Electrochemical Synthesis of Unsymmetric Ketones and Some Related Coupling Reactions

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Summary Halogen can be abstracted electrochemically from organic compounds by reaction with anodic cadmium metal; with a mixture of R^1COX and R^2X the product is the unsymmetric ketone R^1COR^2, and hydrocarbons (R^1_2) and ditin species $R^1_3SnSnR^1_3$ have also been prepared in this way.

A DISADVANTAGE in the preparation of ketones *via* Grignard reagents is that the product ketone may react further to yield a substituted methanol; the reaction of organocadmium compounds with an acid chloride has therefore been favoured, since in this case the reaction does not proceed beyond the ketone.[1] Organocadmium compounds are usually prepared by the action of Grignard reagent upon a cadmium halide, and the resultant mixture is frequently the effective reagent in reaction (1). The mechanism of this reaction has been the subject of some discussion.[1,2]

$$2R^1COX + R^2_2Cd \longrightarrow 2R^1COR + CdX_2 \qquad (1)$$

It was recently shown that cadmium undergoes a smooth electrochemical reaction with alkyl or aryl halides to form the organocadmium halides RCdX, which can be isolated as crystalline adducts with neutral donors.[3] We now report that anodic cadmium acts as a halogen abstraction reagent, and that ketones can be readily produced in this way by its reaction with a mixture of an acid halide and an alkyl or aryl halide. In a typical reaction, benzoyl bromide and ethyl bromide (each 16 mmol) were dissolved in 50 cm^3 of dried diglyme containing 10 mg of tetraethylammonium perchlorate. With a cadmium rod anode (5 cm long, 0·75 cm diam.) and a platinum wire cathode, a voltage of 50 V produced an initial current of 20 mA. After 14 h, 7·5 mmol of cadmium metal had dissolved and a white crystalline material, shown analytically to be $CdBr_2$, deposited on the electrode and in the reaction vessel. After a further 10 h, 9·6 mmol of the metal had dissolved. The weight of $CdBr_2$ recovered (*ca.* 0·5 g) is substantially less than that calculated from the loss of the metal due to its solubility in the reaction solvent. Excess of benzoyl bromide was removed with water, and extraction with diethyl ether, washing with water, followed by distillation gave the product, PhCOEt (6·7 mmol; 64% based on the cadmium lost), which was identical (g.l.c., n.m.r.) with an authentic sample.

The reaction was performed under different conditions, including one at 0 °C, and the ketone was identified in all cases. No attempt has been made so far to optimise either the reaction conditions or work-up procedure; the yield depends *inter alia* on the time of electrolysis and on the current (hence on the composition of the reaction solution). Other unsymmetric ketones prepared by this procedure include MeCOEt (from EtBr and MeCOBr) and PhCOMe (from PhCOCl and MeI, and from MeCOCl and PhCl). The nature of the halogen in the organic halides does not appear to be critical.

The mechanism of the reaction is not clear yet, but two possibilities are worth noting. Since cadmium undergoes oxidative insertion into organohalides,[3] the RCdX species formed may undergo a pseudo-Grignard reaction with the acid chloride. Alternatively, the first step in the reaction may be the formation of an acyl radical as shown in the Scheme.

$$\begin{array}{lll} \mathrm{PhCOX} + \mathrm{Cd_{anode}} & \longrightarrow & \mathrm{Ph\dot{C}{=}O} + \mathrm{\dot{C}dX} \\ \mathrm{Ph\dot{C}{=}O} + \mathrm{RX} & \longrightarrow & \mathrm{PhCOR} + \mathrm{X\cdot} \\ \mathrm{\dot{C}dX} + \mathrm{X\cdot} & \longrightarrow & \mathrm{CdX_2} \end{array}$$

SCHEME. X = halogen

The electrochemical reaction of cadmium with benzoyl chloride (in MeCN) leads to the formation of $CdCl_2$ and benzil, but pure PhCOCl yields a mixture of high melting (presumably polymeric) substances of the type to be expected from the reaction of $\mathrm{Ph\mathring{C}{=}O}$ radicals with PhCOCl.

The reaction is stoicheiometrically analogous to the Wurtz–Fittig reaction (2) and we have carried out a

$$\mathrm{R^1X} + \mathrm{R^2COX} + \mathrm{Cd} \longrightarrow \mathrm{CdX_2} + \mathrm{R^1COR^2} \qquad (2)$$

number of other coupling reactions using anodic cadmium, based on this analogy. Thus the coupling of Pr^nBr and of Bu^nBr (in benzene–methanol) by electrochemical halide abstraction gives n-C_6H_{14} and n-C_8H_{18}, respectively (identified by g.l.c.). Similarly, reactions with Me_3SnCl and Ph_3SnBr (in various solvents) yield Me_3Sn–$SnMe_3$ and Ph_3Sn–$SnPh_3$ (identified by analysis, m.p, and i.r.), respectively.

This electrochemical technique appears to have significant advantage over other methods in that it eliminates the use of the hazardous dialkylcadmium compounds. It also obviates the necessity for the Grignard reagent preparation which normally precedes reaction (1). The availability of temperatures at or below ambient may also be an advantage in certain coupling reactions.

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[1] G. E. Coates and K. Wade, 'Organometallic Compounds,' Methuen, London, 1965, Vol. 1, pp. 144—145, and refs. cited therein.

[2] J. Kollonitsch, *Nature*, 1960, **188**, 140.

[3] J. J. Habeeb, A. Osman, and D. G. Tuck, *J.C.S. Chem. Comm.*, in the press.