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ELECTROREDUCTIVE COUPLING OF METHALLYLCHLORIDE OR METHYL CHLOROACETATE WITH CARBONYL COMPOUNDS CATALYZED BY NICKEL BIPYRIDINE COMPLEXES

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Abstract : An efficient electrosynthesis of homoallyl alcohols or β-hydroxy esters in the presence of catalytic amounts of the $NiBr_2$(2,2'-bipyridine) complex has been developped from mixed electrolysis of methallylchloride, or methylchloroacetate with several carbonyl compounds, using a one-compartment cell equiped of a sacrificial zinc anode.

We recently described an electrosynthetic process (1) using sacrificial anodes of aluminium, magnesium or zinc and DMF as solvent, affording alcohols from organic halides and ketones or aldehydes, according to

$$M - ne^- \longrightarrow M^{n+} \qquad \text{for the anodic process}$$

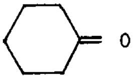
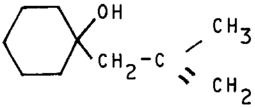
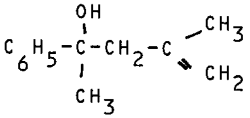
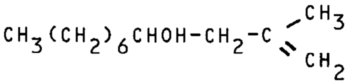
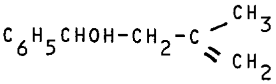
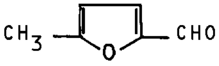
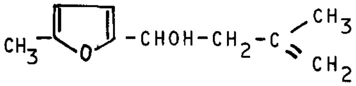
$$RX + 2e^- \longrightarrow R^- + X^- \qquad \text{for the cathodic one}$$

$$R^- + {>}C{=}O \longrightarrow R-\overset{|}{\underset{|}{C}}-O^-$$

If in some cases the yields were almost quantitative, they could be rather low when easily reducible or poorly reactive carbonyls were used or when the electrogenerated R^- were too basic. For example, electrogenerated methallyl anion adds to acetone in excess to give the expected alcohol in 95 % yield, but with cyclohexanone in five molar excess, the yield is only 20 %. We found now that the addition of catalytic (< 5 %) amounts of the complex $NiBr_2$,2-2'bipyridine and the use of a zinc anode greatly enhance the yield of coupling products of methallyl chloride with all kinds of carbonyl compounds tested. The carbonyl compound needs no more to be in excess and the reaction is very clean, the only by-products being RH and in some cases R-R. Table I gives some of the main results, and the yields range from good to excellent. The reaction is thought to go through Ni(II) reduction, oxidative addition of Ni(0) to RX and subsequent reduction of the allylnickel complex. It is expected

TABLE I

Electroreductive coupling of methallylchloride with ketones and aldehydes[a)]

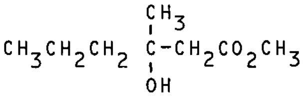
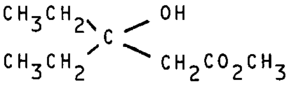
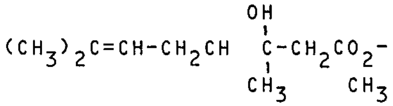
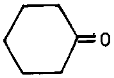
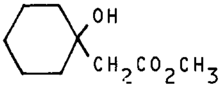
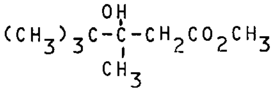
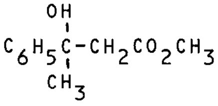
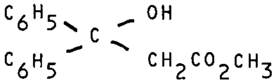
Carbonyl compound	Product (isolated yield[b)])
	 (80 %)
$C_6H_5COCH_3$	 $C_6H_5-C(OH)(CH_3)-CH_2-C(CH_3)=CH_2$ (92 %)
$CH_3(CH_2)_6CHO$	 $CH_3(CH_2)_6CHOH-CH_2-C(CH_3)=CH_2$ (85 %)
C_6H_5CHO	 $C_6H_5CHOH-CH_2-C(CH_3)=CH_2$ (85 %)
	 (50 %)

a) General procedure : DMF 30 ml, nBu_4NBr 1 mmole, $NiBr_2bipy$ 1 mmole, methallylchloride 30 mmoles, carbonyl compound 20 mmoles. At room temperature, a constant intensity (0.15 A) is applied between a zinc anode (5 cm^2) and a glassy carbon cathode (15 cm^2) until the carbonyl compound has disappeared. 1.5 to 2 F/mole of RX are needed.

b) Yield are expressed as isolated alcohol/initial carbonyl compound.

TABLE II

Electroreductive coupling of methyl chloroacetate with ketones [a)]

Carbonyl compound	Product, yield [b)]
$CH_3CH_2CH_2COCH_3$	 $CH_3CH_2CH_2\underset{OH}{\overset{CH_3}{C}}-CH_2CO_2CH_3$ (86 %)
$CH_3CH_2COCH_2CH_3$	 (75 %)
$(CH_3)_2C=CH-CH_2CH_2COCH_3$	 $(CH_3)_2C=CH-CH_2CH\ \underset{CH_3}{\overset{OH}{C}}-CH_2CO_2-CH_3$ (75 %)
	 (80 %)
$(CH_3)_3CCOCH_3$	 $(CH_3)_3C-\underset{CH_3}{\overset{OH}{C}}-CH_2CO_2CH_3$ (65 %)
$C_6H_5COCH_3$	 $C_6H_5\underset{CH_3}{\overset{OH}{C}}-CH_2CO_2CH_3$ (70 %)
$C_6H_5COC_6H_5$	 (60 %)

a) General procedure : DMF 30 ml, nBu_4NBr, 1 mmole, $NiBr_2Bipy$ 1 mmole, ketone 20 mmoles, $ClCH_2CO_2CH_3$ 40 mmoles. At room temperature 0.1 A is applied between a zinc anode and a glassy carbon cathode until the reactants have disappeared.

b) Yields are expressed as isolated alcohol/initial ketone.

that the proposed electrolytic procedure advantages the chemical preparations of homoallyl alcohols involving π-allyl nickel complexes (2), (3) :

- The reaction works catalytically with respect to nickel
- The coupling product is obtained in one step and the delicate preparation of the π-allyl nickel complex is then avoided.
- Milder temperatures and shorter reaction durations can be used.

This procedure can also be applied to the coupling of α-chloroesters with ketones. While in the uncatalyzed electrolysis dichloroacetate adds gently to acetone giving a mixture of chlorohydrine and epoxide with an overall yield of 55 % (4), monochloroacetate gave poor results and acid-base side-reactions became predominant. Addition of catalytic amounts of $NiBr_2$,bipyridine enables the CH_2COOCH_3 anion to couple with a variety of ketones, leading to the expected β-hydroxy alcohols (Table II) in good yields In the same conditions, methyldichloroacetate couples with cyclohexanone to give the corresponding epoxide with a 80 % yield. Work is in progress to elucidate more deeply the mechanism of the reaction and examine its scope and limitation.

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