Tetrahedron Letters No. 11, pp 875 - 878, 1975. Pergamon Press. Printed in Great Britain.

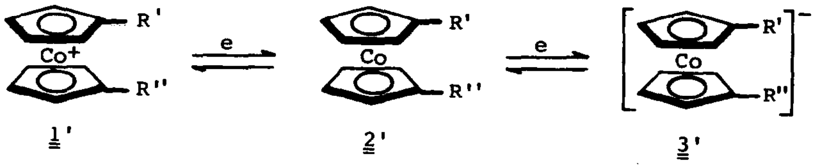
SYNTHESES USING ELECTROCHEMICALLY GENERATED COBALTOCENE OR COBALTOCENE ANION

N. El Murr and E. Laviron

Laboratoire de Polarographie Organique, Faculté des Sciences, 21000 DIJON (France)

(Received in UK 21 January 1975; accepted for publication 5 February 1975)

As we have shown previously[1], substituted or unsubstituted cobalticinium salts 1' are reduced in two reversible stages on a mercury electrode. The first, which had already been described in the case of the unsubstituted compound, corresponds to the reduction to cobaltocene[2,3]; the second, which had never been reported, leads[1] to the very interesting cobaltocene anion 3', the existence of which was later confirmed by Geiger[4].



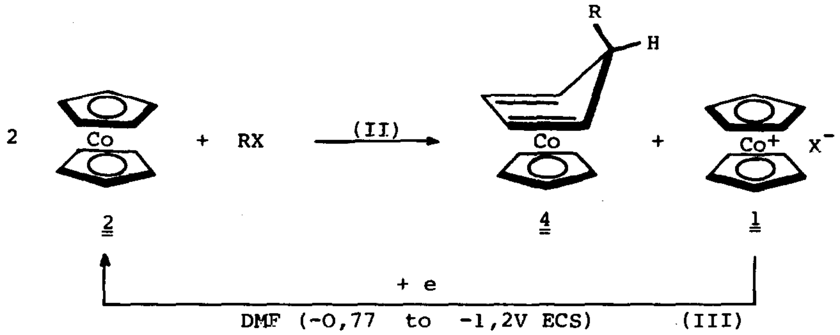
(I)

For the unsubstituted compound (1'; R = R' = H) the half-wave potentials are respectively - 1.20 and - 1.86 V (E.C.S.) in 30 % ethanol-water solutions and - 0.77 and - 1.73 V (E.C.S.) in 0,1 M $(C_4H_9)_4NClO_4$ dimethylformamide.

We wish to report some examples showing the advantages of using electrochemically generated cobaltocene or cobaltocene anions for syntheses in the cobaltocene series.

Preparations starting from cobaltocene.

It has been shown[5-8] that substituted cyclopentadienyl cobalt cyclopentadienes can be prepared by the reaction of an aroyl or alkyl halide RX with cobaltocene. From two moles of cobaltocene, one mole of the product 4 and one mole of the cobalticinium salt are formed.



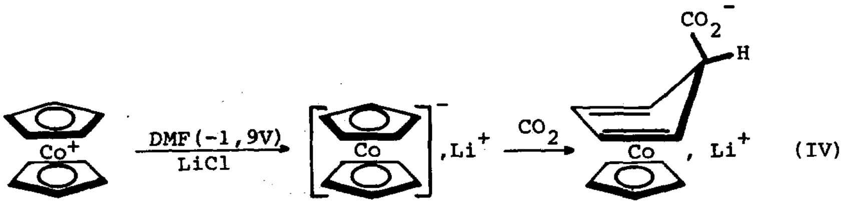
This reaction has two disadvantages : (a) Cobaltocene, being very unstable owing to its oxidability, is difficult to prepare and to manipulate ; it is commercially available but expensive. (b) The yield of the reaction based on cobaltocene is necessarily limited to 50 %.

We have carried out reaction II using cobaltocene generated by electrolysis of the cobalticinium salt 1 (reaction III). 1 is easy to prepare and very stable ; the yield is practically 100 %, since the cobalticinium salt formed is reelectrolyzed until completion of the reaction. Another advantage is the greater velocity of the electrochemical process when the chemical reaction is slow (see table). This feature can probably be explained by the fact that the concentration of cobaltocene decreases more slowly because of the electrochemical regeneration.

Compound		4 a	4 b	4 c	4 d
Substituent R		$CH_2C_6H_5$	$CHClC_6H_5$	CCl_3	CH_2Br
Yields	Electrochemical	95 (20°C)	96 (20°C)	98 (20°C)	90 (20°C)
	chemical	47,5[5] (20°C)	44[6] (40°C)	45[7] (20°C)	45[8] (40°C)
Time	electrochemical	2 h.	7 h.	1 h.	5 h.
	chemical	20 mn.	50 h.	1 h.	5 h.

Preparations starting from the anion.

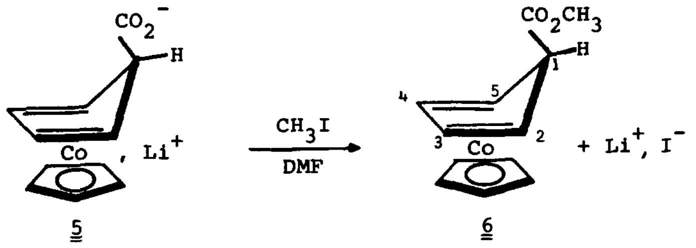
Even more interesting synthetic possibilities are offered by cobaltocene anion 3', as shown for example by the following reaction :



(IV)

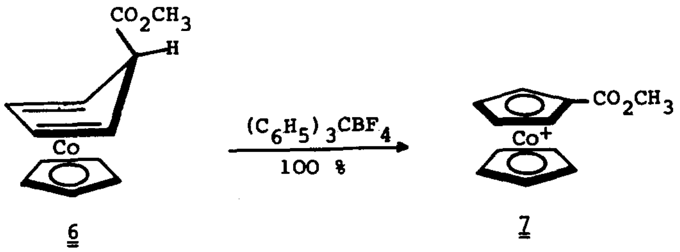
1 3 5

Cyclopentadienylcobalt carboxycyclopentadiene 5 is rather unstable and was converted *in situ* to the methyl ester 6 by the action of methyl iodide[9]. 6 was identified by centesimal analysis and by its spectral properties. [n.m.r, $CDCl_3$, δ p.p.m. : 2.80 H_2,H_5 ; 3.43 CH_3,H_1 ; 4.81 C_5,H_5 ; 5.31 H_3, H_4] [i.r. $\nu_{max.}^{CCl_4}$ 1736 cm^{-1} (CO)].



(V)

Electrochemical oxidation of the ester 6 (E = + 0.05V, 40% ethanol-water, pH 3) gave the methoxycarbonylcobalticinium salt 7 in poor yields (10 %) ; the reaction of 6 with



(VI)

triphenylmethane tetrafluoroborate, however, afforded 7, which we were able to isolate as the hexafluorophosphate or tetraphenylborate in 100 % yield. 7 was characterized by comparison with a sample prepared according to Sheats and Rausch[10], who obtained 7 starting from a mixture of methyl and dimethylcobalticinium salts. Their four step preparation requires at least 50 hours and the overall yield is 27 %. Our method allows 7 to be prepared in 10 hours in 96 % yield (based on the cobalticinium salt).

As this first example demonstrates, reactions involving the anion 3' open a new interesting route to the synthesis of substituted cobalticinium salts, since the direct electrophilic substitution on the cobalticinium nucleus is not possible. In particular we are presently examining its application to the synthesis of homo and hetero disubstituted cobalticinium salts, the preparation of which is difficult[11]. Other reactions of cobaltocene anion and the preparation of other metallocene anions will be investigated later.

REFERENCES

1. N. EL MURR, R. DABARD and E. LAVIRON, *J. Organometal. Chem.*, **47**, C 13 (1973)
2. J.A. PAGE and G. WILKINSON, *J. Amer. Chem. Soc.*, **74**, 6149 (1952)
3. A.A. VLCEK, *Collect. Czech. Chem. Commun.*, **30**, 952 (1963)
4. W.E. GEIGER, *J. Amer. Chem. Soc.*, **96**, 2632 (1974)
5. G.E. HERBERICH and E. BAUER, *J. Organometal. Chem.*, **16**, 301 (1969)
6. G.E. HERBERICH, G. GREIS and H.F. HEIL, *J. Organometal. Chem.*, **22**, 723 (1970)
7. M.L.H. GREEN, L. PRATT and G. WILKINSON, *J. Chem. Soc.*, 3753 (1959)
8. G.E. HERBERICH, E. BAUER and J. SCHWARZER, *J. Organometal. Chem.*, **17**, 445 (1969)
9. S. YONEDA, Z. YOSHIDA and K. FUKUI, *Kogyo Kagaku Zasshi*, **69**, 641 (1966)
10. J.E. SHEATS and M.D. RAUSCH, *J. Org. Chem.*, **35**, 3245 (1970)
11. N. EL MURR and R. DABARD, *J. Organometal. Chem.*, **39**, C 82 (1972)