

Synthesis of Croconic and Hydrocroconic Acids from Di-t-butoxyethyne. Electrochemical Demetallation of a Cyclopentadienyl Organocobalt Complex

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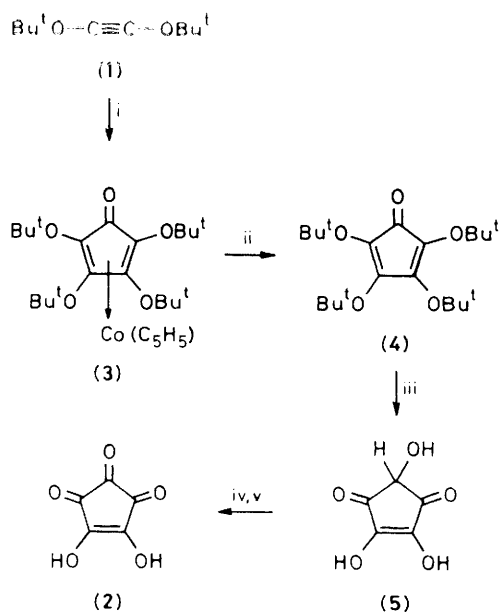
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The electrochemical demetallation of (η -tetra-t-butoxycyclopentadienone)(η -cyclopentadienyl)cobalt, readily available from di-t-butoxyethyne leads to tetra-t-butoxycyclopentadienone which can be converted into hydrocroconic acid by trifluoroacetic acid hydrolysis and then croconic acid by oxidation in basic medium.

As we have already reported,¹ irradiation of a mixture of di-t-butoxyethyne (**1**) and (η -cyclopentadienyl)dicarbonylcobalt at low temperature in pentane solution affords (η -tetra-t-butoxy-

cyclopentadienone)(η -cyclopentadienyl)cobalt (**3**), a suitable precursor for croconic acid (**2**), in 50–58% yield. However, demetallation of this organometallic intermediate by standard



Scheme 1. Reagents: i, $(C_5H_5)Co(CO)_2$, pentane, $-78^\circ C$; ii, electrochemical oxidation at $+0.770$ mV, MeCN- Bu_4NClO_4 ; iii, CF_3CO_2H , CH_2Cl_2 , room temp.; iv, 0.1 M KOH in H_2O , room temp.; v, 0.1 M H_2SO_4 in H_2O , room temp. All new products gave satisfactory analyses or exact mass spectral measurements.

procedures² failed and the highly interesting tetra-*t*-butoxycyclopentadienone (4) could not be isolated. Dimethyl croconate can be prepared from (3) in 47% overall yield by a conventional route but (4) cannot be obtained this way either.

From our previous studies on demetallation by standard methods, it was clear that the electron-rich cyclopentadienone derivative (4) was very sensitive to both the acid and the severe oxidizing conditions of the reaction medium, in which it is completely destroyed.† Therefore, to detach the free ligand (4) from complex (3), very 'redoxselective' conditions should be used, e.g. an electrochemical process. Although electrochemical processes are well recognized as very selective oxidation/reduction procedures,³ they have found little application in the demetallation of organometallic compounds, the reduction of metalloporphyrins and related systems being the only examples reported so far.^{4‡}

A preliminary cyclic voltammetric study of an acetonitrile solution of (3) was carried out first (Figure 1). The voltammogram showed three successive oxidation peaks, but only a very small reduction peak was apparent, indicating the almost complete irreversibility of the electrode process.

For the electrolysis of (3), a working oxidation potential of $+0.770$ V was selected in order to preclude side reactions due to the overlapping of peaks I and II. A solution of (3) in acetonitrile, with tetrabutylammonium perchlorate as supporting electrolyte, was submitted to exhaustive electrolysis. After

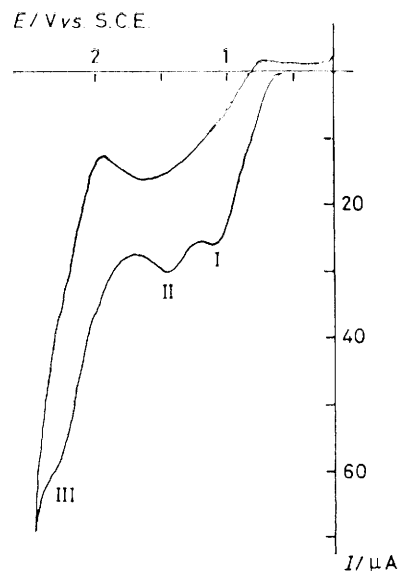


Figure 1. Cyclic voltammetry of (3) in acetonitrile-0.05 M tetrabutylammonium perchlorate (Pt electrode; scan rate 0.1 V s^{-1}). S.C.E. = saturated calomel electrode.

the usual working up, tetra-*t*-butoxycyclopentadienone (4) was isolated in 79% yield as a red solid, m.p. $44^\circ C$.§

In order to complete the preparation of croconic acid (2), it was necessary just to transform (4) into hydrocroconic acid (5), by acidolysis with trifluoroacetic acid (89% yield), the oxidation of (5) to (2) in basic medium being a well documented process.⁵ The overall sequence, which represents the first synthesis of croconic acid (2) by a non degradative method,⁶ is depicted in Scheme 1.

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† *N*-*t*-butylacetamide was the only organic product isolated from the demetallation of (3) with $CuCl_2 \cdot 2H_2O-Et_3N-MeCN$.

‡ A referee informed us that an electrocatalytic system using cobalt for the dimerisation of butadiene was reported in 1971: H. Lehmkuhl, W. Leuchte, and E. Janssen, *J. Organomet. Chem.*, 1971, **30**, 407.

§ Selected spectroscopic and mass spectral data for (4) are as follows: i.r. (CCl_4): ν 1730s, 1665s, and 1635w cm^{-1} ; 1H n.m.r.: (CCl_4) δ 1.24 (s, 18H) and 1.39 (s, 18H); ^{13}C 1H } n.m.r. ($CDCl_3$) δ 196.9, 153.5, 123.7, 84.8, 81.5, 29.2, and 28.9 p.p.m.; u.v.-vis. (pentane): $\lambda_{max}(\epsilon)$ 234(5000) and 460 (193) nm; m.s.: m/e (70 eV) 368(<0.1%), 312(0.5%), 256(3%), 200(25%), 185(3%), 144(100%), and 115(2%).