Pergamon

Tetrahedron Letters, Vol. 38, No. 20, pp. 3565-3568, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00664-3

Electrochemical Activation of Carbon Dioxide: Synthesis of Organic Carbonates.

M. Antonietta Casadei,[a] Achille Inesi,[b] Leucio Rossi[b]*

[a] Dipartimento di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Università "La Sapienza",
P.le Aldo Moro 5, I-00185 Roma, Italy.

[b] Dipartimento di Chimica, Ingegneria Chimica e Materiali, Università degli Studi, I-67040, Monteluco di Roio, L'Aquila, Italy.

Abstract: Electrochemically activated CO_2 reacts, under mild conditions, with primary and secondary alcohols bearing a leaving group at the α-position affording the corresponding cyclic carbonates in high yields; unsubstituted alcohols are converted, after addition of EtI, into the corresponding unsymmetrical ethyl carbonates in moderate to good yields. Tertiary alcohols and phenols are stable to the reagent. © 1997 Published by Elsevier Science Ltd.

Organic carbonates constitute an important and versatile class of compounds. Recently, the synthetic methodologies as well as the possible utilisation have been amply reviewed and discussed.[1] They have widespread application as solvents for a variety of processes and as efficient protecting groups for alcohols and diols.[2] Moreover carbonic esters are widely used in industrial chemistry as monomers for several types of polymers and in the synthesis of pharmaceutical and agricultural chemicals.[1, 3]

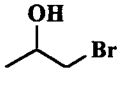
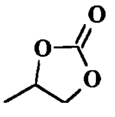
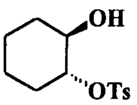
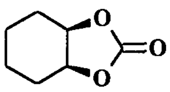
The most relevant known syntheses of organic carbonates involve the direct or indirect use of phosgene, with all the remarkable drawbacks that the use of such a toxic and corrosive reagent entails. Recently, the replacement of phosgene with carbon dioxide in the synthesis of carbonates, starting from hydroxy compounds, has been proposed by several authors.[4] Owing to its thermodynamic stability and relative kinetic inertness, preliminary activation of CO_2 is required, and electrochemical techniques provide solutions to the problem.[5,6] Recently, we proposed the $O_2^{\dot{-}}/CO_2$ system (formed by electrochemical one-electron reduction of dioxygen in dipolar aprotic solvents in the presence of CO_2) as a mild and safe carboxylating reagent for the synthesis of organic carbonates.[7]

In a previous paper,[8] we reported that electrochemically activated CO_2 reacts with amines and EtI, under mild reaction conditions, affording the corresponding ethyl carbamates in high to excellent yields. We now wish to report that this method can be extended to the synthesis of cyclic and linear unsymmetrical carbonates starting from the corresponding alcohols.

In a typical procedure[8], a solution of $MeCN\text{-}Et_4NClO_4$ (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 (-2.1 V *vs.* SCE) that allows the reduction of CO_2 to $CO_2^{\dot{-}}$. At the end of the electrolysis, after bubbling N_2, the alcohol was added and the reaction mixture was allowed to stand at room temperature for the appropriate time before adding, if necessary, a fivefold excess of EtI. Removal of solvent gave a residue which was extracted with Et_2O. The solvent was evaporated and the residue chromatographed on silica gel to afford the corresponding carbonate.

The behaviour of a number of alcohols and phenols was investigated. Aliphatic alcohols bearing a leaving group at the α position were readily converted into the corresponding 2-oxo-1,3-dioxolane in high yields (1.5 F mol^{-1} of substrate were required). The results are reported in Table 1.

Table 1. Carboxylation of Alcohols Bearing a Leaving Group[a]

Entry	Substrate	Product[b]	Yield (%)[c]
1	 **1**	 **2**	90
2	 **3**	 **4**	86

[a] Divided cell, Cu cathode, Pt anode, 0°C; [b] Analyses after 1.5 F mol^{-1} of substrate, no addition of EtI was required, reaction time 6 hours; [c] Yields, based on the starting alcohol, refer to the isolated carbonate.

Table 2. Carboxylation of Alcohol 5 Under Different Reaction Conditions

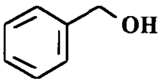
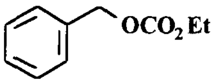
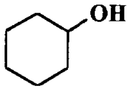
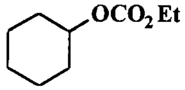
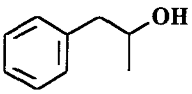
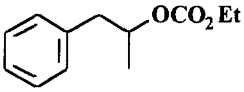
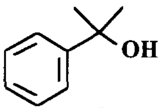
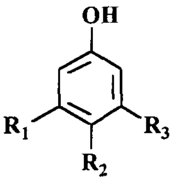
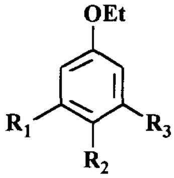
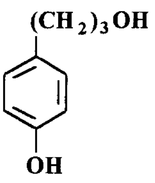
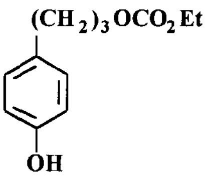

5 **6**

Entry	Reaction conditions[a]	Yield of 6 (%)[b]
1	2.0 F mol^{-1} of 5; rt; 90 min[c]; EtI	55
2	2.0 F mol^{-1} of 5; reflux; 90 min; EtI	27
3	2.0 F mol^{-1} of 5; rt; 90 min; MS 4Å[d]; EtI	69[e]
4	5.0 F mol^{-1} of 5; rt; 90 min; MS 4Å; EtI	71
5	2.0 F mol^{-1} of 5; rt; 2 days; MS 4Å; EtI	68

[a] $MeCN-Et_4NClO_4$ 0.1 mol dm^{-3} (20mL), 5 (1.0 mmol), EtI (5.0 mmol), divided cell, Cu cathode, Pt anode, 0°C; [b] Yields are determined by GC analysis; [c] Time before the addition of EtI; [d] Molecular sieves were activated by heating at 400°C for 24 hours; [e] Carbonate was also isolated in 67% yield.

When the reaction was carried out with 3-phenyl-1-propanol **5** the corresponding ethyl carbonate **6**, formed after addition of EtI (90 min) to the electrolysis mixture, was obtained in 55% yield.
Several attempts were made in order to improve this value. The results are summarized in Table 2.

Table 3. Reaction of Alcohols and Phenols with Electrochemically Reduced CO_2[a]

Entry	Substrate	Product	Yield[b]
1	 **7**	 **8**	54
2	 **9**	 **10**	34
3	 **11**	 **12**	44
4	 **13**	**13**	92
5	 **14a**: R_1=R_3=CH_3; R_3=H **14b**: R_1=R_3=H; R_2=OCH_3	 **15a**: R_1=R_3=CH_3; R_3=H **15b**: R_1=R_3=H; R_2=OCH_3	12[c] 9[d]
6	 **16**	 **17**[e]	50

[a] Reactions were carried out as described in Table 2 entry 5; [b] Yields based on the starting alcohols and phenols refer to the isolated product; [c] Phenol **14a** (78%) was also recovered; [d] Phenol **14b** (76%) was also recovered; [e] Ethylated phenol **17** (21 %) and ethylated phenol **16** (13 %) were also recovered.

Raising the temperature to the reflux temperature results in a lowering of the amount of carbonate recovered (Table 2, entry 2). Better results were obtained when activated 4 Å molecular sieves were added to the system. Ethyl-3-phenylpropyl carbonate **6** was isolated in 69 % of yield (Table 2, entry 3). No further increase of the yield was observed when a larger amount of electricity than 2.0 F mol^{-1} of substrate was used or when long reaction times (2 days) before the addition of EtI were allowed to pass (Table 2, entries 4 and 5).

The methodology with the optimised conditions was extended to other hydroxylated substrates. As shown in table 3, primary alcohols furnished better yields of carbonates with respect to secondary ones (Table 3 entries 2 and 3). A tertiary alcohol was stable to the reagent (Table 3, entry 4), while phenols were only ethylated in poor yields (Table 3, entry 5). Furthermore the stability of phenolic hydroxy groups allows the selective carboxylation of polyhydroxylated compounds (Table 3, entry 6).

The overall mechanism of the reaction is now under study.

Acknowledgement: This work was supported by research grants from M.U.R.S.T. and C.N.R., Rome, Italy.

REFERENCES

1. Shaikh, A.G.; Sivaram, S. *Chem Rev.* **1996**, 96, 951.
2. Greene, T.W.; Wuts, P.G.M. *Protective Groups in Organic Synthesis*, 2nd ed.; John Wiley and Sons, Inc.: New York, 1991; pp. 104-110, 140-141, 165-167, 173-174.
3. Abrams, E.: Carbonic and Chloroformic Esters. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; John Wiley and Sons, Inc.: New York, 1978; Vol. 4, pp 758-771.
4. (a) Oi, S.; Kuroda, Y.; Matsuno, S.; Inoue, Y. *Bull. Chem. Soc. Jpn.* **1993**, 8, 985. (b) Hoffman, W.A. III. *J. Org. Chem.* **1982**, 47, 5209. (c) Dixneuf, P.H.; Bruneau, C. *J. Mol. Catal.* **1992**, 74, 97. (d) Sakai, S.; Fujinamin, T.; Yamada, T.; Furusawa, S. *Nippon Kagaku Kaishi* **1975**, 10, 1789. (e) Ota, H. Jap. Pat. 24, 966, 1970; *Chem. Abstr.* **1970**, 73, 98378j. (f) Sasaki, Y.; Koushita, T. *Shignen Kankio* **1992**, 1 (1), 23. (g) Nisso Petrochem. Ind. Ltd. Jap. Pat. 81, 25, 138, 1979; *Chem. Abstr.* **1981**, 95, 80505t.
5. (a) Aresta, M.; Forti, G. *Carbon Dioxide as a Source of Carbon,* Nato Asi Series, D. Reidel Pub. Comp., Dordrecht 1987, pp 33-55.
6. Casadei, M.A.; Cesa, S.; Micheletti Moracci, F.; Inesi, A. Feroci, M. *J. Org. Chem.* **1996**, 61, 380.
7. Casadei, M.A.; Cesa, S.; Feroci, M.; Inesi, A., Rossi, L., Micheletti Moracci, F. *Tetrahedron* **1997**, 53, 167.
8. Casadei, M.A.; Inesi, A.; Micheletti Moracci, F.; Rossi, L. *Chem. Commun.* **1996**, 2575.

(*Received in UK* 18 *February* 1997; *revised* 3 *April* 1997; *accepted* 8 *April* 1997)