Electrochemical Pinacolisations Modified by Chromium(III)

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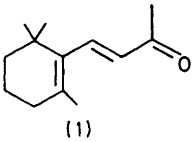
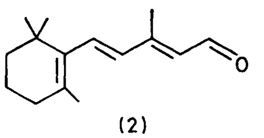
Summary In the presence of Cr^{III} a variety of carbonyl compounds, including polyene compounds such as β-ionone and retinal, are electro-reduced smoothly to pinacols under chemically mild conditions and at relatively low potentials; a mechanism involving reduction of a complex between Cr^{III} and the carbonyl compound is proposed.

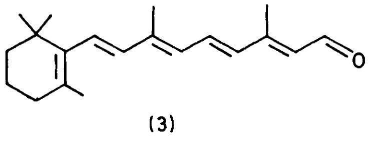
Polyene carbonyl compounds undergo reductive dimerisation to pinacols and olefins chemically[1] and electrochemically.[2] The electrochemical method is both convenient and efficient for the coupling, in the presence of effective proton donors, of β-ionone (**1**), but less efficient for retinal (**3**); in the latter case the pinacol is isolated in low yield (*ca.* 10%). It was recently reported[3] that benzophenone in the presence of chromium(III) chloride hexahydrate was selectively reduced to benzpinacol. Unless a strong proton donor is present, in aprotic media benzophenone is reduced to benzhydrol, hence the presence of chromium(III) apparently favours pinacolisation. This is of considerable synthetic interest and prompts us to report on experiments illustrating the role of chromium(III) in this reaction and its application to the synthesis of polyene pinacols.



(1)



(2)



(3)

Table 1. Peak potentials[a] in the absence ($-E_p$) and presence ($-E_p'$) of $CrCl_3\cdot 6H_2O$.

Carbonyl compound[b]	$-E_p$ (1)[c]	$-E_p$ (2)[d]	$-E_p'$
Ph_2CO	1·24	1·82	0·93
o-MeC_6H_4COPh	1·35	2·06	1·02
p-MeC_6H_4COPh	1·30	1·88	0·98
o-$MeO_2CC_6H_4COPh$	1·20	1·65	0·97
PhCHO	1·34	—	1·02
(**1**)	1·40	1·65	1·05
(**2**)	1·15	1·59	0·90
(**3**)	0·95	1·48	0·70

[a] V *vs.* Ag/AgI. [b] *ca.* 1 mmol dm^{-3} in DMF–Bu_4NI (0·1 mol dm^{-3}), Hg coated Pt bead, 0·4 V s^{-1}. [c] Reversible or quasi-reversible. [d] Irreversible.

In cyclic voltammetry (see Table 1) benzophenone gives reduction peaks at −1·24 (reversible) and −1·82 V (irreversible). Stepwise addition of an equivalent amount of $CrCl_3\cdot 6H_2O$ results in the appearance of two additional peaks; one at −0·58 V due to the quasi-reversible reduction of Cr^{III} to Cr^{II} and the other, which is irreversible, at −0·93 V. The reduction peak at −1·24 V becomes increasingly irreversible as Cr^{III} is added and eventually it disappears. The Cr^{II} reduction process which in the absence of ketone occurs at −1·12 V was not observed.

During the addition of ketone to $CrCl_3\cdot 6H_2O$ both potential and current of the Cr^{III} peak remain unchanged, while a peak appears at −0·93 V with concomitant diminution of the Cr^{II} reduction peak.

Controlled potential coulometry at −0·93 V indicated a 1 F mol^{-1} reaction. Prior electrochemical removal of Cr^{III} from an equimolar mixture of benzophenone and $CrCl_3\cdot 6H_2O$ resulted in the disappearance of the peak at −0·93 V, hence Cr^{III} is essential for the process to occur. That chemical reduction of the ketone by Cr^{II} occurs was disproved by controlled potential electrolysis at −0·60 V of an equimolar mixture of benzophenone and $CrCl_3\cdot 6H_2O$

after which only starting material was recovered. Electrolysis, at constant potential (—1·00 V), of a similar mixture gave a high yield (*ca.* 70%) of crude benzpinacol. Similar results were obtained with anhydrous chromium trichloride. Although reduction is not directly by Cr^{II} it was apparent from the preparative electrolyses that a minimum concentration of Cr^{II} is required. Electrolysis at the correct potential for pinacolisation did not proceed until some of the Cr^{III} had been pre-reduced.

The stereochemical course of Cr^{III}-modified pinacolisation of benzaldehyde resembles that for reduction in acidic solution (Table 2) and is very different from that for reduction in dry DMF (DMF = *NN*-dimethylformamide).

TABLE 2. Preparative scale electrolyses (at potential, $-E$).

Carbonyl compound	$-E^a$/V	Pinacol yield (%) Crude[b]	Pinacol yield (%) Isolated[c]	Alcohol yield (%) Crude
Ph_2CO	1·00[d]	70	55	10
o-MeC_6H_4COPh	0·95[e]	45	26	27
p-MeC_6H_4COPh	0·95[e]	63	25	16
o-$MeO_2CC_6H_4COPh$	0·95[d]	—	—	48
PhCHO	0·90[d]	51 (1·3)[f]	—	—
,,	1·30[g]	60 (14)[f]	—	—
,,	1·30[h]	59 (3·1)[f]	—	—
(**1**)	0·95[e]	75	27 (0·35)[f]	—
(**2**)	0·80[d]	60	25	—
(**3**)	0·80[d]	25	3 (β-carotene)[i]	—

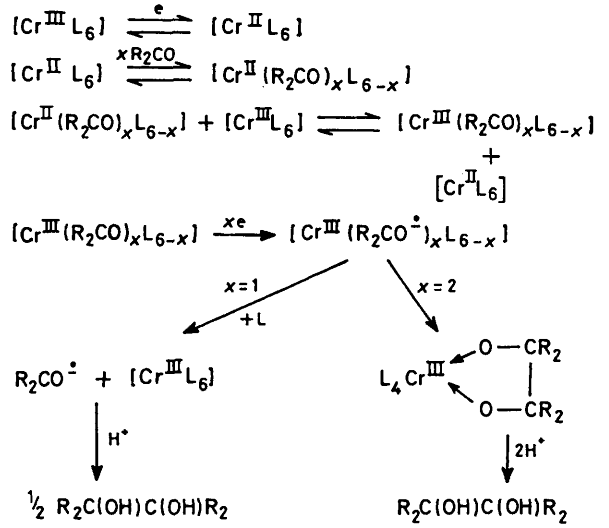
[a] *vs.* Ag/AgI. [b] Based on starting material, measured spectroscopically. [c] Yield of purified product based on starting material. [d] DMF, $NaClO_4$ (0·15 mol dm^{-3}), Hg cathode, divided cell, $CrCl_3 \cdot 6H_2O$ (*ca.* 10^{-2} mol dm^{-3}), carbonyl compound (*ca.* 10^{-2} mol dm^{-3}). [e] As footnote d, undivided cell. [f] Racemic/*meso* ratio of diastereoisomeric pinacols. [g] DMF (dry), $NaClO_4$ (0·15 mol dm^{-3}), Hg cathode, divided cell, carbonyl compound (*ca.* 10^{-2} mol dm^{-3}). [h] DMF, $NaClO_4$ (0·15 mol dm^{-3}), Hg cathode, divided cell, carbonyl compound (*ca.* 10^{-2} mol dm^{-3}), glacial acetic acid (*ca.* 10^{-2} mol dm^{-3}), water (*ca.* 5×10^{-2} mol dm^{-3}). [i] Crude electrolysis product treated with PI_3 in CS_2–pyridine to give β-carotene, purified product, based on retinal.[1b]

The effective shift in electrolysis potential due to addition of Cr^{III} is *ca.* 0·2—0·3 V (Table 1). In practice, this means that for carbonyl compounds which normally reduce at 0·2—0·3 V cathodic of the Cr^{II} peak (*e.g.* acetophenone) no advantage is gained by addition of Cr^{III}; in such cases the current is used to reduce Cr^{II} to Cr^0. The results for substituted benzophenones reveal another limitation. Although the required cyclic voltammetric behaviour is apparent (Table 1), preparative scale electrolysis leads to significant amounts of alcohol for the *ortho*-substituted compounds (Table 2) with a corresponding decrease in pinacol formation.

Cyclic voltammograms for β-ionone (**1**), β-ionylideneacetaldehyde (**2**) and retinal (**3**) are qualitatively similar to that for benzophenone in that stepwise addition of $CrCl_3 \cdot 6H_2O$ also causes the first reduction peak to become irreversible with the appearance of a new peak, albeit small, in the region —0·70 to —1·05 V (Table 1).

Preparative electrolyses (Table 2) at potentials associated with the additional peak gave reasonable isolated yields of the corresponding pinacols and efficient electrochemical conversion is indicated. There is often an advantage in using an undivided cell which provides for regeneration at the anode (platinum) of Cr^{III}.

We propose that in these systems a Lewis acid–base interaction is occurring between the carbonyl compound and Cr^{III}, possibly to form a complex in which the carbonyl group is polarised and therefore easier to reduce. Such complex formation, with the associated polarisation of the carbonyl group, also accounts for the similarities (including stereochemical) with reduction in strongly acidic solution. For benzophenone reduction the effect of *ortho*-substitution can also be explained in terms of hindrance to complex formation. In order for such a complex to be formed the carbonyl compounds must displace the strongly co-ordinating ligands, DMF, and chloride ion. Chromium(II)-catalysed inner-sphere ligand exchange reactions are believed to be operative in DMF solution[4] as in aqueous media[5] and these are probably involved in the formation of a complex between the carbonyl compound and Cr^{III} in the vicinity of the electrode, *i.e.* it is the complex which is, for benzophenone, reduced at —0·93 V. This explains the requirement for some formation of Cr^{II} for smooth pinacolisation. The likely sequence of events is summarised in the Scheme; the ligand L may be DMF or chloride, or both.



SCHEME

The stereochemical result argues in favour of the case with $x \geqslant 2$.

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