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Electrochemical Synthesis of Symmetrical Ketones from Acid Chlorides

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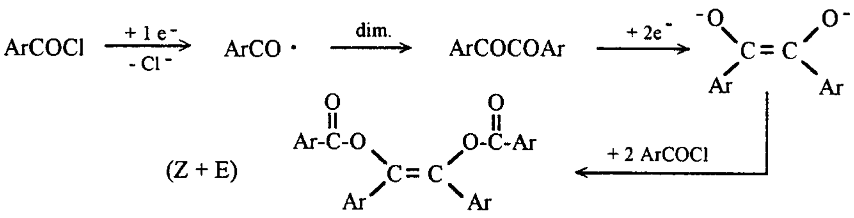
Key words : symmetrical ketones synthesis, acid chloride electroreduction.

Abstract : The electrochemical reduction of aroyl or arylacetyl chlorides was performed in an undivided cell fitted with a stainless steel anode and a nickel foam cathode. The electrolyses were carried out at constant current in acetonitrile as solvent, leading to the corresponding symmetrical ketones.

The possibility of carbon-carbon bond formation by electrochemical syntheses from acid halides has not been extensively explored. As a classical reaction, it has been reported [1, 2, 3] that the electroreduction of aroyl chlorides leads to 1,2-enediol diesters according to the pathway presented in scheme 1 :



Scheme 1

The reaction does not stop at the formation step of the α-diketone since this latter is more easily electroreduced than the starting acid chloride.

In a previous paper [4] we have reported that the electroreduction in acetonitrile of a mixture of an acid chloride (R^1COCl) and an organic halide (R^2X) leads to the unsymmetrical ketone R^1COR^2 when using a catalytic system involving low-valent complexes of nickel with dipyridyl.

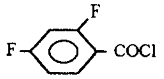
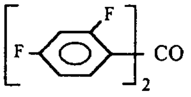
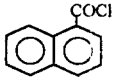
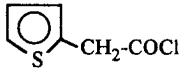
Moreover it has been mentionned [5] that benzoyl chloride or heptanoyl chloride can be electroreduced in acetonitrile into the corresponding aldehyde. In a recent paper [6], the same authors indicate that they obtain 1,3-diphenylacetone as a side product (2-4% yield) of the electroreduction of phenylacetyl chloride.

We present in this paper a new electrochemical synthesis where an acid chloride gives a symmetrical ketone, according to the overall reaction :

$$2\,RCOCl + 2\,e^- \longrightarrow RCOR + 2\,Cl^- + CO$$

This electrochemical coupling of two molecules of acid halide, involving a decarbonylation step, is carried out by the intentiostatic electrolysis of an acetonitrile solution of the acid halide, in an undivided cell fitted with a nickel or stainless steel anode. The results obtained by a typical procedure as described in experimental section, are presented in table 1.

Table 1 : Electrosyntheses of Ketones from Acid Chlorides

Acid chloride	Product		Yield[a]
$PhCH_2COCl$	$(PhCH_2)_2CO$	**1**	80
$PhCOCl$	Ph_2CO	**2**	72
$4\text{-}CH_3\text{-}C_6H_4\text{-}COCl$	$(4\text{-}CH_3\text{-}C_6H_4\text{-})_2CO$	**3**	44
$3\text{-}CH_3\text{-}C_6H_4\text{-}COCl$	$(3\text{-}CH_3\text{-}C_6H_4\text{-})_2CO$	**4**	47
$4\text{-}F\text{-}C_6H_4\text{-}COCl$	$(4\text{-}F\text{-}C_6H_4\text{-})_2CO$	**5**	42
$3\text{-}F\text{-}C_6H_4\text{-}COCl$	$(3\text{-}F\text{-}C_6H_4\text{-})_2CO$	**6**	45
$4\text{-}Br\text{-}C_6H_4\text{-}COCl$	$(4\text{-}Br\text{-}C_6H_4\text{-})_2CO$	**7**	45
		**8**	47
	(1-Naphtyl)$_2$CO	**9**	30
	(2-Thiophen-CH$_2$)$_2$CO	**10**	50

a : yields are given for isolated products in percent *vs.* initial acid chloride.

Symmetrical ketones are formed with moderate yields from aroyl, 1-naphtoyl and 2-thiopheneacetyl chlorides (products **3** to **10**). The best yields were obtained with phenylacetyl and benzoyl chlorides (products **1** and **2**). In all these cases, neither the aldehyde (RCHO), nor the diketone (RCOCOR) have been detected, and the 1,2-enediol diester (RCOO(R)C=C(R)OCOR, see scheme 1) was produced only in small amounts. However the procedure does not work with alkoyl chlorides, as observed from butyryl or heptanoyl chlorides, which were mainly transformed into the corresponding 1,2-enediol diester. The ketone was then formed only with a less than 5% yield.

The cathodic material does not seem to have a particular importance, since the same yields were obtained when replacing the nickel foam cathode by a stainless steel or carbon fiber one.

On the other hand, the nature of the sacrificial anode has a crucial influence. When using a magnesium or aluminium rod as anode, the potential of the cathode stabilized at a value where the direct electroreduction of the acid chloride is classically observed (about - 1.3 V(*vs.*SCE) for ArCOCl and - 2.3 V for $PhCH_2COCl$). In these conditions, only the 1,2-enediol diesters were formed.

When using zinc or iron, the main reaction at the cathode is the electrodeposition of zinc or iron metal from the cations released by the anodic process. Since stainless steel contains iron, nickel and chromium, we have also verified that addition of chromium salts in the solution does not allow the formation of ketone.

Ketones were obtained only when employing a nickel or a stainless steel rod as the sacrificial anode. The potential of the cathode during the electrolysis was in the range - 0.9 to - 1V (*vs.*SCE) which corresponds to a potential level where Fe(II) and Ni(II) species can be electroreduced.

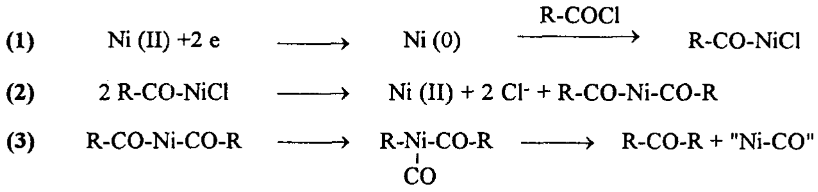
Rieke and co-workers [7,8] have reported that cross-coupling reactions of benzyl halides with acid chlorides can be mediated by stoechiometric amounts of reactive metallic nickel to give benzyl ketones. For some of these experiments, it has been observed a coupling (with decarbonylation) reaction of acid chlorides, leading to symmetrical ketones, but only with poor yields. In connection with that, we have shown that no reaction is obtained if we achieve first an electrolytic nickel-coating of the cathode and then we add the acid chloride.

Consequently we assume that, in our experimental conditions, a reaction occurs between the acid chloride and a low-valent electrogenerated species of nickel, as we have shown in the case of reactions involving a zerovalent nickel-dipyridyl complexe [4]. Moreover, this active nickel species can be involved in a catalytic cycle since the reaction yielding the ketone remains efficient when the nickel or stainless steel anode is replaced in the course of the electrolysis by an iron one, after 10% only of the total electric charge have been engaged.

We observed some differences between a pure nickel and a stainless steel anode. The faradaic yield corresponding to the overall consumption of the acid chloride is higher when using nickel (1.5 to 2 Faraday per mole of RCOCl) than when using stainless steel (2.6 - 2.7 Faraday are then required). In the case of stainless steel, a part of electricity is obviously engaged in the transportation of iron from the anode to the cathode. However, the chemical yield in ketone is slightly lower when using a nickel anode.

We think that the first step of the reaction can be the formation of an acylnickel intermediate resulting from an oxidative addition between the acid halide and a transient electrogenerated low-valent nickel complexe, liganded by the solvent (scheme 2, step 1). A bis acylnickel complex would be obtained with regeneration of divalent nickel (scheme 2, step 2), as it has been already considered for acyl (or aryl) nickel complexes[8,9]. Reductive elimination of nickel liganded by one molecule of carbon monoxide yields the ketone (scheme 2, step 3). During electrolyses, we have found evidence for the release of carbon monoxide and/or metal-carbonyl complexes. If nickel species are undoubtedly required for the ketone formation, we do not exclude that electrogenerated zerovalent iron could be involved in the course of the elimination of carbon monoxide. For the moment, we cannot give more details concerning the mechanism of the reaction.

To conclude, we have shown that acid chlorides can be efficiently converted into ketones, with a very simple electrolytic device, provided that a nickel-containing sacrificial anode is used. Work is currently in progress to achieve other coupling reactions of acid halides by this way.



$$\text{(1)}\quad \text{Ni (II)} + 2\text{ e} \longrightarrow \text{Ni (0)} \xrightarrow{\text{R-COCl}} \text{R-CO-NiCl}$$

$$\text{(2)}\quad 2\text{ R-CO-NiCl} \longrightarrow \text{Ni (II)} + 2\text{ Cl}^- + \text{R-CO-Ni-CO-R}$$

$$\text{(3)}\quad \text{R-CO-Ni-CO-R} \longrightarrow \underset{\text{CO}}{\text{R-Ni-CO-R}} \longrightarrow \text{R-CO-R} + \text{"Ni-CO"}$$

Scheme 2

Experimental part :

Acetonitrile (S.D.S. anhydrous analytical grade) was stored for several days under nitrogen over molecular sieve 0.4 nm. Tetrabutylammonium tetrafluoroborate was dried in vacuo at 70°C for one day before use. The acid chlorides (Aldrich Chimie) were carefully syringed into the electrochemical cell.

In an electrochemical undivided cell, previously described [10] and equipped with a nickel or stainless steel (316 l, 18/8 Ni/Cr) rod as anode surrounded by a cylindrical nickel foam cathode, were added the acid chloride (20 mmol.) and Bu_4NBF_4 (0.5 mmol.) in acetonitrile (40 ml.). Electrolyses were carried out at room temperature, under argon, at constant intensity with a current density of 1.5 $A.dm^{-2}$, until all the reagent was consumed (2.6-2.7 F per mole of acid chloride).

The evolution of carbone monoxide (or metal-carbonyl) was qualitatively evidenced by introducing short-term tube tests in the effluent gaz.

Ketones were isolated by usual work-up procedures (solvent evaporation and acid hydrolysis) and recovered in a pure form by suitable extraction and chromatography on a silica-gel column. They were identified by G.C. analysis, by comparison with authentic samples and on the basis of their spectroscopic data (N.M.R., I.R, M.S.). All the ketones synthetised are known compounds, except the product **8**, for which we give spectroscopic data [11].

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11. Analytical data of **8** : ^1H NMR ($CDCl_3$, 200 MHz) δ_{ppm} = 6.8 (m, 4 H) 7.8 (m, 2 H) ^{19}F NMR ($CDCl_3$, 200 MHz) δ_{ppm} (/$CFCl_3$) = - 107.6 (m) -101.8 (m) MS m/z (relative intensity) = 254 (M, 2), 141 (100), 113 (30) IR (CCl_4) ν_{CO} = 1670 cm^{-1} m.p. = 41.6°C.

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