Electro-organic Reactions. Part 25.† The Role of Chromium(III) in the Modification of Cathodic Pinacolisation

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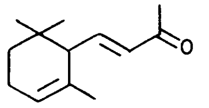
The presence of chromium(III) chloride, both hydrated and anhydrous, profoundly alters the course of cathodic reduction in dimethylformamide solutions of benzophenone, benzaldehyde, β-ionone, β-ionylidene acetaldehyde, and retinal. Pinacolisation is enhanced at the expense of formation of the corresponding alcohol. Furthermore the relevant reduction potential is lowered. The mechanism of the reaction has been investigated using voltammetric and coulometric experiments combined with a detailed analysis of preparative-scale reductions under a variety of conditions. The stereochemical course of the reactions has also been considered. In total the results provide compelling evidence in favour of the key reducible intermediate being a carbonyl compound–Cr^{III} complex which is formed *via* the corresponding Cr^{II} species with homogeneous, inner sphere, re-oxidation playing a crucial role. This is contrary to earlier suggestions invoking the participation of electrogenerated Cr^{II} as the reductant.

Cathodic pinacolisation of carbonyl compounds has been much studied and is especially useful for aromatic aldehydes and ketones.[1] Aliphatic ketones and aldehydes are reduced at inconveniently negative potentials but at low pH the protonated carbonyl function is smoothly reduced at accessible potentials.[2] Conjugation of the carbonyl group, as in αβ-unsaturated aldehydes and ketones, or in polyenyl carbonyl compounds, allows other modes of coupling of the intermediate anion-radicals. For αβ-unsaturated carbonyl compounds cathodic reduction gives predominantly[3] coupling at the β-position to give 1,6-dicarbonyl compounds unless the β-position, or other possible centres for coupling, are hindered. Because of such hindrance by methyl groups it proved possible[4] to pinacolise the α- and β-ionones (**1**) and (**2**) and retinal (**3**). The best yields of pinacol were obtained in acidic conditions [acetonitrile–$Bu_4NOAc{\cdot}HOAc$ (0.1M)] and a major side reaction is cathodic hydrogenation of carbon–carbon and carbon–oxygen double bonds.

Martinet and his co-workers[5] were the first to report that pinacolisation could be expedited by the presence of Cr^{III} salts in the electrolyte. Their preparative-scale cathodic conversion of benzophenone into benzpinacol, in the presence of $CrCl_3{\cdot}6H_2O$, was particularly significant because electrolysis in neutral solution normally gives diphenylmethanol only; the pinacol is only formed (to 60%) under relatively acidic conditions[6] [dimethylformamide–HOAc (4M)] by reduction of protonated benzophenone. Martinet's observation was confirmed and put to synthetic use[7] in the realisation of improved yields for the pinacolisation of β-ionone (**2**), retinal (**3**), and β-ionylideneacetaldehyde (**4**); in the same preliminary publication[7] the mechanism outlined in the Scheme was proposed. The key feature of this hypothesis is the formation of a complex between Cr^{III} and the carbonyl compound combined with inner-sphere electron transfer between Cr^{II} and Cr^{III} species. An alternative view has been expressed by Martinet and his co-workers.[8] They hold that the key reduction step involves an electrogenerated Cr^{II} species which is endowed, through adsorption, with a reactivity that it fails to display in bulk solution. We reject this view and now report in full on experiments which demonstrate that the original hypothesis[7] is essentially correct.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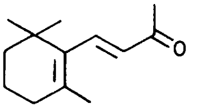
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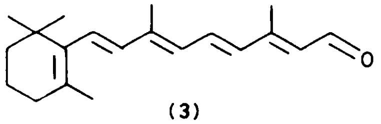
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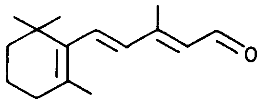
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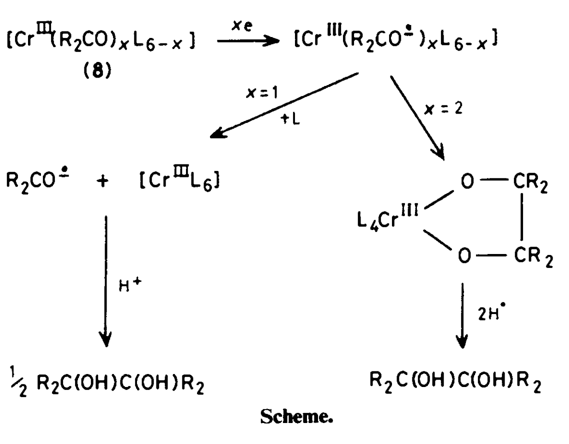

Scheme.

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† Part 24, Q. N. Porter, J. H. P. Utley, P. D. Machion, V. L. Pardini, P. R. Schumacher, and H. Viertler, *J. Chem Soc., Perkin Trans. 1*, 1984, 973.

Table 1. Cyclic voltammetric peak potentials[a] and the effect of added Cr^{III}

Compound	$-E_p^c(1)$	$-E_p^a(1)^b$	$-E_p^c(2)^c$	$-E_p^c(3)$/ additive[d]	ΔE_p^e
$CrCl_3{\cdot}6H_2O$	0.58	0.10	1.12		
Ph_2CO	1.24	1.18[f]	1.82	0.93	0.31
				0.93[g]	0.31
$CrCl_3$	0.66	0.18	1.16		
Fluorenone	0.78	0.70	1.72	0.60—0.74[c]	0.18—0.04[h]
$PhCOCH_3$	1.52	1.45		1.52	0[i]
$2\text{-}MeC_6H_4COPh$	1.35	1.27	2.06	1.02	0.33
$4\text{-}MeC_6H_4COPh$	1.30	1.22	1.88	0.98	0.32
$2\text{-}MeO_2CC_6H_4COPh$	1.20	1.11	1.65	0.97	0.23
β-Ionone (**2**)	1.40	1.29	1.65	1.05	0.35
β-Ionylideneacetaldehyde (**4**)	1.15	0.98	1.59	0.90	0.25
Retinal (**3**)	0.95	0.70	1.48	0.70	0.25

[a] V *versus* Ag–AgI; *ca.* 1 mmol dm^{-3} in DMF–Bu_4NI (0.1 mol dm^{-3}); Hg-coated Pt bead; 0.4 V s^{-1}. [b] Quasi-reversible unless otherwise stated. [c] Irreversible. [d] $CrCl_3{\cdot}6H_2O$ unless otherwise stated. [e] $E_p^c(1) - E_p^c(3)$. [f] Reversible. [g] $CrCl_3$. [h] $-E_p^c(3)$ was 0.60 V when fluorenone was in great excess and 0.74 V when $CrCl_3{\cdot}6H_2O$ was in excess; in the latter case the Cr^{II}–Cr^0 peak (*ca.* −1.12 V) was greatly diminished. [i] The acetophenone reduction peak [$E_p^c(1)$] was unaffected; the peak at −1.45 V was diminished.

Results and Discussion

Cyclic Voltammetric Experiments.—The qualitative effect of Cr^{III} upon the cyclic voltammetry of solutions of benzophenone has been well described by Martinet and his co-workers[8] and by us.[7] Essentially, for cyclic voltammetry in dimethylformamide (DMF) solution, addition of $CrCl_3{\cdot}6H_2O$ causes the reversible reduction peak associated with radical-anion formation to become irreversible and a new irreversible reduction peak is observed which is anodic of the first reduction peak of benzophenone. The 'new peak' is not present in the voltammograms of either $CrCl_3{\cdot}6H_2O$ or benzophenone. This behaviour is found by us to be followed for several carbonyl compounds and is typified in Figure 1 which describes the effect of added Cr^{III} upon the cyclic voltammogram of β-ionone (**2**).

The range of compounds which shows this behaviour is listed in Table 1 which also contains the relevant voltammetric data. It is noteworthy that the new peak [listed as $E_p^c(3)$] appears consistently at 0.25—0.35 V anodic of the first reduction potential [$E_p^c(2)$] of the carbonyl compound. Furthermore the water of crystallisation of chromium chloride hexahydrate is not involved; anhydrous $CrCl_3$ and $CrCl_3{\cdot}6H_2O$ affected the cyclic voltammogram of benzophenone identically.

The formation of a 'new peak' was not observed for acetophenone in the presence of $CrCl_3{\cdot}6H_2O$. In this case the expected reduction potential (−1.52 + 0.35 = −1.17 V) would be similar to the Cr^{II}—Cr^0 potential (−1.12 V). This defines an important limitation in the exploitation of the preparative consequences of the effect of Cr^{III} on carbonyl reductions (see below).

The results of several cyclic voltammetric experiments need separate discussion and are not included in Table 1. The first such experiment involved an examination of the cyclic voltammogram of chromium chloride hexahydrate in dimethylformamide as increasing amounts of benzophenone were added (Figure 2). The important feature of this result is that no increase in current is seen for the Cr^{III}—Cr^{II} couple as the ketone is added. The observation of a 'catalytic current' would have indicated that benzophenone was being reduced at the electrode surface by Cr^{II}, thereby regenerating Cr^{III}. Such behaviour would also be expected to be reflected[9] in a non-linear plot of $i_p/v^{\frac{1}{2}}$ *versus* $v^{\frac{1}{2}}$. In this case, however, a satisfactory linear plot was obtained.

Other voltammetric experiments led to the conclusion that the effect of the chromium(III) chlorides was markedly different from that of other chromium(III) compounds. In this context the voltammetric behaviour of benzophenone in the presence of chromium(III) acetonylacetonate was examined. Chromium(III) acetylacetonate [2mM in DMF–Bu_4NI (0.1M), Hg cathode, 0.3 V s^{-1}] gave irreversible reduction peaks at −1.35 V and −1.70 V. Upon addition of an equivalent amount of benzophenone these were replaced by a single, larger, irreversible peak at

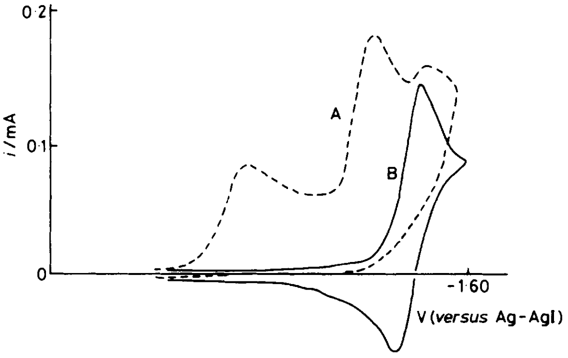


Figure 1. Effect of $CrCl_3{\cdot}6H_2O$ on the cyclic voltammetric reduction of β-ionone (2). [DMF–Bu_4NBF_4(0.1M), Hg bead, 0.3 v s^{-1}, β-ionone *ca.* 2×10^{-3}]: A, β-ionone + $CrCl_3{\cdot}6H_2O$ (1 equiv.); B, β-ionone

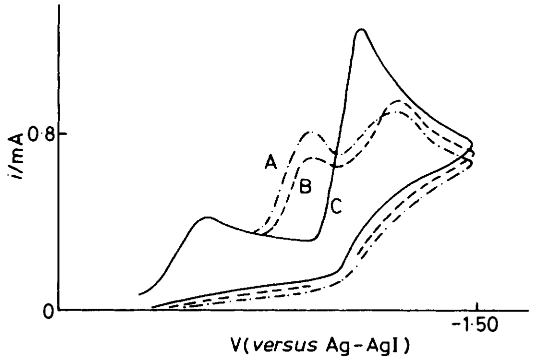


Figure 2. Effect of benzophenone on the cyclic voltammetric reduction of $CrCl_3{\cdot}6H_2O$-[DMF–Bu_4NClO_4(0.1M), Hg bead, 0.2 V s^{-1}, $CrCl_3{\cdot}6H_2O$ *ca.* 1.2×10^{-2}M]; A, $CrCl_3{\cdot}6H_2O$ + Ph_2CO (1 equiv.); B, $CrCl_3{\cdot}6H_2O$ + Ph_2CO (0.5 equiv.); C, $CrCl_3{\cdot}6H_2O$

Table 2. Preparative-scale controlled-potential electrolysis[a] and the effect of added Cr^{III}

Compound–additive	Potential (–V *versus* Ag–AgI)	Product (s) (%) Pinacol	Product (s) (%) Alcohol
Ph_2CO	1.30		80
$Ph_2CO–H_2O$	1.20		75
$Ph_2CO–Cr^{III}$[b]	1.00	70	10
$2\text{-}MeC_6H_4COPh–Cr^{III}$	0.95	46	28
$4\text{-}MeC_6H_4COPh–Cr^{III}$	0.95	56	12
$2\text{-}MeO_2C{\cdot}C_6H_4COPh–Cr^{III}$	0.95		51[c]
β-Ionone (**2**)–Cr^{III}	1.20	75[d]	
β-Ionylideneacetaldehyde (**4**)–Cr^{III}	0.90	60	
Retinal (**3**)–Cr^{III}	0.80	25[e]	

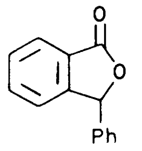
[a] Divided cell, Hg pool cathode, DMF–$NaClO_4$ (0.2 mol dm^{-3}), 3 F mol^{-1}. [b] Equivalent amount of $CrCl_3{\cdot}6H_2O$. [c] Isolation by chromatography caused lactonisation. [d] By u.v. spectroscopy; chromatographic separation gave 27% isolated yield, (±):*meso* = 1:3. [e] After 1 F mol^{-1}; exhaustive electrolysis gave major products characterised by u.v. spectroscopy as 11,12-dihydroretinal ($\lambda^{EtOH}_{max.}$ 245 nm) and 13,14-dihydroretinal ($\lambda^{EtOH}_{max.}$ 292 nm).

–1.25 V. This would suggest that the radical-anion of benzophenone, normally formed at –1.24 V, reacts rapidly with the chromium complex. Similar results have been reported[10] for the reduction of 2,3:6,7-dibenzotropone in the presence of nickel(II) and iron(II) acetylacetonates. Although chromium(III) acetylacetonate does therefore affect the voltammetric behaviour of benzophenone it does so in a significantly different manner to the chromium(III) chlorides.

Chloride ion also appears to participate importantly in the sequence of reactions which give rise to the voltammetric behaviour described in Figure 1 and Table 1. Chromium(III) perchlorate hexahydrate [5mM in DMF–Bu_4NClO_4 (0.1M), Hg cathode, 0.4 V s^{-1}] gave, on cyclic voltammetry, three reduction peaks at –0.72, –1.05, and –1.37 V. The first and second peaks corresponded, in this system, to reduction of Cr^{III} and Cr^{II}, respectively. The origin of the third peak is unknown. One small, broad, anodic peak was observed at –0.13 V if the scan was reversed at –0.9 V and this probably corresponds to the re-oxidation of Cr^{II}. In the presence of benzophenone, in conditions comparable with those used for the chromium chloride experiments, no increase in current for the Cr^{III}–Cr^{II} couple was observed and although the first reduction peak of benzophenone became irreversible only a small peak at –0.9 V appeared. Superimposition of cyclic voltammograms of benzophenone run in the presence of identical amounts of chromium(III) chloride hexahydrate and chromium(III) perchlorate hexahydrate showed that the chloride was about four times more effective in producing the species responsible for the extra reduction peak at *ca.* –0.90 V.

Preparative-scale Electrolyses.—Controlled-potential electrolysis of mixtures of carbonyl compounds and $CrCl_3{\cdot}6H_2O$ at the potential of the 'new peak' evident in cyclic voltammetry gives efficient conversion into the corresponding pinacol. Not only is pinacol formation enhanced in the presence of the Cr^{III} salt but the potentials required are lower. The results of preparative-scale electrolyses are displayed in Table 2. An important requirement for good yields of pinacol is that the catholyte be pre-electrolysed at *ca.* –0.6 V for *ca.* 0.3 F mol^{-1} prior to the addition of carbonyl compound; the significance of the need for some Cr^{II} at the start of the electrolysis is later discussed in detail.

For polyene carbonyl compounds which give acid-sensitive products the possibility of cathodic pinacolisation in neutral solution and at modest potentials is synthetically important. The results in Table 2 also demonstrate that benzophenone alone, in dry or aqueous DMF, gives diphenylmethanol as the only product and this contrasts with the result of electrolysis in the presence of chromium chloride. Also noteworthy is the indication that *ortho*-substituted benzophenones, even in the presence of the Cr^{III} salt, are converted less efficiently into the pinacol and there is an increase in the proportion of alcohol formed. Indeed 2-methoxycarbonylbenzophenone gives only the corresponding alcohol and its lactone (**5**). The preparative results described in this section must be accommodated in any mechanistic rationalisation of the effects of Cr^{III} species on the electrochemical behaviour of carbonyl compounds.


(**5**)

Attempted Reduction with Electrogenerated Cr^{II}.—It was important to determine at an early stage whether or not the key reducing agent was a Cr^{II} species. The absence of a catalytic current for the reduction of Cr^{III} in the presence of benzophenone (see above) suggested that direct reduction by Cr^{II} was not significant. This conclusion was confirmed by the results of further preparative-scale experiments.

A mixture of benzophenone (0.0005 mol) and chromium(III) chloride hexahydrate (0.006 mol) was electrolysed at –0.65 V, the potential at which Cr^{III} is reduced to Cr^{II}. A divided cell was used and the electrolyte was DMF–Bu_4NClO_4 (0.1M); the solution was rigorously degassed and continuously flushed with oxygen-free nitrogen. The cell current fell to the background level after the consumption of 1 F mol^{-1}, *i.e.* a large excess of Cr^{II} was generated *in situ*. Work-up, however, gave only recovered benzophenone in 90% yield.

It is known that benzaldehyde can be pinacolised by Cr^{II} ions[11] and it was found that Cr^{III}-enhanced cathodic pinacolisation was also efficient. This is discussed in detail below but interpretation of the results of such experiments demanded a control experiment in which the likely reactivity of electrogenerated Cr^{II} towards benzaldehyde was established. Consequently Cr^{II}, 0.07M in DMF–$NaClO_4$ (0.1M), was generated by cathodic reduction of the chromium(III) chloride and subsequently stirred for 3 h with an equivalent amount of benzaldehyde. After work-up only benzaldehyde was recovered which is compelling evidence that on the time scale of the chromium(III)-modified reductions (*ca.* 2 h) pinacols are formed

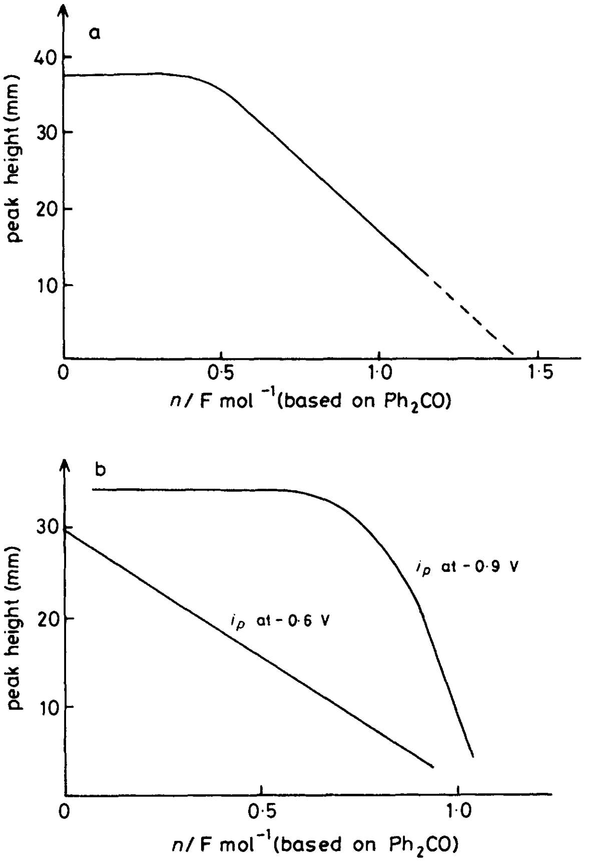


Figure 3. Controlled-potential coulometry: *a*, at -0.95 V (*versus* Ag–AgI) and *b*, at -0.60 V with simultaneous monitoring of i_p at -0.95 V [DMF–Bu_4NClO_4 (0.15M), Hg cathode, Ph_2CO and $CrCl_3$•$6H_2O$ 5.7×10^{-3} M].

by direct electrolysis and not through homogeneous reaction with Cr^{II}.

Coulometry.—Despite the demonstration that direct reduction by Cr^{II} was not important the need for an initial and significant concentration of Cr^{II} in the preparative-scale work requires explanation. The role of Cr^{II} and Cr^{III} species was elucidated by a series of experiments in which the concentrations of key intermediates were monitored as a function of the extent of electrolysis.

The results displayed in Figure 3 are especially revealing. Controlled-potential coulometry of an equimolar mixture of benzophenone and $CrCl_3$•$6H_2O$ was used to measure the number of electrons involved in reduction at -0.93 V, *i.e.* the 'new peak' potential. The working electrode was at -0.93 V throughout but from Figure 3a it is evident that initially only Cr^{III} was being reduced. After *ca.* 0.5 F mol^{-1}, however, the peak at 0.93 V began to decrease linearly with charge consumption and electrolysis was complete at 1.5 F mol^{-1}. Consequently reduction of the species responsible for the peak at -0.93 V is a 1 F mol^{-1} process; this is entirely consistent with the formation of pinacols in the preparative-scale experiments. There is again an indication that prior formation of Cr^{II} is necessary before efficient reduction at -0.93 V can take place. However, the result displayed in Figure 3b shows clearly that the species responsible for the 'new peak' requires the presence of Cr^{III}! Controlled-potential coulometry at -0.60 V was performed and the linear decrease in the peak corresponding to Cr^{III} reduction shows that at this potential Cr^{III} is removed cleanly in the expected 1 F mol^{-1} process. Simultaneous monitoring of the peak current -0.93 V reveals that when the concentration of Cr^{III} falls below a critical level the 'new peak' is decreased until it is not evident in solutions containing only Cr^{II}.

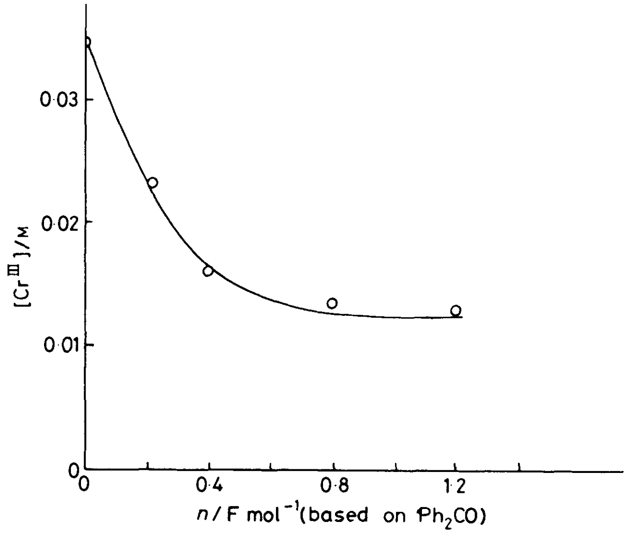


Figure 4. Chromium(III) concentration during electrolysis of benzophenone (0.0350M^{3}) at -0.95 V in DMF–Bu_4NClO_4 (0.1M)

The concentration profile for Cr^{III} during a preparative-scale electrolysis involving benzophenone–$CrCl_3$•$6H_2O$ was constructed by sampling at intervals during the electrolysis, analysing chemically for Cr^{II}, and by subtraction from the initial Cr^{III} concentration arriving at the plot shown in Figure 4. This shows that the Cr^{III} concentration falls sharply over the first 0.4—0.5 F mol^{-1} but decreases slowly thereafter, *i.e.* in the stage of the electrolysis associated with pinacol formation the Cr^{III} concentration is significant and changing only slowly.

The Effect of Proton Donors and Lewis Acids.—The fact that in the presence of chromium chloride the carbonyl compounds are reduced at less cathodic potentials than would otherwise be the case is reminiscent of the reported effect of protonation. The possibility is therefore raised of the chromium chloride polarising the carbonyl group by a Lewis acid–Lewis base interaction. Consequently the effect of proton donors and Lewis acids was explored.

The consequences of added benzoic acid upon the cyclic voltammetric behaviour of benzophenone in DMF–Bu_4NI (0.1M) at a mercury cathode and at a scan rate of 0.3 V s^{-1} are shown in Figure 5. Loss of reversibility of the first reduction peak results from the addition of acid and, significantly, a species is formed which reduces at a lowered cathodic potential. These results are similar to those obtained polarographically[12] and are probably best explained in terms of a benzophenone–benzoic acid complex such as (6).

Controlled-potential electrolysis of an equimolar mixture of benzophenone and benzoic acid, at -1.05 V in DMF–$NaClO_4$ (0.1M), did not proceed to completion. After 0.8 F mol^{-1} the current had fallen to the background level and aqueous work-up resulted in the recovery of benzophenone (58%) and the isolation of diphenylmethanol (29%) and benzpinacol (13%). The facilitation of pinacolisation by polarisation of the carbonyl group is, however, clearly established.

An attempt was made to establish that benzophenone, when complexed through the carbonyl oxygen atom to a Cr^{III} ion, was polarised in such a manner that would explain the lowered

Table 3. Preparative-scale electrolysis[a] of benzaldehyde: added Cr^{III} and stereochemistry

Conditions	Potential (–V *versus* Ag–AgI)	Pinacol (%)[b]	(±):*meso*[c]
Dry DMF[d]	1.30	>90	14
DMF–H_2O (0.42M)[e]	1.30	>90	8.1
DMF–HOAc (0.5M)	1.20	>90	3.8
DMF–HOAc (0.07M)–H_2O (0.42M)	1.30	>90	3.1
DMF–$CrCl_3 \cdot 6H_2O$ (0.07M)	0.90	85	1.3

[a] Conditions as for Table 2. [b] By ^1H n.m.r. spectroscopy on crude product; isolated yields were *ca.* 60%. [c] From integration of the ^1H n.m.r. spectra. [d] Reagent grade DMF dried over activated molecular sieves, 4A. [e] Equivalent to $6H_2O$.

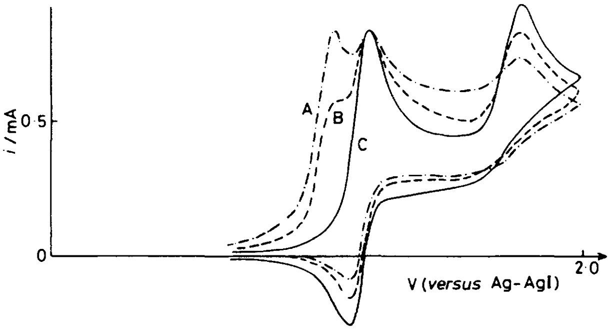
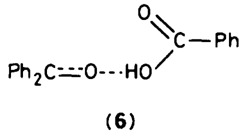


Figure 5. The effect of the addition of benzoic acid on the cyclic voltammetric reduction of benzophenone. [DMF–Bu_4NI (0.1M), Hg bead, 0.3 V s ^{1}, benzophenone *ca.* 2 × 10 ^{3}M^{3}]: A, Ph_2CO + $PhCO_2H$ (1 equiv.); B, Ph_2CO + $PhCO_2H$ (0.5 equiv.); C, Ph_2CO.



(6)

$Cl_3Cr \leftarrow (O{=}CR^1R^2)_x$

(7)

x = 1-3

reduction potentials in the presence of Cr^{III}. A number of complexes of the type **(7)** have been prepared by stirring chromium(III) chloride with the ligand, in benzene solution and in the presence of catalytic amounts of zinc dust.[13] This method was used by us to prepare a complex which is probably $Ph_2CO \cdot CrCl_3$.

An i.r. spectrum of the pale mauve solid obtained confirmed that benzophenone was present in the complex; elemental analysis was not completely satisfactory but was consistent with the proposed formulae. The carbonyl stretching frequency was 1 580 cm ^{1} which must be contrasted with the 1 660 cm ^{1} observed for benzophenone; this is best interpreted in terms of polarisation of the carbonyl group and there is good precedent in the similar and large shift observed for the aluminium chloride–benzophenone complex.[14]

Additional evidence would obviously have resulted from an electrochemical study of the separately prepared complex. However, the common aprotic solvents used for electrochemical work (*e.g.* DMF, MeCN) are themselves Lewis bases which would displace the benzophenone ligand. Other possible solvents, *e.g.* dichloromethane and nitrobenzene, did not dissolve the complex.

A brief examination was also undertaken of the effect of other Lewis acids on the voltammetric behaviour of benzophenone in DMF–Bu_4NI. The addition of $SnCl_4$, $TiCl_4$, and $AlCl_3$ each caused a vigorous and exothermic reaction but no significant change in the potential of the benzophenone reduction peak. Similarly, addition of $ZnCl_2$ and $FeCl_3$ did not modify the voltammetric behaviour of the ketone.

An interesting and relevant observation concerning the preparative consequences of a good choice of proton donor is that of Wightman and his co-workers[15] who showed that in acetonitrile solution diethyl malonate is an excellent proton donor for carbonyl group cathodic reductions and that it promoted efficient pinacolisation of retinal.

The Stereochemical Course of Benzaldehyde Reduction: the Effect of Proton Donors and Cr^{III}.—In DMF solution benzaldehyde reduces at a similar potential to that measured for benzophenone. Furthermore, the expected pinacol is diastereoisomeric and the *meso*:(±) ratio may conveniently be determined by ^1H n.m.r. spectroscopy.[16] This ratio is also known to be sensitive to electrolysis conditions, especially pH, and therefore the influence of Cr^{III} upon the stereochemistry of pinacolisation might be expected to yield mechanistic information.

The addition of chromium(III) chloride hexahydrate to a solution of benzaldehyde (mM) in DMF–BuN_4 (0.1M) causes changes in cyclic voltammetry which are qualitatively similar to those described for other carbonyl compounds (*e.g.* Figure 1). Cyclic voltammetry (Hg cathode, 0.3 V s ^{1}) revealed for benzaldehyde a reduction peak at – 1.34 V with an associated oxidation peak at – 1.25 V (i_p^a/i_p^c 0.4). Addition of successive amounts of the chromium(III) salt was accompanied by the development of an irreversible peak at – 1.20 V.

Preparative-scale electrolysis of benzaldehyde, in DMF–$NaClO_4$ and in the presence of the chromium salt, was carried out at the potential of the 'new peak'. For comparison a number of electrolyses were performed using the same cell and solvent–electrolyte system but with differing proton donors. The results of these experiments are collected in Table 3.

The salient feature of these results is that as the acidity of the electrolyte increases the (±):*meso* ratio decreases. Such ratios, and their variation with electrolyte composition, have been the subject of much detailed discussion[16 18] but no consistent explanation has emerged. However, in this case it can at least be observed that the effect of the chromium(III) salt is in the same direction, but more effective, than protic acids. According to some accounts[18] the high (±):*meso* ratios associated with dry conditions and the presence of alkali-metal ions is symptomatic of the intermediacy of metal-ion-bridged radical-ions whereas for protonated carbonyl compounds it is dimerisation of the first formed and neutral radicals which determines the product stereochemistry.

The Mechanism.—Major features of the results which must be accommodated in any mechanistic hypothesis are: (*a*) the

$$(R^1R^2C{=}O)_x \longrightarrow Cr^{III}L_{(6-x)}$$

(8)

requirement that both Cr^{III} and Cr^{II} be present; (*b*) the lowering of the reduction potential and the attendant promotion of cathodic pinacolisation *vis à vis* alcohol formation; (*c*) the greater effectiveness of $CrCl_3{\cdot}6H_2O$ *versus* $Cr(ClO_4)_3{\cdot}6H_2O$ as a modifier of carbonyl reduction. We have previously proposed the sequence of reactions in the Scheme; the detailed results now presented strongly support this mechanism and disprove the alternative rationalisation presented by Martinet and his co-workers.[8]

The requirement for both Cr^{II} and Cr^{III} is demanded by the way in which the key intermediate (**8**) is formed. Chromium(III) complexes are substitution inert and are usually formed *via* the kinetically labile Cr^{II} complexes with subsequent re-oxidation. Hence the formation of significant concentration of Cr^{II} is a pre-requisite for the eventual formation of (**8**) in which chloride and DMF ligands have been replaced by the carbonyl compound.

Chromium(III) compounds are effective Lewis acids and the lowering of the reduction potential by polarisation of the carbonyl group in complexes such as (**8**) is to be expected. It is the reduction of (**8**) which is responsible for the 'new peaks' described above. In support of this contention it has been demonstrated that polarisation, *e.g.* by protic acids, does result in lowered reduction potentials and furthermore the polarisation of a carbonyl group in the manner required is evident from the lowered carbonyl stretching frequency measured for the benzophenone–$CrCl_3$ complex.

The analogy between protonation and co-ordination to Cr^{III} is further strengthened by the observed similarities in the stereochemical course of the cathodic pinacolisation of benzaldehyde in protic conditions and in the presence of chromium(III) chloride hexahydrate.

The role of the halogen is also important and understandable. Oxidation of the carbonyl compound–Cr^{II} complex, formed rapidly following cathodic reduction of Cr^{III}, must be efficient for the overall reaction to proceed at a useful rate. It is suggested that an inner-sphere electron-transfer process, known [19] to be fast for the $CrCl_2{}^{+}$–Cr^{2+} system, is responsible for the generation of (**8**) from the corresponding Cr^{II} complex. It is the established and considerable effectiveness of chloride as a bridging ion which explains its usefulness *vis à vis* perchlorate.

Within the proposed scheme, the poorer yields of pinacol obtained from *ortho*-substituted benzophenones might be explained by steric hindrance to co-ordination.

The re-oxidation of Cr^{II} to Cr^{III} can also be effected anodically and this has been demonstrated by preparative-scale pinacolisation in an undivided cell equipped with a mercury cathode and a platinum anode. Equivalent amounts of benzophenone and chromium(III) chloride hexahydrate were electrolysed at -0.95 V until 3 F mol^{-1} had been consumed. The electrolyte was DMF–$NaClO_4$ (0.15M). Because of the continual re-oxidation of Cr^{II} the cell current at the end of the electrolysis had fallen by only 40% from the initial value. Work-up gave benzpinacol (90%) and benzophenone (10%). For carbonyl compounds which can tolerate the modest anode potentials associated with Cr^{II} oxidation this is probably the most convenient preparative procedure.

Experimental

Solvents, Electrolytes, and Electrochemical Equipment.—These were essentially as described in earlier papers in the series. Conventional glass H-cells were used with sintered-glass separators; the electrodes were a stirred mercury cathode and a carbon rod anode. One experiment employed an undivided, water-jacketted, cell with a mercury cathode and platinum anode. Controlled-potential coulometric experiments used equipment previously described.[20] In both preparative and electroanalytical experiments the electrolytes were purged with nitrogen before and during the course of the experiment. Electrode potentials were measured against a Ag–AgI(s) reference electrode.

Materials.—Commercial samples of benzaldehyde, acetophenone, benzophenone, fluorenone, and β-ionone were used, with purification if appropriate. Other compounds were prepared using well established methods. Retinal was obtained from the commercially available vitamin A acetate by hydrolysis to the alcohol with subsequent oxidation using activated manganese dioxide. β-Ionylideneacetaldehyde (**4**) was prepared from 3-methyl-5-(2,6,6-trimethylcyclohex-1-enyl)penta-2,4-dienyl 4-nitrobenzoate which was kindly donated by Roche Products Ltd., Welwyn Garden City. The nitrobenzoate ester was saponified and the resulting alcohol converted into the required aldehyde with activated manganese dioxide. The 2- and 4-methyl-benzophenones were prepared from the 2- and 4-methylbenzoic acids by conversion into the acid chlorides and subsequent Friedel–Crafts reaction with benzene.

The chromium salts were obtained commercially, except for anhydrous chromium(III) chloride which was prepared from the hexahydrate by treatment with thionyl chloride.[21]

Electrolyses.—A typical chromium(III)-modified electrolysis is described below.

The Cathodic Conversion of β-*Ionylideneacetaldehyde* (**4**).—Chromium(III) chloride hexahydrate (0.0057 mol) was added to the catholyte [DMF–$NaClO_4$ (0.2M)] contained in the working compartment (volume *ca.* 60 cm^3) of a divided cell. The solution was electrolysed at -0.4 V (*versus* Ag–AgI) until *ca.* 0.3 F mol^{-1} had passed, based on the amount of chromium salt. β-Ionylideneacetaldehyde (0.0034 mol) was then added and the electrolysis continued at -0.90 V until 1.6 F mol^{-1} (based on the aldehyde) had been consumed. During this time the current density fell from 0.007 A cm^{-2} to 0.0007 A cm^{-2}.

The catholyte was shaken with light petroleum (b.p. 60—80 °C) (2 × 100 cm^3), then diluted with water (50 cm^3) and that solution shaken further with light petroleum (4 × 50 cm^3). The combined petroleum extracts were washed with water (4 × 100 cm^3) and dried ($MgSO_4$). Evaporation of the solvent gave a yellow oil (0.58 g) which subsequently crystallised to give the pinacol in 60% yield. Recrystallisation from ethyl acetate–light petroleum gave needles, m.p. 122—128 °C, ν(CCl_4) 3 620 (free OH) and 3 570 cm^{-1} (intramolecularly hydrogen-bonded OH); δ($CDCl_3$) 1.01 (12 H, s), 1.68 (6 H, s), 4,39 (2 H, d, *J* 7 Hz), and 6.0 (4 H, m); *m/z* 438 (*M*, 7%), 420 (*M* − H_2O, 10), and 219 (*M*/2, 100%).

Complex Formation between $CrCl_3$ *and Benzophenone.*—Benzophenone (30 g) and zinc dust (*ca.* 10 mg) were added to anhydrous chromium(III) chloride (5 g) dissolved in dry benzene (30 cm^3). The mixture was stirred for 3 h and then allowed to stand overnight. The resulting sticky solid was removed by filtration and after trituration with light petroleum a pale mauve solid (9 g) was obtained (Found: C, 46.2; H, 3.9; Cl, 25.2. $Ph_2CO{\cdot}CrCl_3$ requires C, 45.8; H, 2.9; Cl, 31.3%), ν(Nujol) 1 595, *1 580*, 1 335, 1 290, and 705 cm^{-1}; *cf. 1 660*, 1 595, 1 320, 1 280, and 705 cm^{-1} for benzophenone.

Determination of Cr^{II} *Concentrations during Electrolysis.*—Samples withdrawn at intervals were added to an aqueous solution of iron(III) chloride which was diluted further to *ca.* 50 cm^3. The solution was then titrated potentiometrically with a standardised solution of cerium(IV) sulphate. From the volume required to re-oxidise Fe^{II} to Fe^{III} the concentration of Cr^{II} in each sample was obtained; the initial concentration of Cr^{III} was known so a complete concentration profile resulted. The method was tested by following the formation of Cr^{III} during electrolysis of chromium(II) chloride hexahydrate at -0.65 V in DMF-$BuNClO_4$ (0.1M). A satisfactorily linear plot was obtained which by extrapolation to zero concentration of Cr^{III} gave *n* 1.05 F mol^{-1}. Separate control experiments also established that benzophenone and benzpinacol did not interfere with the titration.

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