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Reactivity of α,α′-dichloroketones towards anions electrogenerated at carbonium and oxygen atoms. Electrochemically-induced Favorskii rearrangement. Part 2*

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Summary — Electrolyses of solutions containing α,α′-dichloroketones **1a** or **2a** were carried out, on a mercury pool or glassy carbon cathode, at a potential sufficiently negative to allow two-electron cleavage of the C–Cl bond. The effects of the presence of carboxylic acids **3a,b**, phenols **4a–f**, or carbon acid **5** in the solutions were evaluated. Depending on the type of acidic substrate, it was possible to isolate from the cathodic solutions the Favorskii-rearrangement products **9m**, **10m**, **11** and **12**, as well as dechlorinated ketones **1b** and **2b** and the addition products **7m** and **8m**. The conditions under which it was possible, by electrochemical means, to induce the Favorskii rearrangement between dichloroketones **1a** and **2a** and the acidic substrates are discussed. Evidence was gained by voltammetric analysis that the rates of formation of the Favorskii adducts **9a–f** depend on the structures of the corresponding phenols **4a–f**. By employing electrogenerated bases, it was possible to obtain α,β-unsaturated ketones at potentials less negative than required for the direct reduction of **1a** and **2a**.

dichloroketone / Favorskii rearrangement / electroreduction / α,β-unsaturated ketone

Résumé — Réactivité des α,α′-dichlorocétones vis-à-vis d'anions électrogénérés sur des carbanions et des atomes d'oxygène. Réarrangement de Favorskii électrochimiquement induit. *Les électrolyses de solutions contenant les α,α′-dichlorocétones **1a** ou **2a** sont réalisées sur une cathode de mercure ou de verre à un potentiel suffisamment négatif pour permettre la coupure à deux électrons de la liaison C–Cl. Les effets de la présence d'acides carboxyliques **3a,b** ou de phénols **4a–f**, ou de composés à carbone acide **5**, dans les solutions sont évalués. En fonction de la nature de l'acidité du substrat, il est possible d'isoler, des solutions cathodiques, les produits de réarrangement de Favorskii **9m**, **10m**, **11** et **12** à côté des cétones déchlorées **1b** et **2b** et des produits d'addition **7m** et **8m**. Les conditions sous lesquelles, par les moyens électrochimiques, il a été possible d'induire le réarrangement de Favorskii entre les dichlorocétones **1a** et **2a** et les substrats acides sont discutées. Par analyse voltamétrique la preuve est obtenue que les vitesses de formation des adduits de Favorskii **9a–f** sont dépendantes de la structure des phénols correspondants **4a–f**. Par l'utilisation de bases électrogénérées, il a été possible d'obtenir des cétones α,β-insaturées, en opérant à des potentiels moins négatifs que ceux nécessaires à la réduction directe de **1a** et **2a**.*

dichlorocétone / réarrangement de Favorskii / électroréduction / cétone α,β-insaturée

Introduction

Recently we have investigated [1] the reactivity of some anions electrogenerated at carbonium and nitrogen atoms towards α-haloketones. Evidence was provided for the formation of products in agreement with the Favorskii rearrangement [2]. In the present work, we intend to complete the previous study, by investigating the feasibility of an electrochemical activation of α,α′-dichloroketones towards otherwise unreactive acids at oxygen or carbonium atoms.

Among our goals was the formation of carbon–oxygen bonds (synthesis of α,β-unsaturated esters) and carbon–carbon bonds (synthesis of α,β-unsaturated ketones [3]), induced by electrochemical means. Accordingly we investigated the electrochemical behavior of dimethylformamide (DMF) solutions (where tetraethylammonium perchlorate (TEAP) was dissolved as supporting electrolyte) containing α,α′-dichloroketones **1a** and **2a** in the absence and presence of carboxylic acids **3a,b**, phenols **4a–f**, carbon acid **5** and probase **6** [4]. The electrochemical study was carried out by performing voltammetric measurements at various scan

* For Part 1, see [1].

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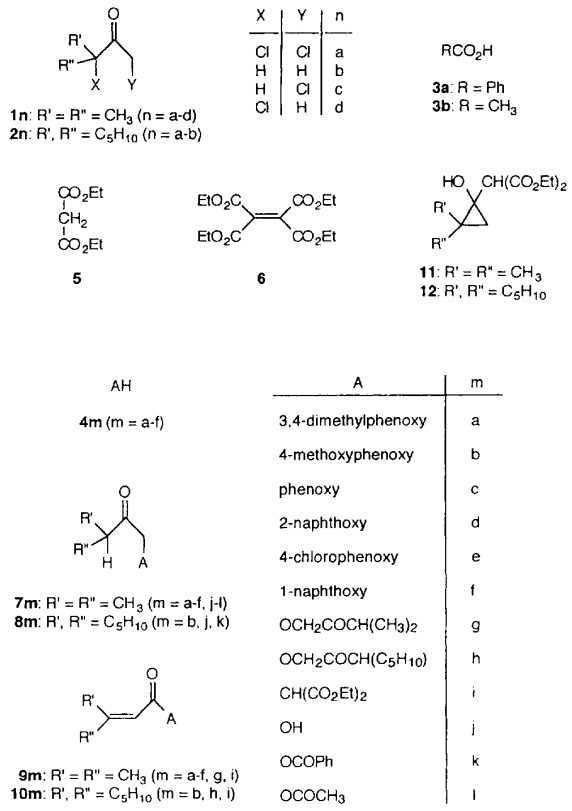


rates, as well as controlled-potential electrolyses. The products of the electrolyses were isolated and identified.

Results and discussion

Electrochemical behavior of solutions containing ketones **1a** *or* **2a**. *Effect of the presence of carboxylic acids* **3a,b**

The electrochemical behavior of α,α'-dihaloketones is strongly dependent not only on the nature of the halogen, but also on the number and kind of alkyl groups at the α and α' positions [5].

The voltammetric curves (Hg cathode) of dichloroketones **1a** and **2a** show two irreversible reduction peaks at potentials $E'_{1a} = -1.48$ V, $E''_{1a} = -1.82$ V, $E'_{2a} = -1.53$ V, $E''_{2a} = -1.88$ V ($c = 5.0 \times 10^{-3}$ mol dm^{-3}, $\nu = 0.2$ Vs^{-1}, see fig 1a). The ratio between the currents of the first peak of **1a** and the one-electron peak of anthracene, recorded under the same conditions, is 1.2. In addition, the ratio between the currents of the first and second peaks of **1a** increases with the scan rate. On the other hand, the voltammetric curves of monochloroketones **1c** and **1d** show only one reduction peak, at potentials $E_{1c} = -1.68$ V and $E_{1d} = -1.85$ V respectively. It follows that the reduction potential for a C–Cl bond at an α-position to a carbonyl group depends both on the nature (primary or tertiary) of the carbon atom, and on the presence of another C–Cl

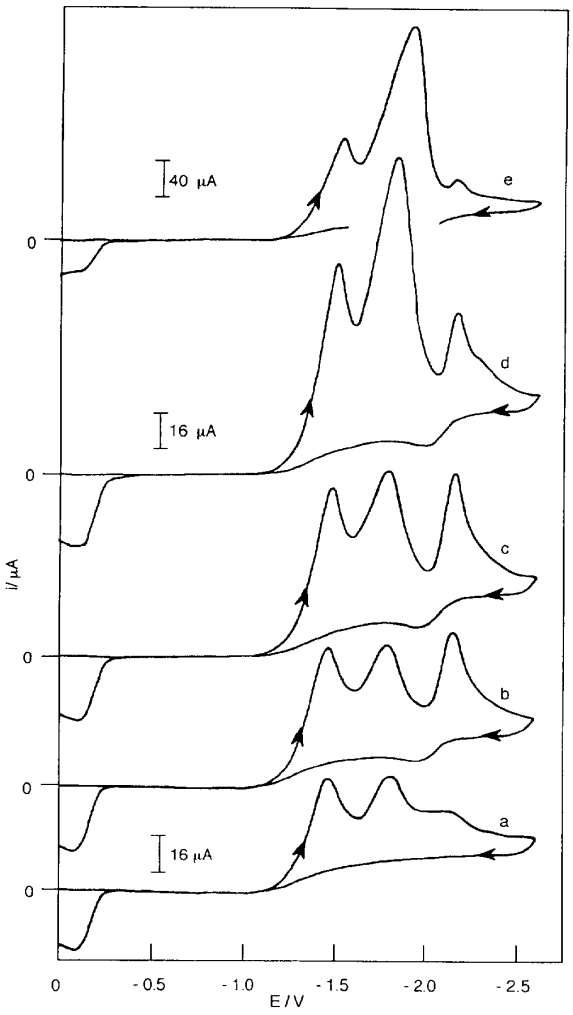


Fig 1a. Cyclic voltammetry curves of DMF/0.1 mol dm^{-3} TEAP solutions of **1a** ($c = 5.0 \times 10^{-3}$ mol dm^{-3}) at a Hg electrode in (a) the absence and (b–e) the presence of **4d** at concentrations of: (b) $c = 1.0 \times 10^{-3}$ mol dm^{-3}; (c) $c = 3.0 \times 10^{-3}$ mol dm^{-3}; (d) $c = 5.0 \times 10^{-3}$ mol dm^{-3}; (e) $c = 7.0 \times 10^{-3}$ mol dm^{-3}; $\nu = 0.2$ Vs^{-1}.

bond at the α' position, which causes a shift towards much more positive values. The voltammetric behavior of **1a** and **2a** at a glassy carbon cathode is similar, ie, two irreversible peaks at potentials $E'_{1a} = -1.67$ V, $E''_{1a} = -1.88$ V and $E'_{2a} = -1.65$ V, $E''_{2a} = -1.90$ V respectively ($c = 5.0 \times 10^{-3}$ mol dm^{-3}, $\nu = 0.2$ Vs^{-1}, see fig 1b).

Solutions containing **1a** were submitted to electrolyses at both Hg and glassy carbon cathodes, at a controlled potential corresponding to the first reduction peak. The voltammetric curves recorded at the end of the electrolyses show that both the first and second reduction peaks have disappeared. From the cathodic solutions, it was possible to isolate compounds **1b**, **7j** and **9g** (see table I, entry 1); in addition, the monochloroketones **1c** and **1d** were found to be absent.

Table I. Coulometric data and yields of the products of the electrochemical reduction at a mercury or glassy carbon cathode of solutions (DMF/0.1 mol dm^{-3} TEAP) of ketones **1a** and **2a** in the absence and presence of carboxylic acids **3a–b**.

Entry	*Ketone*	*Carboxylic acid*[a]	$-E/V^b$	$n_{app}{}^c$	*Products and yields (%)*[d]		
1	**1a**	–	1.5[e]	2.1	**1b** (35)	**7j** (3)	**9g** (5)
2	**1a**	–	1.7[f]	1.9	**1b** (23)	**7j** (13)	**9g** (11)
3	**2a**	–	1.5[e]	2.1	**2b** (33)	**8j** (3)	**10h** (7)
4	**1a**	**3a**	1.5[e]	2.6	**1b** (51)	**7k** (15)	
5	**1a**	**3a**	1.7[f]	2.5	**1b** (47)	**7k** (18)	
6	**1a**	**3b**	1.5[e]	2.6	**1b** (41)	**7l** (10)	
7	**2a**	**3a**	1.5[e]	2.5	**2b** (47)	**8k** (13)	

[a] 1:1 ratio of ketone/carboxylic acid. [b] Compared to SCE. [c] Number of Faraday mol^{-1} obtained by coulometry. [d] Yields with respect to the initial amount of ketone. [e] At mercury cathode. [f] At glassy carbon cathode.

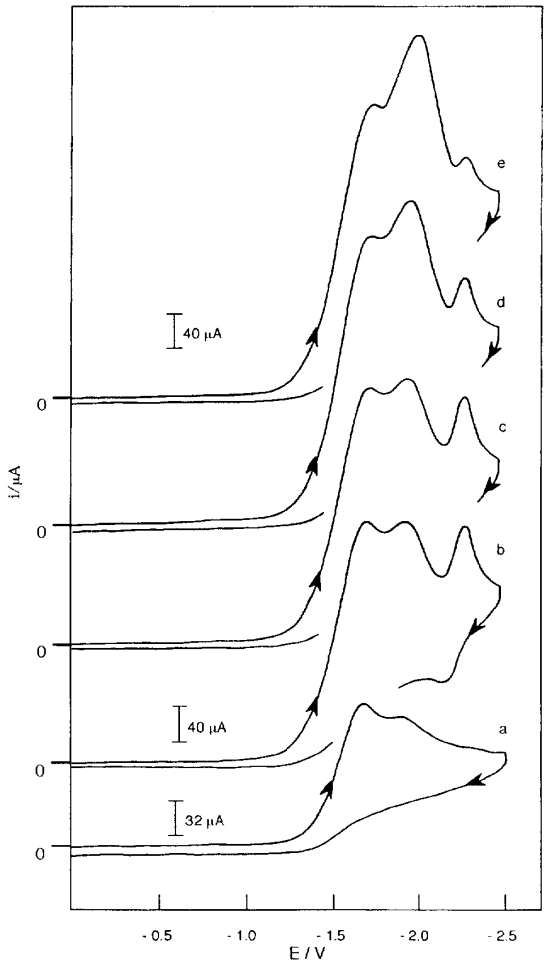
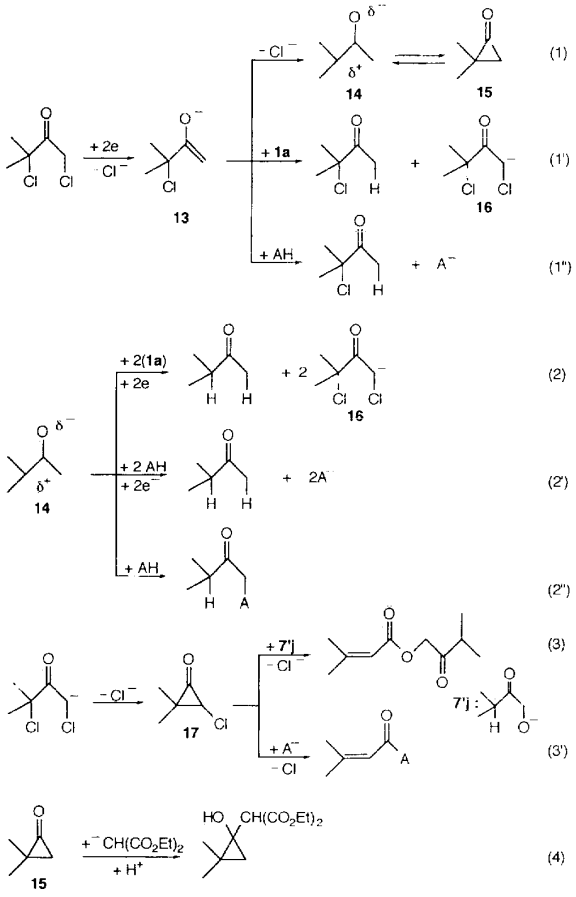


Fig 1b. Cyclic voltammetry curves of DMF/0.1 mol dm^{-3} TEAP solutions of **1a** ($c = 5.0 \times 10^{-3}$ mol dm^{-3}) at a glassy carbon electrode in (a) the absence and (b–e) the presence of **4a** at concentrations of: (b) $c = 7.0 \times 10^{-3}$ mol dm^{-3}; (c) $c = 1.0 \times 10^{-2}$ mol dm^{-3}; (d) $c = 2.0 \times 10^{-2}$ mol dm^{-3}; (e) $c = 3.0 \times 10^{-2}$ mol dm^{-3}; $\nu = 0.2$ Vs^{-1}.

On the basis of the voltammetric and coulometric data, the formation of **1b**, **7j** and **9g** can be described



(irrespective of the nature of the cathode) as a multistep process, involving: (i) the initial electrochemical two-electron cleavage of the first C–Cl bond and the elimination of the second Cl^- anion yielding the zwitterion **14** [5b] (see reaction 1); (ii) the two-electron reduction of the zwitterion at −1.5 V (see reactions 2 and 2′, HA=H_2O), leading to the formation of **1b**; (iii) the addition reaction of adventitious water to the zwitterion, yielding **7j** (see reaction 2″, HA=H_2O).

If the electrolyses at −1.5 V were carried out in the presence of exogenous proton donors (**3a,b**), an

Table II. Coulometric data and yields of the products of the electrochemical reduction of solutions (DMF −0.1 mol dm^{-3} TEAP) of ketones **1a** and **2a** in the presence of substrates **4a–f**, **5** and probase **6**, at a mercury or glassy carbon cathode.

Entry	*Ketone*	*Subst*[a]	*Prob*[b]	−E/V[b]	n_{app}[c]	*Products and yields (%)*[d]		
1	**1a**	**4a**	–	1.5[e]	2.5	**9a** (32)	**7a** (4)	**1b** (32)
2	**1a**	**4a**	–	1.7[f]	2.2	**9a** (29)	**7a** (6)	**1b** (26)
3	**1a**	**4b**	–	1.5[e]	2.6	**9b** (32)	**7b** (5)	**1b** (38)
4	**1a**	**4b**	–	1.7[f]	2.2	**9b** (28)	**7b** (4)	**1b** (32)
5	**1a**	**4c**	–	1.5[e]	2.5	**9c** (26)	**7c** (5)	**1b** (46)
6	**1a**	**4d**	–	1.5[e]	2.5	**9d** (24)	**7d** (5)	**1b** (52)
7	**1a**	**4e**	–	1.5[e]	2.5	**9e** (24)	**7e** (6)	**1b** (43)
8	**1a**	**4f**	–	1.5[e]	2.6	**9f** (24)	**7f** (2)	**1b** (22)
9	**2a**	**4b**	–	1.5[e]	2.6	**10b** (30)	**8b** (10)	**2b** (45)
10	**1a**	**5**	–	1.5[e]	2.4	**9i** (6)	**11** (4)	**1b** (25)
11	**2a**	**5**	–	1.5[e]	2.4	**10i** (7)	**12** (15)	**2b** (30)
12	**1a**	**5**	**6**	1.0[e]	2.0	**9i** (17)		**1a** (10)
13	**2a**	**5**	**6**	1.0[e]	2.0	**10i** (12)		**2a** (15)

[a] The ratio between the concentrations of ketone and substrate is $\rho = 1$. [b] The ratio between the concentrations of ketone and probase is $\rho = 2$. [c] Number of Faraday mol^{-1} obtained by coulometry. [d] Yields with respect to the initial amount of ketone. [e] At mercury cathode. [f] At glassy carbon cathode.

increase was observed both in the value of n_{app} and in the yield of **1b**, and it was possible to isolate the addition products (see reaction 2″, AH = **3a,b**) of benzoic (**7k**) and acetic (**7l**) acids to the zwitterion (see table I, entries 4, 5 and 6). Compound **9g** was isolated in variable yields depending on uncontrollable conditions. It can be regarded as the product of a Favorskii rearrangement operated by **7′j**, anion at the oxygen atom, on monochlorinated cyclopropanone **17** (see reaction 3).

In the cathodic solutions, besides **1b**, **7j** and **9g**, it was possible to detect a complex mixture of products, which were difficult to separate and to identify unambiguously. However, a common feature shared by most of the components of the mixture was a double bond in an α-position to the carbonyl group, ie, $(CH_3)_2C{=}CHCOR$, which can be regarded as produced by nucleophilic attack on the monochlorinated cyclopropanone **17**.

As regards the possibility of establishing which of the two C–Cl bonds undergoes the initial two-electron cleavage, no conclusion can be drawn from the products isolated at the end of the electrolyses, either in the absence or the presence of a substrate. In trying to obtain more information on this subject, electrolyses of **1a**, carried out at −1.5 V, were stopped when only 33%, or 66%, of the amount of electricity needed for the complete reduction of **1a** had flowed through the cell. The voltammograms recorded on the cathodic solutions after these incomplete electrolyses, show that the currents of both the first and second peaks decrease as the electrolysis goes on, but also that the ratio of the currents between the second and first peaks increases.

From the analysis of these cathodic solutions, besides **1a** (as yet not reduced) and **1b**, the presence of monochloroketone **1d** was ascertained (yields: 16% for the 33% electrolysis and 5% for the 66% electrolysis). **1c** was completely absent from these solutions. Therefore monochloroketone **1d** appears to be related to the electrochemical cleavage of the primary C–Cl bond, and can be regarded as one of the reduction products of **1a**.

The formation of **1d** has to be ascribed to the protonation of monochloroanion **13** (see reaction 1′). The absence of **1d** after exhaustive electrolysis indicates that the working potential (−1.5 V) is sufficiently negative to allow a slow reduction of **1d** ($E_p = -1.8$ V), as well as the reduction of **1a**. To confirm this, electrolyses were carried out at −1.5 V on solutions containing both **1a** and **1d** at a 1:1 mole ratio. At the end of the electrolyses, both substances were absent from the cathodic solutions.

1d could be detected in the course of the electrolysis of **1a** run at −1.5 V, thus allowing us to state that the primary C–Cl bond is certainly cleaved as a consequence of electron-exchange between the electrode and substrate. However, is not possible to exclude the possibility that the tertiary C–Cl bond may also be cleaved. In fact, this cleavage would lead to the formation of **1c**, reducible at a potential more positive than **1d**; therefore, during the electrolysis of **1a** at −1.5 V, **1c** would be reduced at a rate sufficiently fast to prevent its detection.

The various results obtained in the electrolyses of **1a** were confirmed for dichloroketone **2a** (see table I, entries 3 and 7).

Electrochemical behavior of solutions containing dichloroketones **1a**, **2a** *and phenols* **4a–f**

Electrolyses of solutions containing both dichloroketone **1a** and phenolic substrates **4a–f** were carried out at a controlled potential corresponding to the first reduction peak of **1a**. From the cathodic solutions (see table II, entries 1–8) we were able to isolate the α,β-unsaturated esters **9a–f**, ie, the Favorskii-rearrangement products of monochlorocyclopropanone **17** induced by the conjugate bases of phenols **4a–f** (see reaction 3′). In addition, the dechlorinated ketone **1b**, (see reaction 2 and 2′, AH = **4a–f**) and the addition products **7a–f** of substrates **4a–f** to zwitterion **14** (see reaction 2″, AH = **4a–f**) were isolated.

The voltammetric curves may provide information about the conditions under which it is possible to

induce electrochemically the Favorskii rearrangement between **1a** and **4a–f**. In fact, on addition of these substrates, the voltammetric curves of **1a** show an increase for both the first and the second reduction peaks, and a third reduction peak appears at a more negative (E''') potential (see figs 1a and 1b). At the end of electrolyses carried out at a potential corresponding to the first voltammetric peak, the voltammetric curves show the presence only of the peak at potential E'''. The voltammetric curves recorded on solutions containing authentic samples of compounds **9a–f** show only one reduction peak at potential E'''. On the contrary, compounds **7a–f**, as well as **1b**, are not reducible under our experimental conditions. Therefore, the presence of peak E''' in the voltammetric curves of solutions containing **1a** and substrates **4a–f** must be ascribed to the formation of coupling products **9a–f**.

The formation of **9a–f** depends on the nucleophilic attack of anions A^- on monochlorocyclopropanone **17** (see reaction 3′), thus requiring the presence of both reactants at adequate concentrations. Therefore, both reactions 1′ and 2 (which cause the formation of dichlorinated anion **16**, and hence monochlorocyclopropanone **17**), as well as reactions 1″ and 2′ (through which A^- is formed), must operate under our experimental conditions. It follows that an excessive increase in the concentration of the phenols causes reactions 1′ and 2 to be no longer competitive with reactions 1″ and 2′, thus hindering the formation of **9a–f**. In fact, when the concentration of **4a–f** is raised beyond a critical value, the current i_3, relative to the reduction of **9a–f**, decreases (see figs 1a and 1b, and table III).

Table III. Current values i_3 (mA) relative to the third reduction peak in the voltammetric curves of **1a** ($c_{1a} = 5 \times 10^{-3}$ mol dm^{-3}) in the presence of phenols (HA): i_3^{I} ($c_{HA} = 1 \times 10^{-3}$ mol dm^{-3}); i_3^{II} ($c_{HA} = 3 \times 10^{-3}$ mol dm^{-3}); i_3^{III} ($c_{HA} = 5 \times 10^{-3}$ mol dm^{-3}); i_3^{IV} ($c_{HA} = 7 \times 10^{-3}$ mol dm^{-3}); i_3^{V} ($c_{HA} = 1 \times 10^{-2}$ mol dm^{-3}); Hg cathode, $\nu = 0.2$ Vs^{-1}.

HA	$pK_a'^{a}$	$pK_a''^{b}$	$pK_a'''^{c}$	i_3^{I}	i_3^{II}	i_3^{III}	i_3^{IV}	i_3^{V}
4a	10.36			22	62	52	45	30
4b	10.20	19.08		20	58	48	42	30
4c	9.95	17.96	18.4	36	54	46	28	7
4d	9.49			32	43	26	6	–
4e	9.38	16.75	16.78	40	43	21	1	–
4f	9.23			42	41	17	–	–

[a] pK_a values in water [6]. [b] pK_a values in DMSO [7]. [b] pK_a values in DMF [7].

For the same concentration of phenol, the value of the current i_3 (see table III), and the yields of **9a–f** (see table II), depend on the protonating power of the phenols. To support this statement, in table III we report the pK_as of these phenols in water, and also in aprotic solvents whenever available in the literature. The total disappearance of the peak at potential E''', and therefore the non-formation of adducts **9d–f**, was observed with substrates **4d–f** at concentrations twice as high as ketone **1a**. To confirm this point, electrolyses were run at a potential $E = -1.5$ V on solutions containing both **1a** and **4f**, at a mole ratio 1:2. At the end of these electrolyses, it was not possible to isolate **9f** from the cathodic solutions.

For all the substrates **4a–f** considered, current i_3, which is proportional to the concentration of the adduct **9a–f** formed, decreases when the scan rate is increased (see fig 2 and table IV). Therefore, in the global process leading to the formation of **9a–f**, there has to be at least one step which is slow with respect to the voltammetric times. In addition, since the dependence of current i_3 on the scan rate is not the same for the different substrates, the slow step must involve the participation of the substrates **4a–f** themselves. Therefore, it is possible to compare the formation rates of compounds **9a–f** by looking at the values of i_3 (see table IV) obtained at the same scan rate.

The results obtained with dichloroketone **1a** were confirmed also for dichloroketone **2a** (see table II, entry 9).

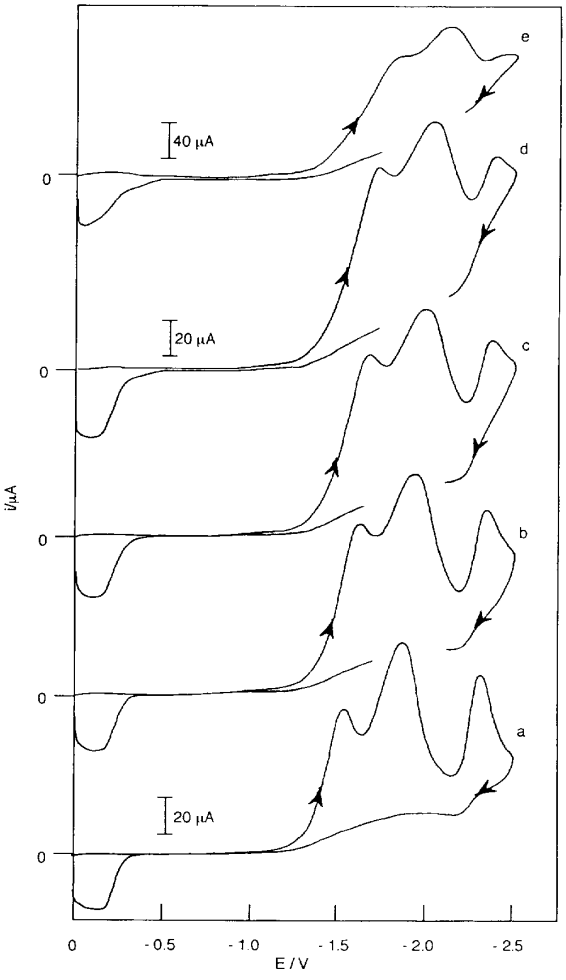


Fig 2. Cyclic voltammetry curves of DMF/0.1 mol dm^{-3} TEAP solutions of **1a** ($c = 5.0 \times 10^{-3}$ mol dm^{-3}) at a Hg electrode in the presence of **4b** ($c = 3.0 \times 10^{-3}$ mol dm^{-3}): (a) $\nu = 0.2$ Vs^{-1}, (b) $\nu = 0.5$ Vs^{-1}, (c) $\nu = 1.0$ Vs^{-1}, (d) $\nu = 2.0$ Vs^{-1}, (e) $\nu = 5.0$ Vs^{-1}.

Table IV. Current values i_3 (mA) relative to the third reduction peak in the voltammetric curves of **1a** ($c_{1a} = 5 \times 10^{-3}$ mol dm^{-3}) in the presence of phenols (HA, $c_{HA} = 3 \times 10^{-3}$ mol dm^{-3}) at different values of scan rate ν (Vs^{-1}). Hg cathode.

HA	ν = 0.2	ν = 0.5	ν = 1.0	ν = 2.0	ν = 5.0	ν = 10.0
4a	62	53	40	26	6	–
4b	58	45	34	24	8	–
4c	54	45	32	21	4	–
4d	43	31	20	5	–	–
4e	43	26	14	–	–	–
4f	41	26	13	–	–	–

Electrochemical behavior of solutions containing **1a** *or* **1b**, *compound* **5** *and probase* **6**

The fact that it was possible to induce electrochemically the Favorskii rearrangement between α,α'-dichloroketones and oxygen acids **4a–f** led to the investigation of whether the same reaction could take place when employing carbon acid **5**, with the aim of inducing the formation of α,β-unsaturated ketones by electrochemical means. For this purpose ketone **1a**, or **2a**, was reduced at a potential of −1.5 V in a solution containing **5** at the same concentration as the ketone. At the end of the electrolysis, besides dechlorinated ketones **1b** and **2b**, it was possible to isolate α,β-unsaturated ketones **9i** and **10i** (see reaction 3′, A = $^-CH(CO_2Et)_2$), as well as Favorskii adducts **11** and **12** (see reaction 4 and table II, entries 10 and 11). The formation of **9i** and **10i** is in agreement with the presence of the intermediate monochlorocyclopropanone **17** in the solution, while the formation of **11** and **12** is in agreement with the presence of intermediate **15**.

To increase the yields of α,β-unsaturated ketones as the only products related to the Favorskii rearrangement, an attempt was made to set up conditions under which the formation of **17** is independent of the formation of **15**. For this purpose, a suitable probase **6** [1] was reduced at E = −1.0 V in a solution containing **1a** or **2a** and the carbon acid **5**. At the end of the electrolysis, compounds **9i** and **10i** were isolated, in yields of 17 and 12% respectively, while **11** and **12** were completely absent from the cathodic solutions (see table II, entries 12 and 13). Therefore, it is reasonable to suppose that the electrogenerated base, derived from the reduction of **6**, deprotonated both **1a** (or **2a**) and **5**, thus inducing the formation of both monochlorocyclopropanone **17** and nucleophile $^-CH(CO_2Et)_2$ under such conditions that the formation of intermediate **15** was prevented.

Conclusions

The electrochemical methodology allowed activation of α,α'-dichloroketones **1a** and **2a** towards acidic substrates which, under conventional conditions, do not react with these haloketones. Actually, at the end of electrolyses carried out on solutions containing both the haloketones and the acidic substrates (carboxylic acids, phenols and a carbon acid), both addition products and Favorskii products could be isolated.

From the voltammetric analysis, evidence was gained that the Favorskii rearrangement can be enhanced, or completely prevented, by varying the ratio between the concentrations of the ketone and the phenol, in a fashion depending on the pK_a of the acid. In addition, it was possible to observe different formation times of Favorskii adducts, depending on the structure of the corresponding phenols.

Finally, through the use of electrogenerated bases, it was possible to activate haloketones by working at a potential less negative than that required for direct reduction of the same ketones.

Experimental section

General

Column chromatography was carried out on Merck silica gel (70–230 mesh, 60 g per 1 g substrate), using a hexane/ethyl acetate mixture, 95:5 to 80:20 depending on the case, as eluent. GLC analyses were performed using a Hewlett-Packard Model 5890 gas chromatograph equipped with a flame ionization detector, a linear temperature programmer and a Hewlett Packard Model 3390A electronic integrator. The column used was a SP 2250 (30 m, 0.32 mm id glass column). GC–MS measurements were carried out on a SE 54 capillary column using a Fisons 8000 gas chromatograph coupled with a Fisons MD 800 mass selective detector. ^1H and ^{13}C NMR spectra were recorded using an AC 200 Bruker spectrometer and $CDCl_3$ as internal standard. All new compounds gave satisfactory elemental analyses (C ± 0.3%; H ± 0.2%). Voltammetric measurements were carried out using an Amel 498 sessile mercury drop electrode (or an Amel glassy carbon electrode) with an Amel 552 potentiostat equipped with an Amel 556 function generator and an Amel 563 multipurpose unit; the curves were displayed on an Amel 863 recorder assisted by a Nicolet 3091 digital oscilloscope. Controlled-potential electrolyses and coulometries were carried out at a mercury pool or glassy carbon cathode with an Amel 552 potentiostat equipped with an Amel 721 integrator. The design of the cells used in the electrochemical techniques, as well as the purification methodologies of the solvent (dimethylformamide, DMF (Fluka)) and supporting electrolyte (tetraethylammonium perchlorate, TEAP (Fluka)), have already been described [1, 8]. The catholyte was degassed and pre-electrolyzed at the working potential before the addition of the depolarizer. The counter electrode was a cylindrical platinum gauze and the reference electrode was of the calomel type described by Fujinaga [9]; its potential was −0.020 V compared with SCE (all the potentials are given with respect to this electrode). All electrochemical measurements were performed at 20.0 ± 0.1 °C in DMF/0.1 mol dm^{-3} TEAP solutions. Compounds **1a** (1,3-dichloro-3-methylbutan-2-one) and **2a** (2-chloro-1-(1-chlorocyclopentyl)ethanone) [3b], **1c** (1-chloro-3-methylbutan-2-one) [10], **1d** (3-chloro-3-methylbutan-2-one) [11] were prepared as described in the literature. Compounds **3a,b** (benzoic and acetic acids), **4a–f** (3,4-dimethoxy, 4-methoxyphenols, phenol, 2-naphthol, 4-chlorophenol, 1-naphthol), **5** (diethyl propanedioate) and **6** (tetraethyl ethenetetracarboxylate) (Fluka) were used as received.

Electrochemistry

• *Reduction of* **1a**: *Hg cathode (entry 1, table I)*
The controlled-potential electrolysis was carried out, at a potential of −1.5 V, by stepwise addition of **1a** (0.212 g,

1.37 mmol) to DMF -0.1 mol dm^{-3} TEAP (35 mL) in such a way that its concentration never exceeded 1×10^{-2} mol dm^{-3}. Each addition of ketone was made when the current dropped from its initial value to that measured after the pre-electrolysis. At the end of the electrolysis, GC-analysis of the cathodic solution showed the presence of **1b** (by comparison with a sample of pure **1b** used as a standard); this was confirmed by GC-MS analysis. The yield of **1b** was 35% (GC yield). The catholyte was separated from ther mercury, mixed with water (50 mL) and extracted with Et_2O (5×30 mL). The organic extracts were washed with water, dried (Na_2SO_4), analyzed by TLC and the solvent evaporated under reduced pressure to give a constant weight of residue. In order to obtain pure samples for analytical and structural characterization, the residue from the work-up of the reduction mixture was submitted to column chromatography. The work-up of the cathodic solution was the same for all the electrolyses. The isolated products and the yields were: **9g** (0.013 g, 0.07 mmol, 5%), **7j** (0.04 g, 0.04 mmol, 3%). Other products were detected that could not be identified. Most of them had ^{1}H NMR signals at $\approx$ 6.23 (br s, 1H), 2.16 (s, 3H) and 2.02 (s, 3H) ppm, characteristic of α,β-unsaturated ketones $(CH_3)_2C{=}CH{-}COR$.

9g: ^{1}H NMR: δ ($CDCl_3$) 5.76 (br s, 1H), 4.72 (s, 2H), 2.67 (sept, J = 7.3 Hz, 1H), 2.14 (s, 3H), 1.89 (s, 3H), 1.11 (d, J = 7.3 Hz, 6H).

^{13}C NMR: δ ($CDCl_3$) 207.69, 165.54, 158.47, 115.06, 65.88, 37.43, 27.37, 20.32, 17.91.

MS m/z (relative intensity): M^+ absent, 141 (15%), 83 (100%), 55 (19%).

7j: ^{1}H NMR: δ ($CDCl_3$) 4.28 (s, 2H), 3.30 (br s, 1H), 2.58 (sept, J = 6.9 Hz, 1H), 1.11 (d, J = 6.9 Hz, 6H).

^{13}C NMR: δ ($CDCl_3$) 207.57, 66.16, 37.19, 17.89.

MS m/z (relative intensity): M^+ absent, 71 (12%), 43 (100%).

• *Reduction of* **1a***: C cathode (entry 2, table I)*

This procedure was similar to the one described for electrolysis at a Hg cathode. The electrolysis potential was -1.7 V. The isolated products (and yields) were: **1b** (23%, GC yield), **9g** (11%), **7j** (13%).

• *Reduction of* **2a***: Hg cathode (entry 3, table I)*

The electrolysis potential was -1.5 V. The isolated products (and yields) were: **2b** (33%, GC yield), **10h** (7%), **8j** (3%).

10h: ^{1}H NMR: δ ($CDCl_3$) 5.69 (br s, 1H), 4.71 (s, 2H), 2.79–2.76 (mc, 4H), 2.21–1.18 (mc, 17H).

^{13}C NMR: δ ($CDCl_3$) 206.93, 165.68, 165.58, 111.91, 66.05, 47.36, 38.02, 29.98, 28.53, 28.16, 27.76, 26.16, 25.68, 25.47.

MS m/z (relative intensity): M^+ absent, 181 (6%); 123 (100%); 83 (45%), 55 (41%).

8j: ^{1}H NMR: δ ($CDCl_3$) 4.26 (s, 2H), 3.20 (br s, 1H), 2.46–2.32 (mc, 1H), 1.81–1.19 (mc, 10H).

^{13}C NMR: δ ($CDCl_3$) 66.33, 47.12, 28.26, 25.57, 25.37.

MS m/z (relative intensity): M^+ absent, 111 (13%), 83 (69%), 55 (100%).

• *Reduction of* **1a** *in the presence of* **3a***: Hg cathode (entry 4, table I)*

The controlled-potential electrolysis was carried out, at a potential of -1.5 V, by stepwise addition of **1a** (0.192 g, 1.24 mmol) and **3a** (0.151 g, 1.24 mmol) to DMF/0.1 mol dm^{-3} TEAP (38 mL) in such a way that their concentrations never exceeded 1×10^{-2} mol dm^{-3}. Each addition of ketone and carboxylic acid was made when the current dropped from its initial value to that measured after the pre-electrolysis. The isolated products (and yields) were: **1b** (51%, GC yield), **7k** (0.039 g, 0.19 mmol, 15%).

7k: ^{1}H NMR: δ ($CDCl_3$) 8.12–7.26 (s, 5H), 4.96 (s, 2H), 2.71 (sept, J = 7.0 Hz, 1H), 1.19 (d, J = 7.0 Hz, 6H).

^{13}C NMR: δ ($CDCl_3$) 205.00, 167.81, 133.16, 129.62, 129.21, 128.24, 66.80, 37.26, 17.74.

MS m/z (relative intensity): M^+ absent, 163 (30%), 135 (3%), 105 (100%), 43 (91%).

• *Reduction of* **1a** *in the presence of* **3a***: C cathode (entry 5, table I)*

The electrolysis potential was -1.7 V. The isolated products (and yields) were: **1b** (47%, GC yield), **7k** (18%).

• *Reduction of* **1a** *in the presence of* **3b***: Hg cathode (entry 6, table I)*

The electrolysis potential was -1.5 V. The isolated products (and yields) were: **1b** (41%, GC yield), **7l** (10%).

7l: ^{1}H NMR: δ ($CDCl_3$) 4.75 (s, 2H), 2.68 (sept, J = 6.8 Hz, 1H), 2.17 (s, 3H), 1.44 (d, J = 6.8 Hz, 6H).

^{13}C NMR: δ ($CDCl_3$) 207.10, 170.19, 66.43, 37.44, 20.40, 17.86.

• *Reduction of* **2a** *in the presence of* **3a***: Hg cathode (entry 7, table I)*

The electrolysis potential was -1.5 V. The isolated products (and yields) were: **2b** (47%, GC yield), **8k** (13%).

8k: ^{1}H NMR: δ ($CDCl_3$) 8.03–7.40 (m, 5H), 4.92 (s, 2H), 2.53–2.38 (m, 1H), 2.38–1.98 (m, 10H).

^{13}C NMR: δ ($CDCl_3$) 212.11, 165.82, 133.23, 129.78, 129.36, 128.36, 67.04, 47.35, 28.12, 25.64, 25.42.

MS m/z (relative intensity): 246 (M^+, 3%), 125 (5%), 124 (100%).

• *Reduction of* **1a** *in the presence of* **4a***: Hg cathode (entry 1, table II)*

The controlled-potential electrolysis was carried out, at a potential of -1.5 V, by stepwise addition of **1a** (0.288 g, 1.86 mmol) and **4a** (0.227 g, 1.86 mmol) to DMF/0.1 mol dm^{-3} TEAP (40 mL) in such a way that their concentrations never exceeded 1×10^{-2} mol dm^{-3}. Each addition of ketone and phenol was made when the current dropped from the initial value to that measured after the pre-electrolysis. The isolated products (and yields) were: **1b** (32%, GC yield), **9a** (0.120 g, 0.59 mmol, 32%), **7a** (0.014 g, 0.07 mmol, 4%).

9a: ^{1}H NMR: δ ($CDCl_3$) 7.14–6.81 (m, 3H), 5.91 (br s, 1H), 2.26 (s, 3H), 2.24 (s, 3H), 2.23 (s, 3H), 1.98 (s, 3H).

^{13}C NMR: δ ($CDCl_3$) 164.99, 158.90, 148.65, 137.51, 133.52, 130.12, 122.63, 118.75, 115.41, 27.35, 20.26, 19.64, 18.94.

MS m/z (relative intensity): 205 ($M^+ + 1$, 2%), 204 (M^+, 10%), 121 (4%), 83 (100%), 55 (21%), 28 (4%).

7a: ^{1}H NMR: δ ($CDCl_3$) 7.03–6.99 (m, 1H), 6.70–6.55 (m, 2H), 4.57 (s, 2H), 2.93 (sept, J = 6.9 Hz, 1H), 2.21 (s, 3H), 2.17 (s, 3H), 1.13 (d, J = 6.9 Hz, 6H).

^{13}C NMR: δ ($CDCl_3$) 211.26, 156.24, 137.98, 130.47, 129.68, 116.32, 111.48, 71.80, 37.03, 19.94, 18.72, 17.87.

MS m/z (relative intensity): 206 ($M^+ + 1$, 9%), 205 (M^+, 71%), 135 (43%), 71 (65%), 43 (100%).

• *Reduction of* **1a** *in the presence of* **4a***: C cathode (entry 2, table II)*

The electrolysis potential was -1.7 V. The isolated products (and yields) were: **1b** (26%, GC yield), **9a** (29%), **7a** (6%).

• *Reduction of* **1a** *in the presence of* **4b**: *Hg cathode (entry 3, table II)*

The electrolysis potential was −1.5 V. The isolated products (and yields) were: **1b** (38%, GC yield), **9b** (32%), **7b** (5%).

9b: ^{1}H NMR: δ ($CDCl_3$) 7.02–6.84 (m, 4H), 5.88 (br s, 1H), 3.76 (s, 3H), 2.21 (s, 3H), 1.95 (s, 3H).

^{13}C NMR: δ ($CDCl_3$) 165.06, 159.12, 157.04, 144.25, 122.40, 115.28, 114.38, 55.46, 27.36, 20.28.

MS m/z (relative intensity): 207 (M^+ + 1, 2%), 206 (M^+, 9%), 124 (52%), 83 (100%), 55 (27%).

7b: ^{1}H NMR: δ ($CDCl_3$) 6.81 (br s, 4H), 4.56 (s, 2H), 3.74 (s, 3H), 2.92 (sept, J = 7.0 Hz, 1H), 1.14 (d, J = 7.0 Hz, 6H).

^{13}C NMR: δ ($CDCl_3$) 211.15, 154.53, 152.23, 115.69, 114.85, 72.40, 55.72, 37.03, 17.87.

MS m/z (relative intensity): 208 (M^+, 25%), 137 (21%), 123 (18%), 71 (24%), 43 (100%).

• *Reduction of* **1a** *in the presence of* **4b**: *C cathode (entry 4, table II)*

The electrolysis potential was −1.7 V. The isolated products (and yields) were: **1b** (32%, GC yield), **9b** (28%), **7b** (4%).

• *Reduction of* **1a** *in the presence of* **4c**: *Hg cathode (entry 5, table II)*

The electrolysis potential was −1.5 V. The isolated products (and yields) were: **1b** (46%, GC yield), **9c** (24%), **7c** (5%).

9c: ^{1}H NMR: δ ($CDCl_3$) 7.41–7.08 (m, 5H), 5.92 (br s, 1H), 2.23 (s, 3H), 1.98 (s, 3H).

^{13}C NMR: δ ($CDCl_3$) 164.71, 159.47, 150.79, 129.20, 125.36, 121.74, 115.29, 27.44, 20.36.

MS m/z (relative intensity): 177 (M^+ + 1, 1%), 176 (M^+, 8%), 83 (100%), 77 (7%), 55 (100%).

7c: ^{1}H NMR: δ ($CDCl_3$) 7.33–6.85 (m, 5H), 4.61 (s, 2H), 2.95 (sept, J = 7.0 Hz, 1H), 1.14 (d, J = 7.0 Hz, 6H).

^{13}C NMR: δ ($CDCl_3$) 158.02, 129.64, 121.67, 114.62, 71.51, 37.07, 17.87.

MS m/z (relative intensity): 178 (M^+, 6%), 107 (7%), 93 (2%), 77 (52%), 71 (23%), 43 (100%).

• *Reduction of* **1a** *in the presence of* **4d**: *Hg cathode (entry 6, table II)*

The electrolysis potential was −1.5 V. The isolated products (and yields) were: **1b** (52%, GC yield), **9d** (24%), **7d** (5%).

9d: ^{1}H NMR: δ ($CDCl_3$) 7.89–7.25 (m, 7H), 5.99 (br s, 1H), 2.28 (s, 3H), 2.00 (s, 3H).

^{13}C NMR: δ ($CDCl_3$) 164.91, 159.79, 148.49, 133.89, 131.39, 129.17, 127.71, 127.60, 126.37, 125.45, 121.52, 118.61, 115.32, 27.53, 20.47.

MS m/z (relative intensity): 226 (M^+, 21%), 144 (98%), 83 (100%), 55 (65%).

7d: ^{1}H NMR: δ ($CDCl_3$) 7.79–7.02 (m, 7H), 4.73 (s, 2H), 2.98 (sept, J = 6.8 Hz, 1H), 1.72 (d, J = 6.8 Hz, 6H).

^{13}C NMR: δ ($CDCl_3$) 155.91, 134.35, 129.81, 128.84, 127.67, 126.85, 126.58, 124.10, 118.50, 107.11, 71.57, 37.14, 17.91.

MS m/z (relative intensity): 229 (M^+ + 1, 5%), 228 (M^+, 40%), 157 (23%), 127 (100%), 101 (8%), 71 (54%), 43 (100%).

• *Reduction of* **1a** *in the presence of* **4e**: *Hg cathode (entry 7, table II)*

The electrolysis potential was −1.5 V. The isolated products (and yields) were: **1b** (43%, GC yield), **9e** (26%), **7e** (6%).

9e: ^{1}H NMR: δ ($CDCl_3$) 7.33–7.03 (m, 4H), 5.87 (br s, 1H), 2.21 (s, 3H), 1.96 (s, 3H).

^{13}C NMR: δ ($CDCl_3$) 164.38, 160.29, 149.29, 130.74, 129.26, 123.12, 114.94, 27.50, 20.44.

MS m/z (relative intensity): 212 (M^+ + 2, 3%), 210 (M^+, 9%), 128 (19%), 83 (100%), 55 (100%).

7e: ^{1}H NMR: δ ($CDCl_3$) 7.26–6.77 (m, 4H), 4.59 (s, 2H), 2.88 (sept, J = 7.0 Hz, 1H), 1.14 (d, J = 7.0 Hz, 6H).

^{13}C NMR: δ ($CDCl_3$) 209.99, 156.50, 129.44, 127.12, 115.83, 71.55, 37.06, 17.78.

MS m/z (relative intensity): 214 (M^+ + 2, 4%), 212 (M^+, 10%), 141 (6%), 127 (8%), 85 (4%), 71 (61%), 43 (100%).

• *Reduction of* **1a** *in the presence of* **4f**: *Hg cathode (entry 8, table II)*

The electrolysis potential was −1.5 V. The isolated products (and yields) were: **1b** (22%, GC yield), **9f** (24%), **7f** (2%).

9f: ^{1}H NMR: δ ($CDCl_3$) 7.91–7.27 (m, 7H), 6.15 (br s, 1H), 2.29 (s, 3H), 2.04 (s, 3H).

^{13}C NMR: δ ($CDCl_3$) 164.78, 160.25, 146.74, 134.68, 127.91, 127.19, 126.23, 126.21, 125.60, 125.37, 121.45, 118.78, 115.01, 27.54, 20.48.

MS m/z (relative intensity): 227 (M^+ + 1, 2%), 226 (M^+, 17%), 144 (64%), 83 (100%), 55 (80%).

7f: ^{1}H NMR: δ ($CDCl_3$) 7.52–6.65 (m, 7H), 4.78 (s, 2H), 3.11 (sept, J = 7.1 Hz, 1H), 1.20 (d, J = 7.1 Hz, 6H).

^{13}C NMR: δ ($CDCl_3$) 211.01, 153.70, 134.69, 130.87, 128.85, 127.57, 126.67, 125.74, 122.30, 121.28, 104.90, 71.82, 37.18, 17.89.

MS m/z (relative intensity): 229 (M^+ + 1, 7%), 228 (M^+, 50%), 157 (27%), 143 (5%), 127 (80%), 71 (52%), 43 (100%).

• *Reduction of* **2a** *in the presence of* **4b**: *Hg cathode (entry 9, table II)*

The electrolysis potential was −1.5 V. The isolated products (and yields) were: **2b** (45%, GC yield), **10b** (30%), **8b** (10%).

10b: ^{1}H NMR: δ ($CDCl_3$) 7.02–6.84 (m, 4H), 5.80 (br s, 1H), 3.77 (s, 3H), 2.88–2.82 (m, 2H), 2.32–2.22 (m, 2H), 2.02–1.62 (m, 6H).

^{13}C NMR: δ ($CDCl_3$) 166.58, 165.34, 157.03, 144.24, 122.50, 114.38, 112.16, 55.55, 38.17, 35.50, 30.02, 27.80, 24.88.

8b: ^{1}H NMR: δ ($CDCl_3$) 6.80 (br s, 4H), 4.55 (s, 2H), 3.73 (s, 3H), 2.70–2.51 (m, 1H), 2.25–1.20 (m, 10H).

^{13}C NMR: δ ($CDCl_3$) 210.12, 154.42, 152.18, 115.65, 114.67, 72.41, 55.70, 46.89, 28.14, 25.74, 25.61.

• *Reduction of* **1a** *in the presence of* **5**: *Hg cathode (entry 10, table II)*

The controlled-potential electrolysis was carried out, at a potential of −1.5 V, by stepwise addition of **1a** (0.285 g, 1.84 mmol) and **5** (0.294 g, 1.84 mmol) to DMF/0.1 mol dm^{-3} TEAP (38 mL) in such a way that their concentrations never exceeded 1×10^{-2} mol dm^{-3}. Each addition of ketone and diester was made when the current dropped from its initial value to that measured after the pre-electrolysis. The isolated products (and yields) were: **1b** (25%, GC yield), **9i** (0.027 g, 0.11 mmol, 6%) [12], **11** (0.017 g, 0.07 mmol, 4%) [12].

• *Reduction of* **2a** *in the presence of* **5**: *Hg cathode (entry 11, table II)*

The electrolysis potential was −1.5 V. The isolated products (and yields) were: **2b** (30%, GC yield), **10i** (7%) [12], **12** (15%) [12].

• *Reduction of* **6** *in the presence of* **1a** *and* **5***: Hg cathode (entry 12, table II)*

The controlled-potential electrolysis was carried out, at a potential of −1.0 V, by stepwise addition of **6** (0.290 g, 0.92 mmol), **1a** (0.285 g, 1.84 mmol) and **5** (0.294 g, 1.84 mmol) to DMF/0.1 mol dm^{-3} TEAP (42 mL) in such a way that the concentration of **6** never exceeded 1×10^{-2} mol dm^{-3} and the concentrations of **1a** and **5** never exceeded 2×10^{-2} mol dm^{-3}. Each addition of substrate was made when the current dropped from its initial value to that measured after the pre-electrolysis. The isolated products (and yields) were: **1a** (0.028 g, 0.18 mmol, 10%), **9i** (0.075 g, 0.31 mmol, 17%).

• *Reduction of* **6** *in the presence of* **2a** *and* **5***: Hg cathode (entry 13, table II)*

The electrolysis potential was −1.0 V. In this case the molar amounts of **2a** and **5** were double that of **6**. The isolated products (and yields) were: **2a** (15%), **10i** (12%).

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