New Electrochemical Synthesis of Ketones from Organic Halides and Carbon Monoxide

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The dissolution of a stainless steel anode provides catalytic nickel species which enable the efficient synthesis of ketones by electrolysis of organic halides in DMF in the presence of bipyridine and carbon monoxide.

Carbon monoxide can be easily coupled with organic halides in carboalkoxy reactions leading to esters or acids.[1] On the other hand the reductive coupling of organic halides with CO yielding ketones or aldehydes is a more difficult reaction which generally needs highly reactive but sensitive species, *e.g.* ketones can be readily obtained by using stoichiometric amounts of tetracarbonyl ferrate anions $Fe(CO)_4^{2-}$ (Collman's reagent[1,2]). The direct use of CO at normal or moderately increased pressure has also been reported for reactions involving organometallic reagents (lithium, aluminium, tin and mercury) as a source of carbanions[1] and very often, a catalytic system based on nickel, palladium and recently rhodium complexes.[3] Electrochemical methods have not been really investigated since Petit *et al.*[4] and Yoshida *et al.*[5] reported the synthesis of aldehydes in moderate yields by electrolysis of mixtures of an organic halide and iron pentacarbonyl. The cathode potential must be low enough (< -2V *vs.* SCE) to allow the electrochemical reduction of iron pentacarbonyl and possibly also the reduction of the organic halide. Here we report a new electrochemical synthesis yielding ketones from organic halides and carbon monoxide in mild reaction conditions, according to the overall reaction shown in eqn. (1).

$$2\,RX + CO + 2e^- \rightarrow RCOR + 2\,X^- \qquad (1)$$

The undivided cell[6] was fitted with a stainless steel (or nickel or iron) rod as the anode which was surrounded by a nickel (or stainless steel) grid as the cathode. In typical experiments the DMF or *N*-methylpyrrolidone (NMP) solution (50 ml) contained Bu_4NBF_4 (1.5 mmol) as supporting electrolyte, $FeCl_2$ (1 mmol), 2,2′-bipyridine (bpy, 1 mmol) and the organic halide RX (20 mmol). The solution was saturated with carbon monoxide by gentle bubbling at normal pressure. The electrolyses were carried out at room temperature and at a constant current (1–2 A dm^{-2}) until GC analysis of samples indicated the consumption of the organic halide which required 1–5 electron-mol per mol of halide. The ketones were recovered by suitable water–organic solvent extraction, purification on silica gel and characterised by GC-MS, ^1H NMR, ^{13}C NMR and IR.

Results reported in Table 1, with benzyl chloride as a model reagent, show that the nature of the sacrificial anode has a crucial importance. With iron, syntheses were not efficient since benzyl chloride was converted mainly to toluene. Dibenzylketone can be obtained in good yields only when the consumption of the anode provides nickel ions as catalytic precursors. Moreover a synergy is observed when iron ions are also released from a stainless steel anode.

Table 1 Influence of the nature of the sacrificial anode on the electrosynthesis of dibenzyl ketone from benzyl chloride[a]

	GC yields (%)		
Anode	$(PhCH_2)_2CO$	$(PhCH_2)_2$	PhMe
Fe	10	30	60
Ni	35	65	trace
Cr18/Ni10/Fe72	60	10	30
Ni80/Cr20	75	15	5
Fe64/Ni36	90	10	trace

[a] For experimental conditions see the text.

During the electrolyses, the potential of the cathode was around -1.2 V *vs.* SCE, corresponding to the reduction of nickel and iron bipyridine complexes as shown by cyclic voltammetry. Metal carbonyl species such as $Ni(CO)_4$ and $Fe(CO)_5$ are reduced at lower potentials (< -2 V *vs.* SCE).[7,8] We thus suppose that the active species is a zerovalent nickel complex associated with both bipyridine and carbon monoxide, *e.g.* $Ni^0bpy(CO)_2$.[9]

Results reported in Table 2 show that ketones were obtained with moderate to good yields depending on the nature of the starting organic halide. The major side-product was the dimer R–R resulting from a reductive homocoupling of RX. In the reactions run at high current density (> 2 A dm^{-2}) the dimer R–R was the major product as observed in the absence of carbon monoxide.[10] This suggests that the solubility of CO[11] and its dissolution rate limit the formation of the zerovalent mixed $Ni^0bpy(CO)_2$ complex.

Conversely, at lower current density (< 1 A dm^{-2}), dimer formation was suppressed but the faradaïc ketone yield was lowered. The reaction even stops when low reactive organic halides were used. This may be due to the formation of inactive complexes overliganded by CO. The reaction started again by stopping the carbon monoxide supply.

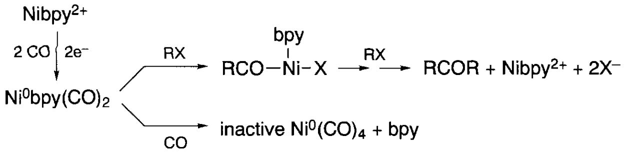
The results are in keeping with the reaction pathway (Scheme 1), already proposed,[12] in which the ketone is obtained *via* an acylnickel intermediate after the oxidative addition of the organic halide onto the zerovalent nickel complex.

We also examined the influence of the ligand nature. In the absence of bpy, the organic halides were converted in low faradaïc yields, mainly to RH and R–R. When the 2,2′-bipyridine was replaced by another ligand such as pyridine,

Table 2 Electrosyntheses of ketones from organic halides and carbon monoxide[a]

RX	Solvent	RCOR Isolated yield (%)	By-products [GC yield (%)]
$PhCH_2Cl$	DMF	80	R–R (10)
$PhCH_2Br$	DMF	70	R–R (15)
$2\text{-}Me\text{–}C_6H_4CH_2Br$	DMF	70	R–R (20)
$4\text{-}MeC_6H_4CH_2Br$	DMF	62	R–R (40)
$2\text{-}Cl\text{–}C_6H_4CH_2Cl$	DMF	75	R–R (10) RH (2)
$Me\text{–}CH{=}CHCH_2Cl$	DMF	$65^{b,c}$	R–R (35)
$Me\text{–}CH{=}CHCH_2Br$	DMF	$60^{b,c}$	R–R (40)
$\substack{Me\\Me}{>}C{=}CHCH_2Cl$	DMF	65^{b}	R–R (35)
$4\text{-}CF_3C_6H_4Br$	NMP	50	R–R (25) RCO_2H (10)
PhI	NMP	25	R–R (20)
$Me(CH_2)_7I$	DMF	50	R–R (40)
$Me(CH_2)_5Br$	NMP	60	R–R (30)
$\substack{Et\\Et}{>}CHI$	DMF	15	R–R (20)

[a] Stainless steel (Fe_{64}/Ni_{36}) anode. For other experimental conditions see the text. [b] For allylic compounds we failed in isolating ketones with satisfactory yields and we only give GC yields. [c] Starting from crotyl halides, analysis proves the presence of a mixture of $(MeCH{=}CHCH_2)_2CO$, $CH_2{=}CHCH(Me)COCH_2CH{=}CHMe$ and $[(CH_2{=}CHCH(Me)]_2CO$.



Scheme 1

triphenylphosphine or cycloocta-1,5-diene unsatisfactory results were obtained. Among the tested ligands, only 1,10-phenanthroline gave the ketone. Nevertheless, the yields were lower than those obtained with bpy.

In conclusion, we have shown that a very simple electrochemical device using a stainless steel sacrificial anode provides a catalytic system, which, in the presence of carbon monoxide, converts organic halides into symmetrical ketones in mild reaction conditions.

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