigation was extended to 1,2-diols for which one of the two carbon atoms bearing the hydroxy group was always primary, while the other could be secondary (**1e**), tertiary (**1d**), or also primary (**1c**). In all cases, the transformation of the 1,2-diols into cyclic carbonates has been confirmed (Table 1, entries 11–13). As regard diols *meso*-**1b**, (−)-**1b**, **1c–e**, HPLC or GC analyses of the reaction mixture obtained by treatment with solution a gave evidence for the formation of linear carbonates **2b–e** besides cyclic carbonates **3b–e**. Subsequent work-up of the mixture, and isolation of the reaction products, showed that only cyclic carbonates **3d,e** are obtained from diols **1d,e**. In these cases, to a good approximation, the yield of the isolated cyclic carbonates corresponds to the sum of the yields obtained for linear and cyclic carbonates by the HPLC or GC analyses performed on the reaction mixture. It may be suggested that a linear carbonate is an intermediate in the transformation of diols into cyclic carbonates (Scheme 3).

To support this hypothesis, linear monocarbonate **2c**, prepared by an independent route,[6] has been added to solution a, without the subsequent addition of any alkylating agent. GC analysis of the reaction mixture showed that **2c** was quantitatively converted into cyclic carbonate **3c** (Table 1, entry 14).

## Conclusions

The transformation of 1,2-diols into alkane-1,2-diyl carbonates may be carried out without employing toxic and pol-

**Table 1** Synthesis of cyclic carbonates **3a–e** by addition of **1a–e**, **2c** to $CH_3CN$ solutions of $C_2O_6^{2-}$ (a), $CO_3^{2-}$ (b), $HCO_3^-$ (c)

| Entry | Substrate | Solution | Products and yields (%)[a] | | |
|---|---|---|---|---|---|
| 1 | *meso*-**1a** | a | *cis*-**3a**(19)[20][44][b] | | *meso*-**1a** (62)[75][40][b] |
| 2 | *meso*-**1a** | b | *cis*-**3a** [20][45][b] | | *meso*-**1a** [72][42][b] |
| 3 | *meso*-**1a** | c | *cis*-**3a** [22][44][b] | | *meso*-**1a** [66][37][b] |
| 4 | (±)-**1a** | a | *trans*-**3a** (10)[15] | | (±)-**1a** (60)[83] |
| 5 | (±)-**1a** | b | *trans*-**3a** [12] | | (±)-**1a** [70] |
| 6 | (±)-**1a** | c | *trans*-**3a** [16] | | (±)-**1a** [83] |
| 7 | *meso*-**1b** | a | *cis*-**3b** (9)[13] | **2b** (8)[13] | *meso*-**1b** (46)[60] |
| 8 | *meso*-**1b** | b | *cis*-**3b** [20] | | *meso*-**1b** [67] |
| 9 | *meso*-**1b** | c | *cis*-**3b** [17] | | *meso*-**1b** [63] |
| 10 | (−)-**1b** | a | *trans*-**3b** (4)[10] | **2b** (6)[12] | (−)-**1b** (32)[64] |
| 11 | **1c** | a | **3c** [9] | **2c** [22] | **1c** [68] |
| 12 | **1d** | a | **3d** (25)[19] | **2d** [6] | **1d** (56)[68] |
| 13 | **1e** | a | **3e** (21)[14] | **2e** [8] | **1e** (55)[75] |
| 14 | **2c** | a | **3c** [100] | | |

[a] Procedure 1, isolated yields are given in parentheses, HPLC (GC in entries 7–11, 14) yields in brackets. [b] Procedure 2, HPLC yields.

luting reactants, at room temperature, in fairly short times, by means of acetonitrile solutions containing $C_2O_6^{2-}$, $CO_3^{2-}$, or $HCO_3^-$ anions in the presence of tetraalkylammonium cations. These solutions are readily prepared by electrochemical or chemical routes. The transformation is characterized by complete retention of the absolute configuration of the starting diols. Although the process yield is not high (20%), most of the 1,2-diol not turned into carbonate remains unchanged at the end of the reaction. A simple procedure to recycle this unreacted 1,2-diol has been elaborated and a better conversion (45%) from diols into carbonates has been achieved.

## Experimental

Controlled-potential electrolyses were carried out with an AMEL 552 potentiostat equipped with an AMEL 721 integrator. The cells used have already been described.[7] The counter electrode was a cylindrical platinum gauze and the reference electrode was the calomel type described by Fujinaga *et al*,[8] its potential was −0.02 V *vs.* SCE (saturated calomel electrode). Acetonitrile (Carlo Erba) and tetraethylammonium perchlorate (TEAP, Fluka) were purified as previously described.[7] All starting diols as well as *cis*- and *trans*-2,3-diphenyloxirane are commercially available; bromohydrins *erythro*- and *threo*-2-bromo-1,2-diphenylethanol were synthesized according to Dalton *et al.*[9] Column chromatography (cc) was performed on Merck silica gel 70–230 mesh (100 g per 1 g of crude mixture). HPLC analyses were carried out on a Perkin Elmer system composed of a Series 200 LC pump, a 235 Diode Array Detector and a Nelson 1022 Data Station, using a Merck Hibar LiChrocart (250-4, 7 μm) RP-18 column. A $CH_3CN$–$H_2O$ mixture in a linear gradient from 35 : 65 to absolute $CH_3CN$ over 20 min was used as eluent. The flow rate was 1 mL $min^{-1}$. GC analyses were carried out with a Perkin Elmer 8500 GC using a J & W fused silica megabore DB-WAX (30 m) column in the temperature range 70–200 °C. Quantitative HPLC and GC analyses were performed with the internal standard method. IR spectra were recorded with a Perkin Elmer Paragon 1000 FT-IR. $^1$H-NMR spectra were recorded as solutions in $CDCl_3$, using an AC 200 Bruker spectrometer and $Me_4Si$ as internal standard. MPs were taken on a Tottoli apparatus and are uncorrected. All new compounds gave satisfactory elemental analyses (C ± 0.3%, H ± 0.2%, N ± 0.2%).

### Electrochemistry

**Carboxylation promoted by reduction of $O_2$ in the presence of $CO_2$.** Solution a has been obtained by electrolysis carried out using a mercury pool cathode at −1.0 V, on a 0.1 M $CH_3CN$ solution of TEAP (60 ml) maintained at 25 °C, with $O_2$ and $CO_2$ being simultaneously bubbled through.

After flowing 3.0 F $mol^{-1}$ of substrate, the current was switched off, $N_2$ was bubbled through the solution for 5 min and the substrate **1a**–**e**, **2c** (1 mmol) was added to 20 ml of solution a. After 1 h, a fivefold molar excess of ethyl iodide was added (except in the case of **2c**) and the solution was maintained under stirring at room temperature for 24 h, giving solution A.

*Procedure 1*. A 1 ml sample of solution A was taken off for HPLC or GC analysis whose results are given in Table 1. The remaining solution was evaporated under reduced pressure and the residue extracted with diethyl ether (3 × 30 mL). The combined organic layers were dried ($Na_2SO_4$) and the solvent removed under reduced pressure. Cc of the residue allowed separation of the reaction products for their characterization (IR, NMR, TLC). *cis*- and *trans*-4,5-Diphenyl-1,3-dioxolan-2-one (**3a**),[10] *cis*- and *trans*-4,5-dimethyl-1,3-dioxolan-2-one (**3b**),[11] ethyl 2-hydroxyethyl carbonate (**2c**),[12] 1,3-dioxolan-2-one (**3c**),[13] 4-phenyl-1,3-dioxolan-2-one (**3e**)[14] are known compounds; product assignment was determined by their analytical data compared to authentic samples or literature data.

*Procedure 2*. As regards the substrate *meso*-**1a**, solution A was evaporated under reduced pressure. Solution a (20 ml) and subsequently EtI were added to the residue and the mixture was worked-up as before. This procedure was repeated once again. The final solution was analysed by HPLC (Table 1).

*meso-1,2-Diphenylethane-1,2-diol* (*meso-**1a***). Cc of the residue (222 mg) gave *cis*-**3a**, (47 mg, 19%) and starting *meso*-**1a** (134 mg, 62%).

(±)*-1,2-Diphenylethane-1,2-diol* [(±)-***1a***]. Cc of the residue (234 mg) gave *trans*-**3a**, (24 mg, 10%) and starting (±)-**1a** (128 mg, 60%).

*meso-Butane-2,3-diol* (*meso-**1b***). Cc of the residue (160 mg) gave *cis*-**3b** (11 mg, 9%), ethyl 3-hydroxybut-3-yl carbonate **2b** (12 mg, 8%) and starting *meso*-**1b** (40 mg, 46%). *R**, *S**-**2b**: oil; IR (film): *ν* 3450 and 1745 $cm^{-1}$; $^1$H-NMR *δ*: 4.65 (1H, m, C*H*OH, *J* = 6.3 Hz, 6.3 Hz), 4.17 (2H, q, $CH_2O$, *J* = 7.1 Hz), 3.95 (1H, m, CHOCO, *J* = 6.3 Hz, 6.3 Hz), 2.15 (1H, br s, OH), 1.25–1.10 (9H, m, 3 × $CH_3$).

(−)*-Butane-2,3-diol* [(−)-***1b***]. Cc of the residue (125 mg) gave *trans*-**3b**, (7 mg, 4%), ethyl 3-hydroxybut-2-yl carbonate **2b** (11 mg, 6%) and starting (−)-**1b** (29 mg, 32%). *R*,*R*-**2b**: oil; IR (film): *ν* 3450 and 1745 $cm^{-1}$; $^1$H-NMR *δ*: 4.59 (1H, m, C*H*OH, *J* = 6.3 Hz, 6.3 Hz), 4.18 (2H, q, $CH_2O$, *J* = 7.1 Hz), 3.76 (1H, m, CHOCO, *J* = 6.3 Hz, 6.3 Hz), 2.07 (1H, br s, OH), 1.30–1.13 (9H, m, 3 × $CH_3$).

*2-Phenylpropane-1,2-diol* (***1d***). Cc of the residue (140 mg) gave 4-methyl-4-phenyl-1,3-dioxolan-2-one **3d**[15] (48 mg, 25%) and starting **1d** (82 mg, 56%). **3d**: oil; IR (film): *ν* 1800 $cm^{-1}$; $^1$H-NMR *δ*: 7.28 (5H, br s, arom), 4.41 (2H, s, $CH_2O$), 1.82 (3H, s, $CH_3$).

*1-Phenylethane-1,2-diol* (***1e***). Cc of the residue (165 mg) gave 4-phenyl-1,3-dioxolan-2-one **3e** (30 mg, 21%), and starting **1e** (62 mg, 55%).

*erythro-2-Bromo-1,2-diphenylethanol* (*erythro-**5a***). The HPLC analysis of the electrolyzed solution gave: *trans*-**3a** (62%), *trans*-2,3-diphenyloxirane (28%) and starting *erythro*-**5a** (9%).

*threo-2-Bromo-1,2-diphenylethanol* (*threo-**5a***). The HPLC analysis of the electrolyzed solution gave: *cis*-2,3-diphenyloxirane (63%), starting *threo*-**5a** (15%), *cis*-**3a** (5%), *trans*-2,3-diphenyloxirane (4%), and *trans*-**3a** (2%).

**Carboxylation promoted by reduction of $CO_2$.** Solution b has been obtained by electrolysis carried out using a copper cathode at −2.1 V on a 0.1 M $CH_3CN$ solution of TEAP (60 ml) maintained at 0 °C, with $CO_2$ being bubbled through.

After flowing 3.0 F $mol^{-1}$ of substrate, the current was switched off, $N_2$ was bubbled through the solution for 5 min and the substrate *meso*-**1a**, (±)-**1a**, *meso*-**1b** (1 mmol) was added to 20 ml of solution b. After 1 h, a fivefold molar excess of ethyl iodide was added and the solution was maintained under stirring at room temperature for 24 h, giving solution B. The work-up of solution B was carried out according to procedures 1 and 2 (the latter for *meso*-**1a**). The results of HPLC or GC analyses are reported in Table 1. The HPLC analysis of the electrolyzed solution from *threo*-**5a** gave: *cis*-2,3-diphenyloxirane (42%), *cis*-**3a** (37%), starting *threo*-**5a** (8%), *trans*-**3a** (4%), *trans*-2,3-diphenyloxirane (3%).

### Chemistry

**Synthesis of 2d,e.** The availability of monocarbonates **2d,e** was necessary for their identification during the instrumental analysis of the appropriate reaction mixtures. They were prepared by reacting equimolar amounts of the corresponding diols **1d,e** and ethyl chloroformate according to usual procedures[6] and purified by column chromatography.

*Ethyl 2-hydroxy-2-phenylpropyl carbonate* (**2d**). Oil; IR: $\nu$ 3470 and 1750 $cm^{-1}$, $^1$H-NMR $\delta$: 7.25–7.15 (5H, m, arom), 4.23 (2H, s, $CH_2O$), 4.13 (2H, q, $CH_2CH_3$, $J = 7.2$ Hz), 2.46 (1H, br s, OH), 1.54 (3H, s, $CH_3C$), 1.23 (3H, t, $CH_2CH_3$, $J = 7.2$ Hz).

*Ethyl 2-hydroxy-2-phenylethyl carbonate* (**2e**). Oil, IR (film): $\nu$ 3500 and 1740 $cm^{-1}$, $^1$H-NMR $\delta$: 7.30–7.25 (5H, m, arom), 4.92 (1H, dd, CHOH, $J = 4.0$ Hz, 8.0 Hz), 4.25 (1H, dd, $CHCH_2$, $J = 4.0$ Hz, 1.2 Hz), 4.13 (2H, q, $CH_2CH_3$, $J = 7.2$ Hz), 4.11 (1H, dd, $CHCH_2$, $J = 8.0$ Hz, 1.2 Hz), 3.16 (1H, br s, OH), 1.26 (3H, t, $CH_2CH_3$, $J = 7.2$ Hz).

**Carboxylation promoted by reaction with tetraethylammonium hydrogencarbonate.** *meso*-**1a**, (±)-**1a**, *meso*-**1b** (1 mmol) were added to a suspension of tetraethylammonium hydrogencarbonate[3] (1 mmol) in $CH_3CN$ (20 ml). After 1 h, a fivefold molar excess of ethyl iodide was added and the mixture was maintained under stirring at room temperature for 24 h, giving solution C. Work-up of the latter was carried out according to procedures 1 and 2 (the latter for *meso*-**1a**). The results of HPLC and GC analysis are reported in Table 1.

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