Tetrahedron Letters,Vol.26,No.22,pp 2633-2636,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

ELECTROCATALYZED CARBOXYLATION OF ORGANIC HALIDES BY A COBALT-SALEN COMPLEX.

Jean-Claude FOLEST, Jean-Marc DUPRILOT, Jacques PERICHON*
Laboratoire d'Electrochimie Organique (U.A. n° 329 du CNRS),
Université Paris-Val de Marne - Avenue du Général de Gaulle - 94010 CRETEIL Cedex, France.

Yvette ROBIN et Jacques DEVYNCK,
Laboratoire d'Electrochimie Analytique et Appliquée (U.A. n° 216 du CNRS),
E.N.S.C.P., 11 rue Pierre et Marie Curie - 75231 PARIS Cedex 05, France.

ABSTRACT

The carboxylation of benzylic and allylic chlorides by CO_2 in tetrahydrofuran + hexamethylphosphoramide (40% - 60%) is electrocatalyzed by a cobalt Schiff-base complex Co(Salen). The reactions were performed by controlled-potential electrolysis at the R-Co (Salen) reduction potential. The yield of the carboxylic acid formation has been calculated.

Controlled potential electrolysis of organic halides in the presence of carbon dioxide generally gives low yields of the corresponding carboxylates. The best results are obtained with benzylic or allylic halides, but esters are formed by a side reaction between the carboxylate and the unreacted organic halide (1,2).

It is well known that some of the strongly nucleophilic coordination compounds of low oxidation state of transition metals form CO_2 adducts and CO_2 insertion compounds (3). Whereas it was shown that carboxylic acids can be obtained from such compounds, the electrochemical carboxylation of organic halides RX has only been demonstrated in the case of nickel complexes. We have shown that the electrochemical reduction :

$$ArX + CO_2 + 2e \rightarrow ArCO_2^- + X^-$$

(in which ArX is an aryl halide) is catalyzed by zerovalent complexes Ni(O)Ln (L = triphenylphosphine) prepared by electrochemical reduction of the phosphinated Ni(II) complexes (4-5). The carboxylation thus proceeds through the formation of $ArNiXL_{n-2}$, and high yields of $ArCO_2^-$ in presence of CO_2 are obtained.

In contrast, low yields were obtained with benzylic or allylic halides and the reaction led mainly to dibenzyl or diallyl (6). In the case of α-chloroethylbenzene, the main product is styrene, resulting from a β-elimination in the Ni(O) insertion compound (4).

Reduction of organic halides can also be catalyzed by Schiff base-cobalt complexes. Electrochemical studies (7) have shown that cobalt-bis-salicylidene iminate (or Co(Salen) in its reduced form (Co(I)) permits the catalytic reduction of benzylic, aliphatic or allylic halides, leading to the same kind of dimers as Ni(O) phosphine complexes. Furthermore, the CO_2 adduct of Co(I) Salen has been described and isolated (8-9).

These results indicate that carboxylation could be possible with such cobalt complexes. This study was undertaken to investigate the electroreduction of some alkyl halides in the presence of CO_2 and to select experimental conditions where carboxylic acids could be obtained with significantly better yield than with other complexes.

The electrolysis was performed at the reduction potential of R Co (Salen) in a CO_2 saturated solution of RX and Co(II) Salen under a CO_2 pressure of 1 or 2 atm.

EXPERIMENTAL

The solvent was a mixture of tetrahydrofuran (THF) 40% and hexamethylphosphoramide (HMPA) 60%. The supporting electrolyte was $LiClO_4$. The electrolysis cell has been previously described (7). The anodic compartment contained 25 ml of solvent and 0.8 g (0.3M) of $LiClO_4$. The anode was a platinum grid. The cathodic compartment contained the same quantity of electrolyte and 0.2M of RX (5 mmol) and 10^{-2}M of Co(Salen) (0.25 mmol) with a mercury pool as cathode. Solutions were dehydrated with CH_3MgCl, according to a previously described procedure (7) ($E_{Ag/Ag^+} - E_{SCE} = -0.680 \pm 0.005$ V in this medium).

After exchange of two moles of electrons per mole of RX, the solution was hydrolyzed by HCl and the organic products extracted with dimethylether. The volatile products of electrolysis (RX,RR,RH) were analyzed by GPC ; carboxylic acids were characterized by acid-base titration and RMN after isolation.

Quantitative results are given in the following table :

RX	RX/Co(Salen)	Electrolyte	P_{CO_2}(atm)	$E_{electrolysis}$ ref : Ag/Ag^+	RCOOH%(1)
$C_6H_5CH_2Cl$	10	$LiClO_4$(n.d.)	1	-2,3V	50
$C_6H_5CH_2Cl$	20	$LiClO_4$(d)	2	-2,3V	62
$C_6H_5CH(Cl)CH_3$	20	$LiClO_4$(d)	2	-2,1V	65
$C_6H_5CH = CHCH_2Cl$	20	$LiClO_4$(d)	2	-2,3V	97
$CH_3CH = CHCH_2Cl$	10	$LiClO_4$(d)	2	-2,4V	63
$CH_2 = C(CH_3)CH_2Cl$	10	$LiClO_4$(d)	2	-2,4V	62

(n.d.) non dehydrated (H_2O) - 5.10^{-2}M ; (d) : dehydrated -
(1) expressed as percent of the initial RX.

The above data show that high yields were obtained with the allylic and benzylic halides after dehydration of the solvent. The presence of water decreases the yield of carboxylate and increases the amount of RH, as illustrated by the following example :

RX	Media (water content)	RH (%)	RR (%)	RCOOH (%)
$C_6H_5CH_2Cl$ P_{CO_2} = 2 atm	$1\text{-}5.10^{-2}M$	10	2	50
	anhydrous (CH_3MgCl)	< 1	< 1	62

These preliminary experimental data show that carboxylation of organic halides can be obtained with particularly high yields by electrolysis with Co(Salen) as catalyst and benzylic and allylic halides as substrate. These results allow us to predict similar reactions with other halides of the same class. Co Salen thus appears to be an efficient catalyst in the dehydrated HMPA-THF mixture.

Nevertheless it should be noted that no carboxylation was observed either with an aliphatic halide (experiments were performed with bromohexane) or with bromostyrene. With halobenzenes, high yields of benzoic acid were obtained with Ni-phosphine complexes whereas carboxylation was insignificant with Co Salen.

The process involved in the carboxylation with Co Salen is not yet well understood. The first reaction is the reduction of Co(II)Salen, followed by alkylation by RX :

$$\text{Co(II)Salen} + e \rightarrow \text{Co(I)Salen}^-$$

$$\text{Co(I)Salen}^- + RX \rightarrow R\ \text{Co(III)Salen} + X^-$$

The overall carboxylation reaction is :

$$R\ \text{Co(III)Salen} + CO_2 + 2e \rightarrow R\ CO_2^- + \text{Co(I)Salen}^-$$

The reaction can proceed through an adduct of the Co complex and CO_2 or through a reaction of the carbonium resulting from the dissociation of reduced R-Co(Salen).

The adduct of Co Salen and CO_2 described by Fachinetti and Floriani (8) was observed only under CO_2 pressure and its formation in solution must be proved.

ACKNOWLEDGMENT - This work was supported by "Le Groupement Scientifique pour la Valorisation du CO_2".

REFERENCES.

1 - a. M. BAIZER and J. SHRUMA, J. Org. Chem. (1972) 37, 1951.
b. D. TYSSEE and M. BAIZER, J. Org. Chem. (1974) 39, 2819.

2 - S. WAWZONEK and J.M. SHRADEL, J. Electrochem. Soc. (1979), 126, 401.

3 - R.P.A. SNEEDEN in "Comprehensive organometallic Chemistry", G. WILKINSON ed., vol. 8, Pergamon Press, Oxford (1982).

4 - M. TROUPEL, Y. ROLLIN, S. SIBILLE, J.F. FAUVARQUE and J. PERICHON, J. Chem. Research (S), (1980), 26.

5 - M. TROUPEL, Y. ROLLIN, J. PERICHON and J.F. FAUVARQUE, Nouv. J. Chim. (1981) 5, 621.

6 - J.M. DUPRILOT, F. BEDIOUI, J.C. FOLEST, C. BIED-CHARRETON, J. DEVYNCK, J. Organomet. Chem. (in the press).

7 - M. TROUPEL, Thèse de Doctorat, Université Paris-Val de Marne - CRETEIL (1980).

8 - G. FACHINETTI and C. FLORIANI, J. Am. Chem. Soc. (1978), 100, 7405.

(Received in France 15 January 1985)