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The $O_2^{\cdot -}/CO_2$ System as Mild and Safe Carboxylating Reagent Synthesis of Organic Carbonates

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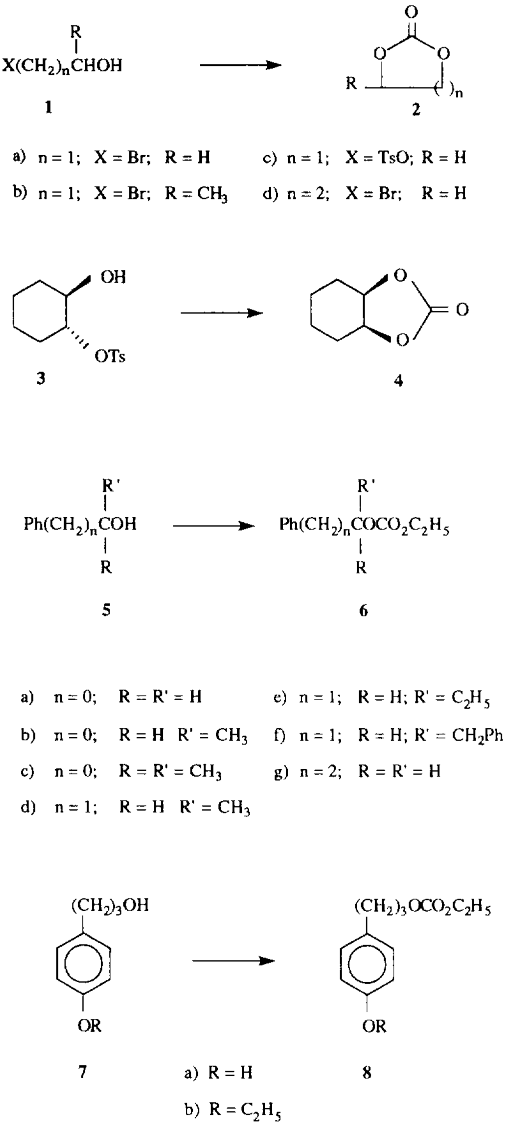
Abstract: The $O_2^{\cdot -}/CO_2$ system, originating from electrochemical one-electron reduction of dioxygen in dipolar aprotic solvents and in the presence of CO_2, converts primary and secondary alcohols bearing a leaving group at α or β position into the corresponding cyclic carbonates in high to excellent yields. Unsubstituted alcohols are also converted, but in unsatisfactory yields, into the corresponding alkyl ethyl carbonates after completion of the reaction by addition of EtI. Tertiary alcohols and phenols are stable to the reagent, thus allowing selective carboxylation of polyhydroxy derivatives. CH-acid containing compounds undergo different reactions, if any, with the reagent but in the cases under study the formation of carboxylation products has never been observed. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

We have recently shown[1] that superoxide ion, electrogenerated by reducing dioxygen in dipolar aprotic solvents, activates carbon dioxide giving a carboxylating species able to convert NH-protic carboxamides bearing a leaving group at the appropriate position into the corresponding oxazolidine- or 1,3-oxazine-2,4-diones.[2] In the case of the five-membered heterocycles, which represent a class of biologically active compounds,[3] high to excellent yields were attained under a number of experimental conditions, including the addition of the substrate after the current was switched off. If compared with the known syntheses of oxazolidine-2,4-diones,[4] the electrochemically promoted carboxylation-cyclization process needs milder conditions and the use of inexpensive and safe reagents, assuming the role of a convenient, environmentally friendly approach, which can also be applied to substrates bearing electrophoric groups more easily reducible than dioxygen.

At present we are engaged in defining the scope and generality of the new carboxylating procedure taking into account other classes of compounds than carboxamides. In this paper we report the results obtained by studying OH and CH-acid containing compounds (Schemes 1 and 2). Apart from their usefulness as protective groups for phenols and alcohols,[5] in particular in sugar[6] and nucleoside[7] chemistry, carbonic esters are widely used in industrial chemistry as, for example, in the synthesis of pharmaceutical and agricultural chemicals, as solvents for natural and synthetic polymers and in the electronic industry, as starting materials in the preparation of polycarbonate resins.[8] The most important syntheses of organic carbonates need the direct or indirect (*via* chloroformates) use of phosgene,[5,8] with all the considerable drawbacks that such a toxic and corrosive reagent involves. Otherwise, carbonates are prepared by metal assisted carbonylation of hydroxy compounds,[8] but also this approach has disadvantages, in particular with respect to the environmental impact. If the $O_2^{\cdot -}/CO_2$ system works well with hydroxy compounds, a new convenient access to organic carbonates might therefore be opened.

Scheme 1



RESULTS AND DISCUSSION

Stability of the reagent. As stated before, we have previously shown that the reagent survives the electrolysis time required for its preparation but no attempt was made to establish its shelf-life.[1] We started the present study with a few initial experiments. O_2 was reduced in the presence of CO_2 in MeCN -0.1 mol l^{-1} TEAP and samples of this solution were stored both at room temperature (20-22°C) with exclusion of moisture and in a refrigerator (4-5°C) in a sealed bottle. The activity of the reagent in these samples was tested by reaction with *N*-benzylchloroacetamide as standard compound,[1] and the yield of 3-benzyloxazolidine-2,4-dione at different times was compared with that obtained by using the freshly prepared reagent. The yield of oxazolidinedione at zero time observed in several runs was in the range 82-88% and, independently of the storage temperature, does not change significantly during a period of six weeks. This is interesting with respect to the usefulness of the reagent in synthetic chemistry and once ascertained the generality of its use, it makes also conceivable its marketing.

Table 1. Synthesis of Carbonates from Alcohols and $O_2^{\cdot-}/CO_2$ (MeCN -0.1 mol l^{-1} TEAP; Pt anode; Hg cathode; E= -1.0 V)

Entry	Subs.	Meth.[a]	n[b]	Products (yield%)[c]
1	**1a**	A	1.0	**2a** (94) [94]
2	**1a**	B	1.2[d]	**2a** (83) [80]
3	**1a**	B[e]	1.2	**2a** (81) [81]
4	**1b**	A	1.0	**2b** (92) [90]
5	**1b**	B	1.2	**2b** (95) [90]
6	**1c**	B	1.2	**2a** (85) [82]
7	**1d**	B	1.2	**2d** (86) [86]
8	**3**	A	1.0	**4** (90) [87]
9	**3**	A[f]	1.0	**4** (88) [87]
10	**3**	B	1.2	**4** (87) [83]
11	**5a**	A	1.0	**5a** (33), **6a** (33), BA[g] (21)
12	**5a**	B	0.2	**5a** (82), **6a** (15), BA (2)
13	**5a**	B	0.4	**5a** (66), **6a** (24), BA (5)
14	**5a**	B	0.6	**5a** (58), **6a** (32), BA (7)
15	**5a**	B	0.8	**5a** (55), **6a** (35), BA (9)
16	**5a**	B	1.0	**5a** (55), **6a** (35), BA (9)
17	**5a**	B	1.2	**5a** (56), **6a** (35), BA (9)
18	**5a**	B	1.5	**5a** (56), **6a** (34), BA (10)
19	**5a**	B	2.0	**5a** (52), **6a** (32), BA (14)
20	**5b**	B	1.0	**5b** (68), **6b** (24)
21	**5c**	B	1.0	**5c** (97)
22	**5d**	B	1.0	**5d** (64), **6d** (25)
23	**5e**	B	1.0	**5e** (73), **6e** (19)
24	**5f**	B	1.0	**5f** (77), **6f** (20)
25	**5g**	B	1.0	**5g** (54), **6g** (37)
26	**7a**	B	2.0	**7a** (30), **7b** (3) **8a** (43), **8b** (7)

[a] Method A: O_2 was reduced in the presence of both CO_2 and the substrate. Method B: O_2 was reduced in the presence of CO_2 and the substrate was added after the current was switched off. [b] Number of Faraday/mol of substrate. [c] GC (entries 1-10) or HPLC (entries 11-26) analysis. Values in square brackets refer to isolated yields. [d] By using 1.0 F/mol some unreacted substrate was still present in the reaction mixture. [e] Pt was used as cathode. [f] DMF was used as solvent. [g] BA = benzaldehyde.

Reactions with hydroxy compounds. Synthesis of organic carbonates. The behaviour of a number of alcohols and phenols toward the $O_2^{\cdot-}/CO_2$ system has been investigated. By analogy with the carboxamides previously studied,[1] ω-substituted alcohols were tested at first. Primary and secondary aliphatic alcohols bearing a leaving group at α or β position (**1**,**3** Scheme 1) are smoothly converted into the corresponding 1,3-dioxolan- or 1,3-dioxan-2-ones. High to excellent yields of cyclic carbonates are attained in every case, independent of the experimental conditions (Table 1, entries 1 - 10). In particular, the addition of the substrate at the beginning of the electrolysis or after the current was switched off (*cfr.* entries 1,4 and 8 *vs* 2,5 and 10) and the nature of both the cathode (*cfr.* entries 2 and 3) and the solvent (*cfr.* entries 8 and 9) do not significantly change the chemical yield of the products. The stereochemical outcome of the carboxylation-cyclization process is shown by the formation of the *cis*-fused bicyclic carbonate **4** as the only diastereomer which originates from *trans*-1,2-cyclohexanediol derivative **3**. The intervention of an S_N2 step in the reaction pathway is supported by the observed unreactivity of the *cis*-isomer of **3** toward the carboxylation process.

Less satisfactory results were obtained in the case of alcohols **5**, lacking leaving groups as substituents. According to procedure B, which involves addition of the substrate after the current was switched off, the corresponding alkyl ethyl carbonates, formed by addition of EtI to the electrolysis mixture, were recovered in chemical yields not exceeding 35-40% (Table 1). In an attempt to improve these values, we have investigated their dependence, under otherwise identical conditions, on the amount of electricity passed through the cell. Using benzyl alcohol **5a** as model compound, the data reported in Table 1 (entries 12-19) were collected. Quite surprisingly, the maximum chemical yield of **6a** (35%) is attained at 0.8 Faraday per mole of **5a** and it remains almost unchanged up to 1.5 F/mol as do the yields of starting **5a** (55%) and benzaldehyde[9] (9%), which are the only accompanying products in the reaction mixture. At 2.0 F/mol the amounts of **5a** (52%) and **6a** (32%) slightly decrease and in parallel the yield of benzaldehyde (14%) increases. The current efficiency moves in the opposite direction with respect to the chemical yield: higher (and satisfactory) values are measured at low current consumptions. Therefore, in some cases it may be more convenient to work under these conditions and arrange the recycling of the substrate. When treated according to procedure A, which involves the reduction of dioxygen in the presence of both CO_2 and the substrate, **5a** gives 33% **6a** and 21% benzaldehyde after 1.0 F/mol has been consumed but only 33% **5a** is recovered unchanged, other unknown products being also present in the reaction mixture. It appears that competitive reactions between superoxide and the alcohol, including oxidation,[10] occur under these conditions thus discouraging the use of procedure A with substrates as **5**.

No mechanistically oriented investigations have been carried out. Nevertheless, based on the available data, some hypotheses can be put forward. The formation of **4** from **3** strongly supports the intervention of a monoalkyl carbonate (or its anion) intermediate which, at least in principle, can competitively undergo alkylation (to dialkyl carbonate) or dissociation (to CO_2 and the starting alcohol or its anion).[11] The presence of a leaving group in the starting molecule allows the intermediate to directly evolve to the end-products and very high yields of cyclic carbonates are attained in the case of both primary and secondary alcohols. On the contrary, when leaving groups are absent an external electrophile is necessary to complete the carboxylation process and it must be added to the electrolysis mixture after some time has elapsed in order to prevent its reaction with the carboxylating species.[12] The concentration of the surviving intermediate thus establishes the yield of dialkyl carbonate. In turn, the concentration of the monoalkyl carbonate depends on both steric factors and nucleophilicity of the substrate (or its anion). Accordingly, the higher the steric hindrance the lower the yield of carbonate arising from alcohols **5** (Table 1. Tertiary alcohol **5c** does not react at all). Furthermore, separate experiments (see Experimental) have demonstrated that phenols are unreactive toward the carboxylation reaction.

The stability of phenolic hydroxy groups allows the selective carboxylation of polyhydroxylated compounds such as **7a** which is converted into the corresponding carbonate exclusively at the terminal alcoholic group, the phenol end of the molecule being only partially converted into the ethyl derivative after addition of the alkylating reagent.

Reaction with carbon acids. Unsubstituted carbon acids of very low acidity (di- or triphenylmethane, phenylacetonitrile, *etc.*) are stable toward the reagent. Substrates of the same type but bearing a leaving group undergo nucleophilic displacement of the latter. For example, compound **9** yields a mixture of alcohol **5g** and carbonate **10** (Scheme 2, Table 2), the latter possibly arising from the former *via* carboxylation and alkylation by starting **9**. Different reaction pathways are observed if a leaving group is present at α or β position with respect to the acidic centre. In these cases, β-elimination or cyclization reactions follow the initial deprotonation, and also unfavourable acid-base equilibria are shifted because of the formation of stable end-products. Thus, chloroalkyl phenyl ketones **11** and **13** are converted in good yield into the corresponding vinyl and cyclopropyl ketones **12** and **14**, respectively.

Scheme 2

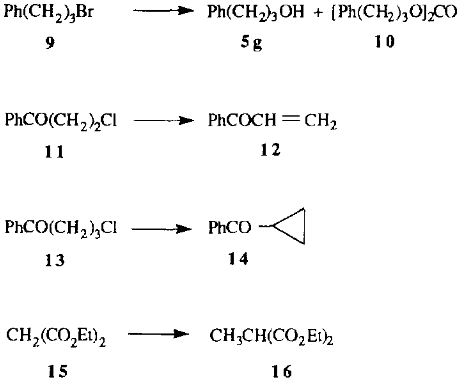


Table 2. Reaction of $O_2^{\cdot-}/CO_2$ with Carbon Acids. (MeCN - 0.1 mol l^{-1} TEAP; Pt anode; Hg cathode; E = -1.0 V)

Entry	Substrate	n[a]	Products (yield%)[b]
1	**9**	1.2	**9** (36), **5g** (26), **10** (22)
2	**11**	1.2	**12** (80)
3	**13**	1.2	**13** (10), **14** (70)
4	**15**	1.5	**15** (73), **16** (22)

[a] Number of Faraday/mol of substrate. [b] HPLC (entries 1-3) or GC (entry 4) analysis.

On the other hand, malonate **15** upon sequential treatment with the reagent and MeI is converted into its methyl derivative **16** only to a very limited extent, the remaining part being unchanged **15** (Table 2, entry 4). The acidity of diethyl malonate is about three order of magnitude higher than that of primary and secondary alcohols,[13] so that the unreactivity of **15** toward the reagent cannot be ascribed to this parameter. Possibly, the poor nucleophilicity of the malonate anion is responsible for its stability to $O_2^{\cdot-}/CO_2$ so that only the large excess of MeI promotes its partial conversion into **16** and no traces of carboxylation products are observed.

CONCLUSIONS

The electrochemical, one-electron reduction of dioxygen carried out in dipolar aprotic solvents and in the presence of carbon dioxide gives a reagent which behaves as a base, nucleophile or carboxylating agent, depending on the structural features of the substrate. From a synthetic point of view, the most important application results from its carboxylating ability which had previously been discovered and applied to the synthesis of biologically active oxazolidine-2,4-diones from carboxamides and has now been extended to the synthesis of organic carbonates from alcohols. In particular, alcohols bearing a leaving group at α or β position are converted into cyclic carbonates in excellent yields. The stability of the reagent allows the addition of the substrate after its preparation has been completed and the current switched off, thus widening its use to substrates more easily reducible than dioxygen.

If compared with the conventional syntheses of organic carbonates which require the use of phosgene or chloroformates, the $O_2^{\cdot-}/CO_2$ system works under very mild and safe conditions and thus represents a new useful approach to the synthesis of such class of compounds.

EXPERIMENTAL

General. The electrochemical apparatus, the cells and the reference electrode were described elsewhere.[14] The values of the working potential are given relative to SCE. *N,N*-Dimethylformamide (DMF, Aldrich) was distilled from activated alumina under reduced pressure. Acetonitrile (Carlo Erba RS for HPLC) was distilled twice from CaH_2 and P_2O_5 respectively and stored under activated molecular sieves. Tetraethylammonium perchlorate (TEAP, Fluka) was purified as already described.[14] Column chromatography (c.c.) was performed on Merck silica gel (70-230 mesh; 100 g per 1 g of reaction mixture). GC analyses were carried out with a Perkin Elmer 8500 GC using a SGE fused silica megabore BP 5 (25 m) column in the temperature range 45 - 110°C. HPLC analyses were carried out on a Perkin Elmer system made up from a Series 200 LC pump, a 235C Diode Array Detector and a Nelson 1022 data station, using a Merck Hibar LiChrocart (250 - 4; 5 μm) RP-18 column. A MeCN - H_2O mixture in linear gradient from 30 : 70 to 100 : 0 in 20 min was employed. In the analysis of the reaction solution from **9**, a MeOH - H_2O mixture in linear gradient from 30 : 70 to 90 : 10 was used. Quantitative HPLC and GC analyses were carried out with the internal standard method. IR spectra were recorded on a Perkin Elmer 281B grating spectrophotometer. ^{1}H-NMR spectra were recorded for solutions in $CDCl_3$, using an AC 200 Bruker spectrometer and Me_4Si as internal standard. M.p.s were taken upon a Tottoli apparatus and are uncorrected. All new compounds gave satisfactory elemental analyses (C ± 0.3%; H ± 0.2%; N ± 0.2%).

Chemistry. Substrates **1a,b,d**, **3**, **5a-e,g**, **7a**, **9**, **11**, **13** and **15** were commercially available. 2-Hydroxyethyl *p*-toluenesulfonate **1c**[15] was prepared by reacting equimolar amounts of 2-bromoethanol and silver *p*-toluenesolfonate in MeCN under reflux for 2 days and purified by c.c. ($CHCl_3$-AcOEt 8:2 as eluent).*cis*-2-Hydroxycyclohexyl *p*-toluenesulfonate was prepared by reacting equimolar amounts of *cis*-1,2-cyclohexanediol and *p*-toluenesulfonyl chloride in pyridine at room temperature for 24 h. The compound was purified by c.c. (light petroleum-AcOEt 7:3 as eluent): IR ν (film) 3460 and 1600 cm^{-1}; ^{1}H-NMR δ (ppm) 1.2 - 2.0 (m, 8H, 4 x CH_2), 2.0 (bs, 1H, OH), 2.43 (s, 3H, CH_3), 3.7 - 3.9 (m, 1H, C*H*OH), 4.6 -4.7 (m, 1H, C*H*OTs), 7.33 (d, 2H, arom) and 7.80 (d, 2H, arom).

1,3-diphenyl-2-propanol **5f**[16] was prepared by reducing 1,3-diphenylacetone with $NaBH_4$ in MeOH and purified by c.c. (light petroleum - AcOEt 3 : 2 as eluent).

Electrochemistry. The controlled-potential electrolyses were carried out at -1.0V in DMF (or MeCN) - 0.1 mol l^{-1} TEAP (50 ml) where O_2 and CO_2 were simultaneously bubbling. According to procedure A the substrate (2 mmol) was added at the beginning of the electrolysis.

According to procedure B, at the end of the electrolysis N_2 was bubbled for 5 min into the solution and then the substrate (2 mmol) was added. When necessary (**5a** - **g**, **7a**, **15**), 10 min after the current was switched off (procedure A) or the substrate was added (procedure B) a fivefold molar excess of alkylating agent was also added and the mixture was mantained under stirring at room temperature overnight to ensure that, independently of the nature of the substrate, the reaction goes to completion. A 2 ml sample of the electrolyzed solution was taken off for HPLC or GC analysis, the solvent was removed under reduced pressure from the remaining solution and the residue was extracted with Et_2O (5 x 30 ml). H_2O (100 ml) was added to the insoluble in ether and the mixture was extracted with $CHCl_3$ (3 x 50 ml). The extracts were dried (Na_2SO_4) and the solvent evaporated under reduced pressure. The residues were analyzed (IR, NMR and TLC) and combined if they have the same composition. C.c. of the mixtures allowed the separation of the reaction products for their characterization.

Reactions with substituted alcohols 1,3. The ^{1}H-NMR spectra of the residue from the ethereal extracts of the solutions arising from **1a** - **d** and **3** showed only the signals relative to the corresponding cyclic carbonates **2**, **4** (isolated yields in the range 80 - 94 % of theoretical values) as ascertained by comparison with authentic samples. 1,3-dioxolan-2-one **2a** and 4-methyl-1,3-dioxolan-2-one **2b** are commercially available; 1,3-dioxan-2-one **2d** [m.p. 44-45°C (ether); lit.[17] m.p. 47.0 - 47.5°C] and hexahydrobenzo[1,3]dioxolan-2-one **4** [m.p. 37-39°C (light petroleum); lit.[18] m.p. 38-39°C] were prepared according to the literature. The employed procedure together with the experimental conditions and the yields of the cyclic carbonates are reported in Table 1 (entries 1-10).

cis-2-Hydroxycyclohexyl *p*-toluenesulfonate was also submitted to procedure B. After the usual work up, only starting material and *cis*-1,2-cyclohexanediol were recovered in 67 and 15% yield, respectively.

A separate experiment was performed on **3** in order to verify its reactivity toward the system O_2/CO_2 without flowing of current. **3** (1 mmol) was dissolved in MeCN (25 ml) where O_2 and CO_2 were simultaneously bubbling. The mixture was mantained under stirring at room temperature for 2h. After the usual work up, **3** was quantitatively recovered.

Reactions with alcohols 5,7a. *Benzyl alcohol* ***5a***. C.c. (light petroleum - AcOEt 3:2 as eluent) of the residue from the combined extracts obtained in the reaction carried out according to procedure A gave benzyl ethyl carbonate **6a**[19] (100 mg, 29%), benzaldheyde (33 mg, 16%) and unreacted **5a** (56 mg, 27%). HPLC analysis of the reaction solution is reported in Table 1 (entry 11). In order to define the optimum of the current amount to employ for the carboxylation process, an electrolysis was carried out according to procedure B by using 100 ml of MeCN - 0.1 mol l^{-1} TEAP. After the flow of 0.2 F per mol of **5a**, N_2 was bubbled through the solution for 5 min, a sample (5 ml) was taken off and added to the alcohol (0.2 mmol). This solution was stirred for 10 min and then a fivefold molar excess of EtI was added. Other samples were taken off at 0.4, 0.6, 0.8, 1.0, 1.2, 1.5 and 2.0 F respectively and treated as above. All the solutions were mantained under stirring at room temperature overnight and then analyzed by HPLC. The results are reported in Table 1 (entries 12-19). C.c. of the residue from the combined extracts obtained in the reaction carried out after flowing 1.0 F / mol gave **6a** (100 mg, 29%), benzaldehyde (10 mg, 5%) and unreacted **5a** (110 mg, 53%).

A separate experiment was performed on **5a** in order to verify its reactivity toward the system O_2/CO_2 without flowing of current. **5a** (1 mmol) was dissolved in MeCN (25 ml) where O_2 and CO_2 were simultaneously bubbling. After 1h, a fivefold molar excess of EtI was added and the mixture was mantained under stirring at room temperature overnight. After the usual work up, **5a** was quantitatively recovered.

1-Phenylethanol ***5b***. C.c. of the residue from the combined extracts (light petroleum - AcOEt 4:1 as eluent) gave ethyl 1-phenylethyl carbonate **6b**[20] (75 mg, 20%) and unreacted **5b** (115 mg, 49%). **6b**: IR (film) ν: 1745 and 1610 cm^{-1}; ^{1}H-NMR δ (ppm) 1.20 (t, 3H, CH_3), 1.53 (d, 3H, CH_3CH), 4.13 (q, 2H, CH_2O), 5.70 (q, 1H, CH) and 7.30 (s, 5H, arom).

2-Phenyl-2-propanol ***5c***. ^{1}H-NMR spectra of the residues from the two extracts showed only the signals of the starting **5c**, that was recovered quantitatively.

1-Phenyl-2-propanol ***5d***. C.c. of the residue from the combined extracts (light petroleum - AcOEt 4:1 as eluent) gave ethyl 1-phenylpropan-2-yl carbonate **6d** (95 mg, 24%) and unreacted **5d** (145 mg, 56%). **6d**: IR (film) ν: 1745 and 1610 cm^{-1}; ^{1}H-NMR δ (ppm) 1.0 - 1.5 (m, 6H, 2 x CH_3), 2.87 (t, 2H, CH_2Ph), 4.17 (q, 2H, CH_2O), 4.6 - 5.2 (m, 1H, CH) and 7.23 (s, 5H, arom).

1-Phenyl-2-butanol ***5e***. C.c. of the residue from the combined extracts (light petroleum - AcOEt 4:1 as eluent) gave ethyl 1-phenylbutan-2-yl carbonate **6e** (72 mg, 17%) and unreacted **5e** (190 mg, 66%). **6e**: IR (film) ν: 1740 and 1600 cm^{-1}; ^{1}H - NMR δ (ppm) 0.8 - 2.8 (m, 8H, CH_2 + 2 x CH_3), 2.87 (t, 2H, CH_2Ph), 4.17 (q, 2H, CH_2O), 4.6 - 5.2 (m, 1H, CH) and 7.23 (s, 5H, arom).

1,3-Diphenyl-2-propanol ***5f***. C.c. of the residue from the combined extracts (light petroleum - AcOEt 9:1 as eluent) gave ethyl 1,3-diphenylpropan-2-yl carbonate **6f** (105 mg, 19%) and unreacted **5f** (240 mg, 59%). **6f**: IR (film) ν: 1740 and 1600 cm^{-1}; ^{1}H-NMR δ (ppm) 1.13 (t, 3H, CH_3), 2.85 (d, 4H, 2 x CH_2Ph), 4.05 (q, 2H, CH_2O), 4.8 - 5.3 (m, 1H, CH) and 7.13 (s, 10H, arom).

3-Phenylpropanol ***5g***. C.c. of the residue from the combined extracts (light petroleum - AcOEt 4:1 as eluent) gave ethyl 3-phenylpropyl carbonate **6g**[20] (140 mg, 35%) and unreacted **5g** (100 mg, 39%). **6g**: IR (film) ν: 1750 and 1610 cm^{-1}; ^{1}H-NMR δ (ppm) 1.27 (t, 3H, CH_3), 1.7 - 2.3 (m, 2H, CH_2), 2.70 (t, 2H, CH_2Ph), 4.17 (q, 2H, CH_2O) and 7.17 (s, 5H, arom).

3-(4-Hydroxyphenyl)propanol ***7a***. C.c. of the residue from the combined extracts (light petroleum - AcOEt 7:3 as eluent) gave ethyl 3-(4-ethoxyphenyl)propyl carbonate **8b** (24 mg, 5%), ethyl 3-(4-hydroxyphenyl)propyl carbonate **8a** (137 mg, 32%), 3-(4-ethoxyphenyl)propanol **7b** (10 mg, 3%) and unreacted **7a** (60 mg, 21%).
7b: m.p. 36 - 38°C; IR (nujol) ν: 3260 and 1610 cm^{-1}; ^{1}H-NMR δ (ppm) 1.33 (t, 3H, CH_3), 1.6 - 2.1 (m, 2H, CH_2), 2.3 - 2.8 (m, 3H, CH_2Ph + OH), 3.60 (t, 2H, CH_2OH), 3.97 (q, 2H, CH_2O), 6.73 (d, 2H, arom) and 7.07 (d, 2H, arom).
8a: IR ($CHCl_3$) ν: 3340, 1740 and 1610 cm^{-1}; ^{1}H-NMR δ (ppm) 1.30 (t, 3H, CH_3), 1.7 - 2.3 (m, 2H, CH_2), 2.63 (t, 2H, CH_2Ph), 4.0 - 4.5 (m, 4H, 2 x CH_2O) 5.7 - 6.3 (bs, 1H, OH), 6.73 (d, 2H, arom) and 7.10 (d, 2H, arom).
8b: IR (film) ν: 1750 and 1610 cm^{-1}; ^{1}H-NMR δ (ppm) 1.2 - 1.7 (m, 6H, 2 x CH_3), 1.8 - 2.3 (m, 2H, CH_2), 2.70 (t, 2H, CH_2Ph), 3.8 - 4.5 (m, 6H, 3 x CH_2O), 6.80 (d, 2H, arom) and 7.20 (d, 2H, arom).

Phenol. The ^{1}H-NMR spectra of the residues from the two extracts showed the signals relative to the unreacted phenol and to ethyl phenyl ether, whose yields were obtained by HPLC (69 and 22%, respectively).

The results of the HPLC analyses carried out on the solutions from **5b** - **g** and **7a** are reported in Table 1 (entries 20 - 26).

Reactions with carbon acids. *1-Bromo-3-phenylpropane 9*. C.c. of the residue from the combined extracts (light petroleum-AcOEt 4:1 as eluent) gave **9** (110 mg, 29%), di(3-phenylpropyl) carbonate **10** (50 mg, 17%) and **5g** (51 mg, 20%). **10**: IR (film) ν: 1750 and 1600 cm^{-1}; ^1H-NMR δ (ppm) 1.8-2.3 (m, 4H, 2 x CH_2), 2.70 (t, 4H, 2 x CH_2Ph), 4.43 (t, 4H, 2 x CH_2O) and 7.17 (s, 10H, arom).

2-Chloroethyl phenyl ketone 11. C.c. of the residue from the ethereal extract (light petroleum - AcOEt 4:1 as eluent) gave phenyl vinyl ketone **12**[21] (180 mg, 71%).

3-Chloropropyl phenyl ketone 13. C.c. of the residue from the combined extracts (light petroleum - AcOEt 7:3 as eluent) gave cyclopropyl phenyl ketone **14**[22] (170 mg, 61%) and unreacted **13** (28 mg, 8%).

Diethyl malonate 15. In the ^1H-NMR spectrum of the residue from the ethereal extract (250 mg) are present only the signals relative to diethyl methylmalonate **16** (17%) and unreacted **15** (62%).

The results of HPLC and GC analyses of the solutions from **9**, **11**, **13**, and **15** are reported in Table 2.

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