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### Preliminary communication

## Electrochemical synthesis of ketones from acid chlorides and alkyl and aryl halides catalysed by nickel complexes

H. Marzouk, Y. Rollin, J.C. Folest, J.Y. Nédélec and J. Périchon

*Laboratoire d'Electrochimie, Catalyse et Synthèse Organique (U.M. No. 28), C.N.R.S., 2, rue Henri Dunant, 94320 Thiais (France)*

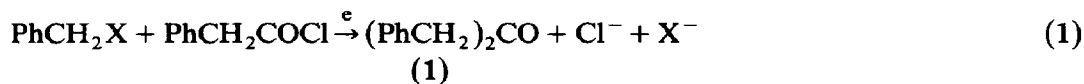
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### Abstract

The nickel-catalysed electrochemical cross-coupling of acid chlorides and alkyl or aryl halides in acetonitrile affords unsymmetric ketones in good to high yields. The reaction can be performed under very simple and mild conditions in a diaphragmless cell. A zinc rod as the sacrificial anode has been found to be the most efficient.

The coupling of organometallic reagents with acid chlorides is a straightforward method of preparing ketones [1]. Many transition metal catalysts have been used either to increase the reactivity of the acid halide towards the organometallic [2], or to allow the reaction to occur without requiring the preliminary formation of an organometallic reagent [3]. Unlike the chemical syntheses, the electrochemical synthesis of ketones from acid chlorides and organic halides is not well documented, only two short papers having appeared, a decade ago, on such direct electroreductive couplings [4]. More recently, direct electrochemical syntheses of ketones from organic halides and acid anhydrides have been described [5]. We report here on a promising new nickel-catalysed electrochemical coupling reaction of acid chlorides with benzyl, allyl, and aryl halides under mild conditions to give unsymmetric ketones.

A preliminary investigation of the features of the reaction has been devoted to the coupling of  $\text{PhCH}_2\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) with  $\text{PhCH}_2\text{COCl}$  (eq. 1). Several parameters have been studied, and the results are given in Table 1.



It was first found that there is very little cross-coupling in the absence of a catalyst, either in a divided cell or in a diaphragmless one equipped with a magnesium or zinc consumable anode. Among the many catalysts and redox

Table 1

Electrochemical synthesis of dibenzylketone from  $\text{PhCH}_2\text{COCl}$  and  $\text{PhCH}_2\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) under various conditions <sup>a</sup>

Entry	$\text{PhCH}_2\text{COCl}$	X	Anode (electrochem. conditions <sup>b</sup> )	$\text{PhCH}_2\text{COCH}_2\text{Ph}$		Conversion of $\text{PhCH}_2\text{X}$ (b/)
	$\text{PhCH}_2\text{X}$			Faradic yield (%) <sup>d</sup>	Chemical yield (%) <sup>e</sup>	
1	1	Br	c	53	44	100
2	1	Br	Mg (A)	145	32	100
3	1	Br	Mg (B)	140	35	90
4	1	Br	Zn (A)	93	80	78
5	1	Br	Zn (B)	98	95	100
6	1	Cl	Zn (B)	49	95	52
7	1	Cl	Mg (B)	12	18	80
8	5	Cl	Mg (B)	55	96	70
9	10	Cl	Mg (B)	35	95	70
10	5	Br	Mg (B)	65	98	100
11	1.5	Br	Al (A)	nd	16	nd
12	1.5	Br	Cd (A)	nd	$\epsilon < 5$	nd

<sup>a</sup> Undivided cell;  $\text{PhCH}_2\text{X}$  (10 mmol);  $\text{CH}_3\text{CN}$  (25 ml);  $\text{NiBr}_2\text{bpy}$  (0.5 mmol); bpy (1 mmol); cathode: gold or vitreous carbon; under argon; room temperature; nd: not determined. <sup>b</sup> A: Constant current electrolysis ( $I$  0.1 A);  $\text{NBu}_4\text{BF}_4$  ( $2 \times 10^{-2} M$ ). B: Controlled potential electrolysis ( $-1.6$  V);  $\text{NBu}_4\text{BF}_4$  ( $10^{-1} M$ ). <sup>c</sup> Electrolysis in divided cell at  $-1.6$  V with  $3 \times 10^{-1} M$   $\text{NBu}_4\text{BF}_4$ ; gold cathode. <sup>d</sup> Amount of formed ketone relative to the electricity passed. <sup>e</sup> Amount of ketone relative to consumed  $\text{PhCH}_2\text{X}$ .

mediators we have tested [6\*], only  $\text{NiBr}_2\text{bpy}$  (bpy = 2,2'-bipyridyl) gave promising results in the preliminary experiments. Cyclic voltammetry analysis clearly shows that each compound rapidly adds oxidatively to the  $\text{Ni}^0$  complex electrogenerated at  $-1.25$  V vs. SCE, the reaction of  $\text{PhCH}_2\text{COCl}$  being slightly faster than that of  $\text{PhCH}_2\text{X}$ . From the latter dibenzyl is readily formed, as expected [7], whereas the reaction of  $\text{PhCH}_2\text{COCl}$  leads to a stable bis-acyl nickel, which is reduced at a more cathodic potential ( $< -1.5$  V vs. SCE).

In a divided cell, a moderate yield of the expected ketone is obtained in the reduction of a 1/1  $\text{PhCH}_2\text{COCl}/\text{PhCH}_2\text{Br}$  mixture in 0.01 M  $\text{NBu}_4\text{BF}_4$  acetonitrile solution containing the catalyst (Table 1, entry 1). We then turned to the recently proposed consumable anode electroreduction process in the hope of increasing the yield, in addition to taking advantage of the demonstrated ease of the procedure [8]. The nature of the anode has been found to be quite important. Thus, with Mg the yield of dibenzyl ketone **1** was satisfactory only when an excess of acid chloride up to five times the amount of the benzyl halide was used (entries 3, 10 and 7–9, Table 1), whereas high Faradic and chemical yields were obtained from a 1/1 reagent mixture when a Zn rod was used as the anode. In addition, chemical reduction of the product as well as the reagents occurs on the electroscoured magnesium rod, especially in constant current electrolysis at medium current density [9]. Other metals (Cd, Mn, Al) were tried without success. The role of the metallic ions in this reaction has not been clearly revealed so far, and current studies are aimed at elucidating the mechanism.

\* Reference number with asterisk indicates a note in the list of references.

Table 2

Nickel-catalysed electrochemical synthesis of unsymmetric ketones from acid halides and alkyl or aryl halides <sup>a</sup>

Entry	RCOCl	R'X	RCOR'			
			anode (conditions <sup>b</sup> )	faradic yield (%) <sup>c</sup>	chemical yield (%) <sup>d</sup>	conversion of R'X (%)
1	PhCH <sub>2</sub> COCl	PhCH <sub>2</sub> Br	Zn (A)	93	80	78
2	CH <sub>3</sub> CH <sub>2</sub> COCl	PhCH <sub>2</sub> Br	Zn (A)	60	62	100
3	CH <sub>3</sub> CH <sub>2</sub> COCl	PhCH <sub>2</sub> Br	Mg(A)	nd	48	100
4	PhCH <sub>2</sub> COCl	CH <sub>2</sub> =CCH <sub>3</sub> CH <sub>2</sub> Cl	Zn (A)	26	nd	nd
5	PhCH <sub>2</sub> COCl	CH <sub>2</sub> =CCH <sub>3</sub> CH <sub>2</sub> Cl	Mg(A et B)	$\epsilon < 5\%$		
6	CH <sub>3</sub> CH <sub>2</sub> COCl	PhI	Zn (A)	35	90	30
7	CH <sub>3</sub> CH <sub>2</sub> COCl	PhI	Mg(A)	$\epsilon$		
8 <sup>e</sup>	PhCH <sub>2</sub> COCl	PhI	Mg(B)	10	35	60
9 <sup>e</sup>	PhCOCl	PhCH <sub>2</sub> Br	Mg(B)	nd	70	95
10 <sup>e</sup>	CH <sub>3</sub> CH <sub>2</sub> COCl	PhCH <sub>2</sub> Br	Mg(B)	nd	65	nd

<sup>a</sup> Undivided cell; R'X (10 mmol); RCOCl (10 mmol); NiBr<sub>2</sub>bpy (0.5 mmol); bpy (1 mmol); CH<sub>3</sub>CN (25 ml); gold or vitreous carbon cathode; under argon; room temperature; nd: not determined. <sup>b</sup> A: Constant current electrolysis (I = 0.1 A); NBu<sub>4</sub>BF<sub>4</sub> (2 · 10<sup>-2</sup> M). B: Controlled potential electrolysis (-1.6 V); NBu<sub>4</sub>BF<sub>4</sub> (10<sup>-1</sup> M). <sup>c</sup> Amount of ketone relative to the passed electricity. <sup>d</sup> Amount of ketone relative to consumed R'X. <sup>e</sup> RCOCl/R'X = 5.

The optimized experimental conditions for the model reaction [10\*] appear to be of general application in view of the results of the ketone syntheses already investigated, involving interaction of benzyl, allyl, and aryl halides with alkoyl and aroyl halides (see Table 2). Satisfactory yields were obtained, though the condition by these reactions were not optimized.

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- The reduction potentials of the reagents are (*E* volt/SCE; gold cathode; 0.01 M solution in CH<sub>3</sub>CN): PhCH<sub>2</sub>Br (-1.83); PhCH<sub>2</sub>Cl (-2.31); PhCH<sub>2</sub>COCl (-2.2). Mediators or catalysts having their reduction potential close to but higher than that of PhCH<sub>2</sub>COCl have been examined (*E* volt/SCE): perylene (-1.67); anthracene (-1.96); benzophenone (-1.78); bpy (-2.2); Co salen (-1.45); PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> + PPh<sub>3</sub> (-0.9). All afforded less than 15% (mediators) and 30% (transition metal catalysts) of **1**, whatever the other parameters were.
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- 9 C. Saboureau, M. Troupel, J. Perichon, submitted to *J. Applied Electrochem.*
- 10 A typical preparative experiment was as follows. In a cylindrical cell equipped with a zinc rod as the anode and a vitreous carbon gauze as the cathode are mixed RX (10 mmol), RCOCl (10 mmol), NiBr<sub>2</sub>bpy (0.5 mmol), bpy (1 mmol) and NBu<sub>4</sub>BF<sub>4</sub> (0.5 mmol) in CH<sub>3</sub>CN (25 ml). The electrolysis is carried out under 0.1 A, at room temperature, under argon, until all the RX is consumed. The usual work-up gives the ketone. All the products gave satisfactory analyses.