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ELECTROSYNTHESIS OF KETONES FROM ORGANIC HALIDES AND ANHYDRIDES

by Esther d'INCAN, Soline SIBILLE, Jacques PERICHON

Laboratoire d'Electrochimie, Catalyse et Synthèse Organique (U.M. n° 28)
C.N.R.S. 2, rue Henri-Dunant 94320 THIAIS (France)

Marie-Odile MOINGEON and Jacques CHAUSSARD
S.N.P.E. Le Bouchet
91710 VERT-LE-PETIT (France)

Abstract :

The electroreduction of benzylic and allylic halides in the presence of anhydrides affords ketones in moderate to good yields. The electrolysis is performed in an undivided cell, under constant current, using an aluminium or magnesium anode.

Electroreductive acylation of halogen compounds should be an extremely useful tool for the synthesis of ketones. Benzylic halides have been reported to couple with aliphatic acid chlorides (1) or with acetic anhydride (2) by controlled potential electrolysis in acetonitrile or DMF, using the standard two-compartments procedure. In previous communications, we reported that the use of sacrificial anodes of magnesium or duralumin in an undivided electrolytic cell enhanced the yield of coupling products between electrogenerated carbanions from organic halides and electrophiles such as carbon dioxide (3), ketones or aldehydes (4) in DMF. We wish now to report that allyl and benzylketones can be obtained by electroreduction of organic halides in DMF in the presence of anhydrides (5), by the same electrolytic procedure, according to :

$$RX + 2e \longrightarrow R^- + X^-$$

$$Mg \longrightarrow Mg^{2+} + 2e$$

$$R^- + R'COOCOR' \longrightarrow RCOR' + R'CO_2^-$$

In a typical experiment, 30 mmoles of the halide, an excess of the anhydride and 1 mmole of tetrabutylammonium iodide or tetrafluoroborate as supporting electrolyte are dissolved in 25 ml of DMF. When acetic anhydride is the substrate, the solvent may even consist of a 4:1 mixture of anhydride and DMF. The cell is immersed in a cooling bath to keep the temperature of the electrolyte in the range of 0°C to 10° C. A constant current intensity (0,4 A) is applied between a rod of magnesium or duralumin (1 cm diameter) as the anode and a cylindrical grid of stainless steel or nickel (20 cm^2) as the cathode, until 3 to 4 mole of electrons per mole of halide are passed. An acid hydrolysis (refluxing 1 h in H_2SO_4 20 %) destroys the excess of anhydride and releases the ketone from the enol ester which may be formed. After ether extraction, the ketone is purified by column chromatography or distillation and is identified by its spectral features (IR, ^{H}NMR).

Aliphatic anhydrides as well as benzoïc anhydride, allylic and benzylic halides gave satisfactory results (Table I). This electrolytic procedure which needs only a current generator is specially easy to work up. It proved to be suitable for the preparation, with good yields, of benzylketones of synthetic utility in the field of pharmaceuticals or fragancies.

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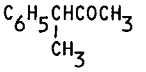
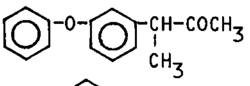
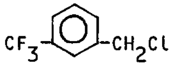
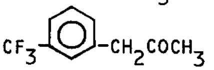
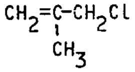
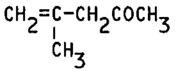
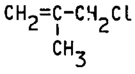
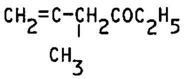
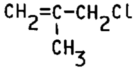
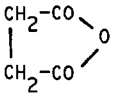
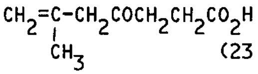
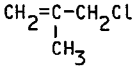
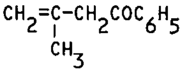
Table 1

Electroreductive coupling of organic halides with anhydrides in DMF

Halide (mmoles)	Anhydride (mmoles)	Anode	Product (yield[a])
$C_6H_5CH_2Cl$ (30)	$CH_3COOCOCH_3$ (300)	Mg	$C_6H_5CH_2COCH_3$ (80 %)
$C_6H_5CH_2Cl$ (30)	$CH_3COOCOCH_3$ (120)	Al	$C_6H_5CH_2COCH_3$ (50 %)
$C_6H_5CH_2Cl$ (30)	$C_2H_5COOCOC_2H_5$ (150)	Mg	$C_6H_5CH_2COCH_2CH_3$ (75 %)
$C_6H_5CH_2Cl$ (30)	$C_6H_5COOCOC_6H_5$ (40)	Mg	$C_6H_5CH_2COC_6H_5$ (25 %)
$C_6H_5CH_2Cl$ (87)	$tC_4H_9COOCOCH_3$[b] (400)	Mg	$C_6H_5CH_2COtC_4H_9$ (15 %) $C_6H_5CH_2COCH_3$ (30 %)
$C_6H_5CHCl_2$ (30)	$CH_3COOCOCH_3$ (300)	Mg	$C_6H_5CHClCOCH_3$ (17 %)
$C_6H_5CHClCH_3$ (71)	$CH_3COOCOCH_3$ (650)	Mg	 $C_6H_5CH(CH_3)COCH_3$ (70 %)
 (143)	$CH_3COOCOCH_3$ (784)	Mg	 (94 %)
 (52)	$CH_3COOCOCH_3$ (650)	Mg	 (58 %)
 $CH_2{=}C(CH_3){-}CH_2Cl$ (30)	$CH_3COOCOCH_3$ (300)	Mg	 $CH_2{=}C(CH_3){-}CH_2COCH_3$ (75 %)
 $CH_2{=}C(CH_3){-}CH_2Cl$ (30)	$C_2H_5COOCOC_2H_5$ (150)	Mg	 $CH_2{=}C(CH_3){-}CH_2COC_2H_5$ (75 %)
 $CH_2{=}C(CH_3){-}CH_2Cl$ (30)	 (40)	Mg	 $CH_2{=}C(CH_3){-}CH_2COCH_2CH_2CO_2H$ (23 %)
 $CH_2{=}C(CH_3){-}CH_2Cl$ (30)	$C_6H_5COOCOC_6H_5$	Mg	 $CH_2{=}C(CH_3){-}CH_2COC_6H_5$ (30 %)

[a] isolated yield based on initial halide

[b] prepared in situ from pivaloylchloride and sodium acetate.

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