REVIEWS

Applications of Chromium(II) Salts in Preparative Organic Chemistry

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The applications of chromium(II) salts to the reduction of alkyl halides, unsaturated systems, epoxides, acyloxyketones, and nitro compounds are reviewed.

1. Chromium(II) Reagents
2. Reduction of Alkyl Halides
3. Reduction of Unsaturated Substances
4. Reduction of Epoxides
5. Reduction of Acyloxyketones
6. Reduction of Nitro Compounds

Die praktische Anwendbarkeit der Chrom(II)-Reduktion von Alkyl Halogeniden, ungesättigten Systemen, Epoxyden, Acyloxyketonen, und Nitro-Verbindungen wird beschrieben.

The reactions of the lower valency states of transition metal ions such as chromium(II) with organic substrates have been studied for many years[1]. A number of synthetic applications have developed from these studies. It is the purpose of this review to describe some of these applications in preparative organic chemistry.

One of the earliest reports of the application of chromium(II) chloride was in 1916[2] when it was shown that, in an inert atmosphere, it reduced maleic and fumaric acids to succinic acid. Treatment of the chromium(II) chloride solution with sodium hydroxide gave a suspension of chromium(II) hydroxide which reduced cinnamic acid to phenylpropanoic acid. Nitrous oxide was reduced by both alkaline and acidic solutions of chromium(II) to ammonia whilst an oxime, benzaldoxime, was reduced under alkaline conditions at 100° to benzylamine. During the 1920's salts of the lower valency states of chromium, titanium and vanadium were utilised[3-5] in the generation of free radicals from, for example, triphenyl carbinol. Dimeric products arising from radical coupling were observed in the reduction of other substances such as aromatic α,β-unsaturated ketones. Even benzaldehyde is slowly reduced by chromium(II) to hydrobenzoin. However other applications of the reagent were spasmodic. Thus in 1934 an application to the reduction of unsaturated iminochlorides to Schiff's bases was described[6]. In 1945 the use of chromium(II) chloride in the dehalogenation of 5,6-dibromo-3-keto steroids was described[7]. A preparation of diacrydyl from 5-chloroacridine using chromium(II) sulphate was reported in 1949[8]. Other applications reported at this time involved the use of the reagent in the reduction of epoxyketones[9]. Studies of the inorganic chemistry of the system and in particular of the importance of bridging complexes in redox reactions have been reflected in a clearer understanding of the mechanism of these reductions[1]. As a result of this many new applications of the reagent have been developed. In this review we shall classify the applications of the reagent to organic chemistry in terms of the organic substrate.

1. Chromium(II) Reagents

The chromium(II) ion is readily prepared by the reduction of chromium(III) salts by zinc and hydrochloric acid in an inert atmosphere. The zinc is usually activated by amalgamation or with copper sulphate[10]. A chromium(II) chloride solution has a light blue colour. Related procedures have been described employing a 'Jones' reductor[11]. Electrolytic reduction may be used[12] or the dissolution of chromium metal in, for example, perchloric acid[13]. The solution may be standardised against ferric sulphate. The ferrous ion which is formed is then titrated with standard dichromate using for example, *p*-diphenylamine sulphonic acid, as an indicator. Alternatively a potentiometric method can be used[14].

Most reductions proceed at room temperature under nitrogen or carbon dioxide. Care must be taken to exclude oxygen. Indeed chromium(II) chloride is sometimes used as a cleaner and more efficient alternative to alkaline pyrogallol in removing traces of oxygen from nitrogen. The scope of chromium(II) reductions are dependant both on the complexed

state of the chromium(II) and on the other ions such as halide present in the solution[15,16]. Concentrated solutions of chromium(II) perchlorate, will decompose water at room temperature[13]. This can present a potential hazard.

A number of chromium(II) reagents have been developed. Chromium(II) chloride, sulphate and perchlorate are similar in their scope. However more recently a chromium(II) ethylenediamine reagent has been introduced which appears to be an exceedingly efficient reducing agent[17,18]. On the other hand chromium(II) acetate, a relatively insoluble salt produced from chromium(II) chloride by the action of sodium acetate, is a milder reducing agent reacting under relatively neutral conditions[19]. Chromium(II) hydroxide is a powerful reducing agent[2].

Reduction with Chromium(II) Chloride:
Chromium(II) chloride was prepared by reduction of chromium(III) chloride (12 g) in water (15 ml) and 12 *N* hydrochloric acid (25 ml) with excess granulated zinc under nitrogen. Amalgamated zinc dust, prepared by shaking zinc dust (10 g) with mercury(II) chloride (0·8 g) in water (10 ml) containing conc. hydrochloric acid (0.5 ml) for 5 min and then decanting the supernatent liquid, has also been recommended for this reduction. The blue solution was filtered under nitrogen through a plug of glass wool into a solution of the substrate (0·01 mol) in redistilled acetone (50 ml). After an appropriate time (1–4 hr, T.L.C. control) at room temperature or under reflux, the solution was poured into water and the organic substrate recovered in ether or chloroform. It was advisable to back extract the organic phase with dil. hydrochloric acid to remove traces of chromium salts, and then with aqueous sodium hydrogen carbonate before drying and recovering the organic substrate.

Chromium(II) Acetate:
Powdered chromium metal (9 g) in 6*N* hydrochloric acid (100 ml) was stirred until reaction was complete. A solution of sodium acetate (50 g) in deoxygenated water (100 ml) was added under nitrogen with stirring and cooling. The pink precipitate of chromium(II) acetate (10 g) was washed under nitrogen with air-free water.

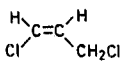
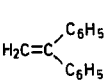
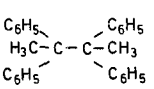
Chromium(II) Ethylenediamine Perchlorate:
A solution of dimethylformamide (40 ml) and ethylenediamine (1 ml) was flushed with nitrogen. Chromium(II) perchlorate (0.8*N* solution; 5 ml), prepared from chromium metal and dil. perchloric acid, was added to give a clear blue-purple solution. The substrate (0.5*M* in dimethylformamide; 1 ml) was added and the reduction was complete when the colour of the solution changed from purple to red.

A co-solvent such as acetone, methanol or ethanol, tetrahydrofuran, dimethylformamide or dimethyl sulphoxide is often used. These can affect the course of a reaction. Mechanistic studies have indicated that reduction involves a series of one-electron transfer steps across bridging anions to an organochromium intermediate formed from an organic radical[20]. The addition of hydrogen donor reagents such as *n*-butyl mercaptan or hypophosphorus acid can modify the reaction particularly to favour the reduction of the intermediate radical over elimination reactions[21].

2. Reduction of Alkyl Halides

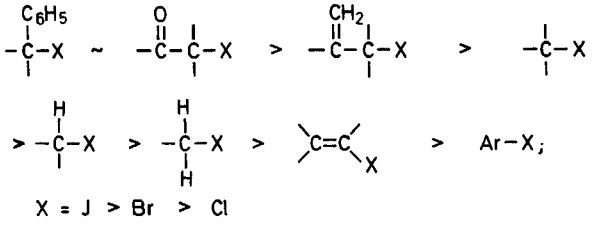
The reduction of alkyl halides by chromium(II) salts represents one of the best known applications of these reagents. Some examples of the systems that have been reduced are presented in the Table.

Table. Reduction of Alkyl Halides by Chromium(II) Salts

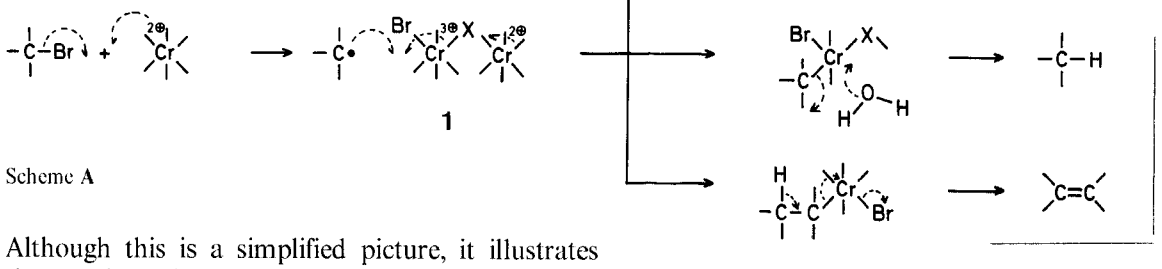
Substrate	Reducing Agent and Solvent	Product	Yield (%)	References
$H_3C-CH_2-CH_2-Br$	$CrSO_4$ / DMF	$H_3C-CH_2-CH_3$		20
$Cl-CH_2-COOH$	$CrCl_2$ / H_2O	$H_3C-COOH$		4
$H_2C=CH-CH_2-Br$	$CrSO_4$ / H_2O / THF	$H_2C=CH-CH_3$	95	16
	$CrCl_2$ / THF	$H_2C=CH-CH_2-CH_2-CH=CH_2$	83	
	$CrSO_4$ / DMF	$H_2C=CH-CH_3$		20
$Br-CH_2-CH_2-Br$	$CrSO_4$ / DMF	$H_2C=CH_2$		20
$Br-CH_2-CH_2-OH$	$CrCl_2$ / H_2O	$H_2C=CH_2$		55
$Br-CH_2-CHBr-CH_2-Cl$	$CrSO_4$ / DMF	$H_2C=CH-CH_2-Cl$ (5 min)		20
$H_2C=CBr-CH_2-Br$	$CrSO_4$ / DMF	$H_2C=CH-CH_3$	74	20
		+		
		$H_2C=C=CH_2$	26	
	$CrSO_4$ / dioxan			15
$C_6H_5-CH=CH-CCl=N-C_6H_5$	$CrCl_2$	$C_6H_5-CH=CH-CHO$		6

[1] For a review of the inorganic chemistry see, inter alia,
H. Taube, *Advances in Inorganic Chemistry and Radiochemistry* **1**, 1 (1959).
A. G. Sykes, *Advances in Inorganic Chemistry and Radiochemistry* **10**, 153 (1967).
For earlier reviews see:
J. K. Kochi, *Rec. Chem. Progr.* **27**, 207 (1966).
L. F. Fieser, M. Fieser, *Reagents for Organic Synthesis*, John Wiley and Sons, New York, 1967, p. 149 and vol. 2 p. 75.
J. R. Hanson, E. Premuzic, *Angew. Chem.* **80**, 271 (1968); *Angew. Chem. Internat. Ed.* **7**, 247 (1968).

The rates of reduction and the products are dependant on the structure of the organic halide as well as the nature of the chromium(II) species. A reactivity order for various types of halide has been proposed.



Whereas arylalkyl halides and allylic halides give both monomeric and dimeric products, α-halocarbonyl compounds often give simple reduction products. On the other hand compounds with an adjacent halogen, hydroxyl or other anionic substituent give rise to olefins. In the presence of suitably oriented α,β-unsaturated ketones, cyclization reactions can occur. The formation of these products can be rationalized in mechanistic terms (Scheme **A**). The first stage involves the attack of the chromium(II) ion on the halogen atom. The second stage involves migration of the alkyl residue to form a new chromium-carbon bond. This process is accompanied by a one-electron transfer from a second chromium(II) ion through a bridging anion (**1**). The subsequent decomposition of this intermediate (**1**) by elimination, protonolysis or attack on unchanged organic halide can account for the majority of the products.

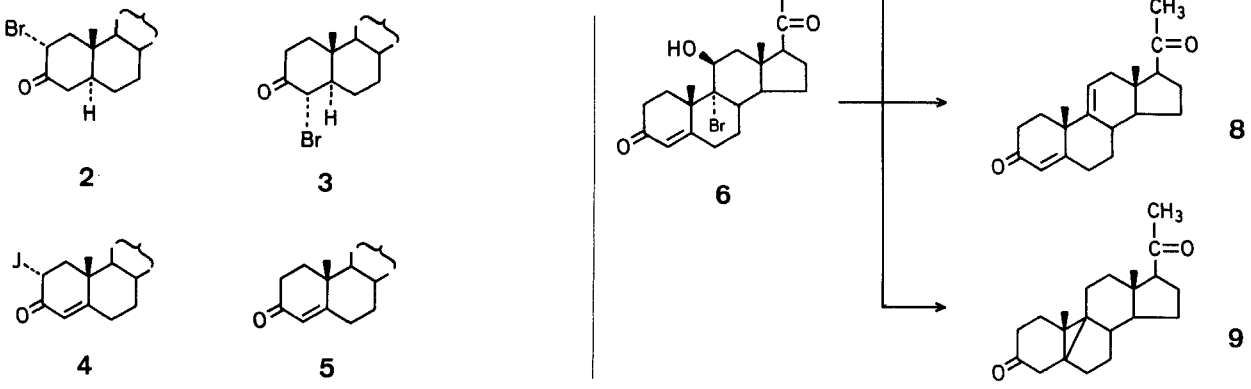


Scheme A

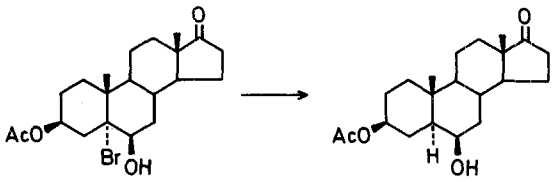
Although this is a simplified picture, it illustrates the way in which bridging anions, complexing solvents and hydrogen donors may influence the reaction pathway. The formation of such a complex may also account for double bond isomerizations that have been observed. Geminal, vicinal and 1,3-dihalides can be reduced by chromium(II) salts to generate carbenes[23], alkenes and cyclopropanes by α, β or γ-reductive elimination of the halogen atoms[24].

Some further examples will serve to illustrate the uses of the reagent. The first product of bromination of a 3-keto steroid is the 2-bromo-3-keto steroid (e.g. **2**). If the 4α-bromo steroid (**3**) is required[25], reduction of the 2,4-dibromoketone with excess chromium(II) acetate removes the C-2 bromine to afford a facile means of preparing the 4-bromo compound. The reagent also found application[26] in a sequence for converting 3-keto steroids to the Δ^4-α,β-unsaturated ketones (**5**). The 2,4-dibromoketone, on reaction with sodium iodide, afforded a 2-iodo-Δ^4-α,β-unsaturated ketone (**4**). The iodine was then reduced out with chromium(II) chloride or with zinc to give the unsaturated ketone (**5**). In some instances 2-chloro-3-keto steroids were also reduced.

An illustration of the effect of added hydrogen donors is provided by the reduction of 9α-bromo-11β-hydroxy steroids (**6**). In the reduction of 9α-bromo-11β-hydroxyprogesterone (**6**) with chromium(II) acetate three products were observed[27]. These were 11β-hydroxyprogesterone (**7**), the $\Delta^{9(11)}$-olefin (**8**) and the 5,9-cyclosteroid (**9**) – the product of organometallic addition across the α,β-unsaturated ketone. In the presence of an added hydrogen donor such as butanethiol or hypophosphorus acid, 11β-hydroxyprogesterone (**7**) was obtained in 80% yield.



The use of *n*-butanethiol and chromium(II) acetate in the reduction of a 5α-bromo-6β-hydroxysteroid (**10**) permitted[28] the removal of the bromine and the isolation of the 6β-hydroxy-steroid(**11**).



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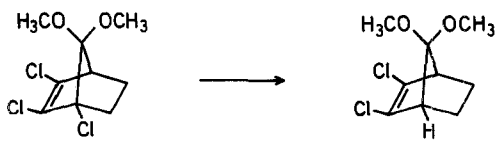
5,9-Cyclopregn-1-ene-11β,17α,21-triol-3,20-dione 11β,21-Diacetate[27]:
A chromium(II) chloride solution (228 ml) (from chromic chloride, 60 g) was added in three portions over 45 min. to a solution of 9α-bromopregna-1,4-diene-11β,17α,21-triol-3,20-dione 11β,21-diacetate (7·6 g) in acetone (600 ml) at 25°. A slow stream of carbon dioxide was bubbled through the reaction mixture during the whole operation. The reaction mixture was then diluted with water, filtered, and the precipitate was washed with water and dried. The crude product was recrystallised several times from ethyl acetate/methanol to give analytically pure cyclosteroid; yield: 2.82 g; m.p. 186—191°; $[\alpha]_D = +254°$.

3β-Acetoxy-6β-hydroxyandrostan-17-one (11)[28]:
3β-Acetoxy-5α-bromo-6β-hydroxyandrostan-17-one (4·07 g) was added to a solution of chromium(II) acetate (5·3 g, 5 equiv.) in dimethyl sulphoxide (redistilled, 75 ml) under oxygen-free nitrogen in the presence of *n*-butyl mercaptan (1·60 ml, 8 equiv.). The deep purple mixture was stirred at 28° for 2 hr and then poured into water (200 ml). The steroid was recovered in dichloromethane. After chromatography on alumina, 3β-acetoxy-6β-hydroxyandrostan-17-one; m.p. 183—184° $[\alpha]_D^{24} = +42°$, was obtained.

Chromium(II) perchlorate and ethylenediamine react rapidly in aqueous dimethylformamide to form a purple ethylenediamine complex. The chromium(II) ion complexed with this ligand has a greatly enhanced ability to reduce even primary alkyl halides. Thus it will reduce primary alkyl bromides to alkanes and aryl bromides and iodides to arenes at rates which are at least a hundred times faster than for chromium(II) alone[17,18]. Another reducing agent is the chromium(II) ethanolamine complex which will reduce primary alkyl chlorides. Spectroscopic evidence has been presented for the formation of alkyl chromium species in these reductions which then undergo protonolysis.

An interesting example of the application of the chromium(II) reagent is in the removal of a bridgehead halogen[29]. Thus reduction of the chloro-acetal (**12**) resulted in the removal of the bridgehead halogen in preference to the vinylic halogens.



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Chromium(II) chloride is particularly useful for dehalogenation reactions. The dehalogenation of vicinal dihalides by chromium(II) ions proceeds much faster than the reaction with the corresponding monohalides and leads to the formation of olefins[30]. The stereospecific *trans* elimination of vicinal dibromides by chromium(II) can be induced by the use of dimethyl sulphoxide or pyridine as a solvent or by the use of excess ethylenediamine as a ligand. There have been a number of preparative uses of this in the introduction and protection of double bonds in the steroid series as, for example, the Δ^5-double bond. Under certain conditions the method permits[31,32] a smooth sequence in the conversion of Δ^5-3-hydroxy steroids to the Δ^4-3-ketones by the addition of bromine, oxidation to the ketone and reductive elimination with chromium(II) chloride. In the preparation of 16α-acetoxyprogesterone by this route, the 16α-acetoxyl group was stable to the acidic chromium(II) chloride in contrast to the elimination of 16α,17α-epoxides shown by this reagent.

The reductive elimination of steroidal bromofluorides (e.g. **13** and **14** giving **15** and **16** respectively) has been studied[33] in an effort to selectively remove the bromine atom to give a fluoro-steroid. With chromium(II) chloride vicinal halohydrins such as 9α-bromohydrocortisone acetate (**17**) gave the $\Delta^{9(11)}$-olefin (**18**)[34]. However the problem was overcome and a successful route to the 11β-fluorosteroids established[27] by reduction with chromium(II) acetate in the presence of *n*-butanethiol.

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J. B. Conant, L. F. Small, B. S. Taylor, *J. Amer. Chem. Soc.* **47**, 1959 (1925).
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[10] G. Rosenkranz, O. Mancera, J. Gatica, C. Djerassi, *J. Amer. Chem. Soc.* **72**, 4077 (1950).
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W. Traube, E. Burmeister, R. Stahn, *Z. Anorg. Chem.* **147**, 50 (1925).
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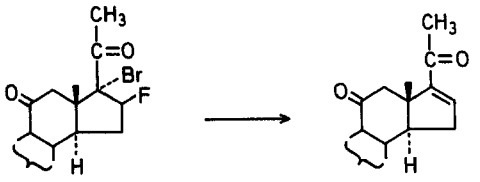
A. I. Vogel, *Quantitative Inorganic Analysis*, Longmans, London, 1951, p. 326.
[15] C. E. Castro, *J. Amer. Chem. Soc.* **83**, 1601 (1961).
[16] L. H. Slaugh, J. H. Raley, *Tetrahedron* **20**, 1005 (1964).
[17] J. K. Kochi, P. Mocadlo, *J. Amer. Chem. Soc.* **88**, 4094 (1966).



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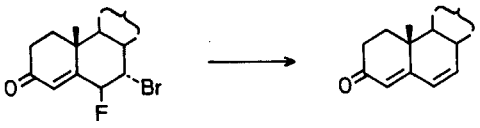

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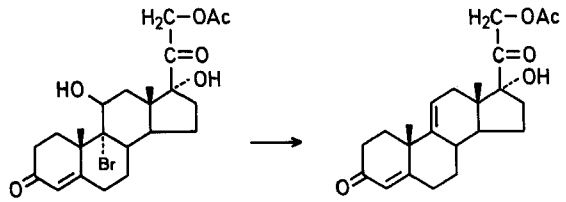

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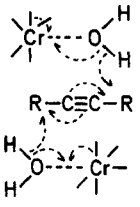
3. The Reduction of Unsaturated Substances

There are a number of examples of the reduction of multiple bonds by the lower valency states of transition metal ions. The reduction of acetylenes by chromium(II) sulphate in dimethylformamide leads to *trans* substituted olefins with the intervention of intermediates such as (**19**)[35]. Thus acetylene dicarboxylic acid, phenylpropiolic acid, propargyl alcohol, but-1-yn-3-ol and butyn-1,4-diol are reduced quite rapidly to the *trans* olefins.



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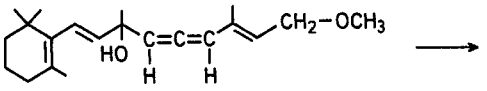
Phenylacetylene and but-2-yn-1-ol react less rapidly, whilst diphenylacetylene is relatively inert. The ease of reduction depends on the presence of an accessible co-ordination site in the molecule. In the case of carboxylic acids spectroscopic evidence clearly implicates these functions in complex formation. There is also a report of the specific reduction of an α-hydroxyallene (**20**) to an olefin (**21**) during a vitamin A synthesis[37].

[18] J. K. Kochi, D. M. Singleton, L. J. Andrews, *Tetrahedron* **24**, 3503 (1968).

[19] M. R. Hatfield, *Inorg. Synth.* **3**, 148 (1950).



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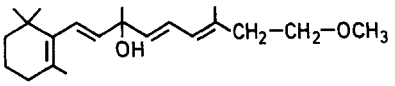

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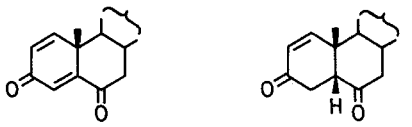
Chromium(II) sulphate will reduce unsaturated dicarboxylic acids such as maleic and fumaric acid to the saturated succinic acid[38]. The reduction of ene-1,4-diones to the saturated 1,4-diketones and α,β-unsaturated-γ-arylketones to saturated γ-arylketones by acidic solutions of chromium(II) has also been reported[3]. In the majority of cases the yields are high although dimeric products have been isolated in certain cases. However, simple α,β-unsaturated ketones are not reduced by chromium(II) chloride. Ammoniacal chromium(II)[39] or the chromium(II) ethylenediamine complex[17] are required in order to reduce α,β-unsaturated ketones. Ammoniacal chromium(II) solutions reduced benzaldehyde to benzylamine, acetophenone to α-phenylethyl alcohol and mesityl oxide to methyl isobutyl ketone. In this system dimeric products were not detected. As an example of the selectivity of the reduction of ene-1,4-diones by chromium(II) chloride, cholesta-1,4-diene-3,6-dione (**22**) is reduced to 5β-cholest-1-ene-3,6-dione (**23**)[40]. Here complex formation between the two carbonyl groups leads to the formation of the *cis* A/B ring junction. However the ability of the two carbonyl groups to complex with a single chromium species is not mandatory for reduction. Linear steroidal 3,5-diene-2,7-diones such as (**24**) afford the non-conjugated 4-ene-2,7-diones (**25**).



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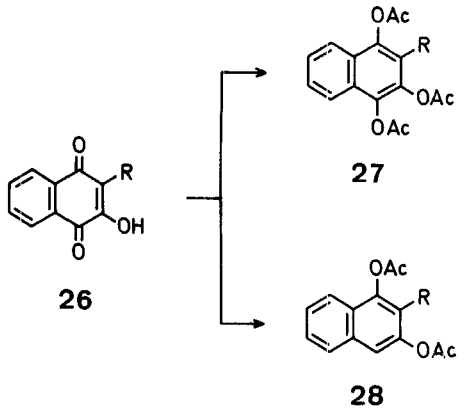
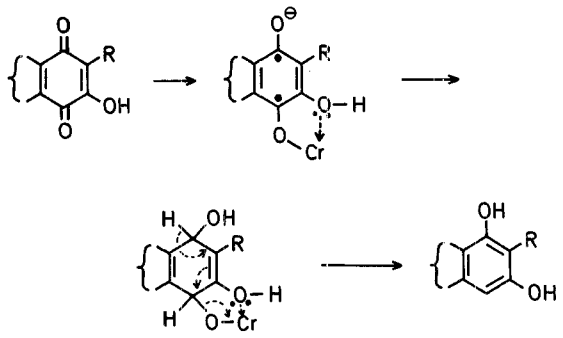
5β-Cholestane-3,6-dione[40]:
Cholest-4-ene-3,6-dione (503 mg) in tetrahydrofuran (70 ml) was heated under reflux with 0.1 *N* chromium(II) chloride (120 ml) in an atmosphere of nitrogen. The solution was diluted with water and the product was recovered in ether. 5β-Cholestane-3,6-dione (250 mg) crystallised from acetone as needles; m.p. 170—172 °; $[\alpha]_D^{20} = -62.5$.

Benzoquinones and naphthoquinones are reduced to the corresponding dihydroxyarenes[41]. Reduction of 2-alkyl-3-hydroxy-1,4-naphthoquinones (**26**) with chromium(II) acetate in neutral solution in the absence of a hydrogen donor gave, after acetylation 1,3,4-triacetoxy-2-alkylnaphthalenes (**27**). However with chromium(II) chloride in the presence of hypophosphorus acid as a hydrogen donor, the 4-oxygen function was eliminated. Thus 2-hydroxy-3-methyl-1,4-naphthoquinone (**26**, R=CH_3) gave 1,3-dihydroxy-2-methylnaphthalene (**28**).



A possible rationalisation for this is set out in Scheme **B**. This provides a simple route to 2-alkyl-1,3-dihydroxynaphthalenes – an oxygenation pattern found in some natural products.



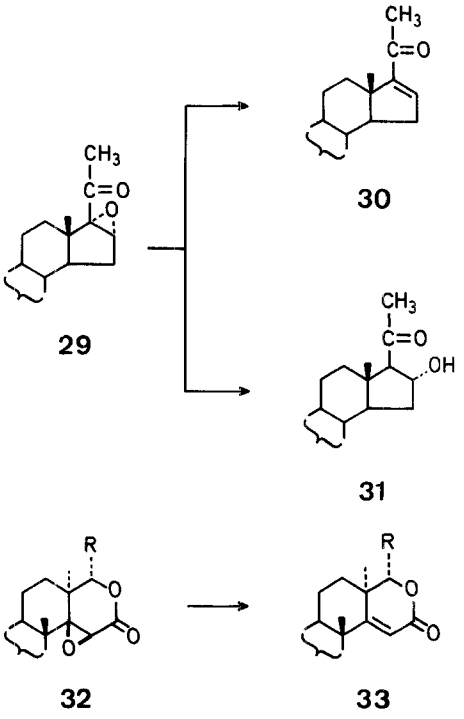
Scheme **B**

4. Reduction of Epoxides

A number of α-epoxyketones have been reduced by acidic solutions of chromium(II) chloride or chromium(II) acetate. Whereas chromium(II) chloride leads to the formation of the α,β-unsaturated ketone, use of chromium(II) acetate under less acidic conditions enables the β-hydroxy ketone to be isolated. For example, reduction of 16α,17α-epoxyprogesterone (**29**) with chromium(II) chloride gives 16-dehydroprogesterone (**30**) whilst with chromium(II) acetate 16α-hydroxyprogesterone (**31**) is isolated[42].

16α-Hydroxyprogesterone (31)[42]:
16,17-Epoxypregn-4-ene-3,20-dione (2.0 g) and chromium(II) acetate (4·4 g) in acetic acid (45 ml) and water (15 ml) were stirred under an atmosphere of carbon dioxide for 14 hr. Water was added and the steroid was recovered in dichloromethane. The 16α-hydroxyprogesterone; yield: 1.35 g; m.p. 218–222°; crystallised from acetone.

Chromium(II) chloride has been used in the removal of an epoxide group in the limonoid group of triterpenes where ring D takes the form of an α,β-epoxy-δ-lactone, (e.g. the conversion of **32** to **33**)[43].



Isolated epoxides are reduced by the chromium(II)-ethylenediamine reagent although they are relatively inert to the milder chromium(II) systems. The chromium(II) chloride reduction of ergosterol acetate epidioxide (**34**) has been studied[44]. Ergosteryl acetate (**35**), a dimeric steroid (**36**) and a 5α-hydroxy-6β-ethoxysteroid (**37**) were amongst the products that were formed.

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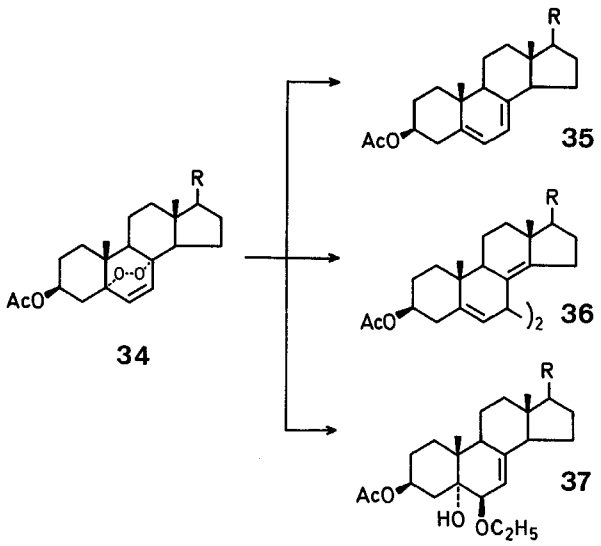
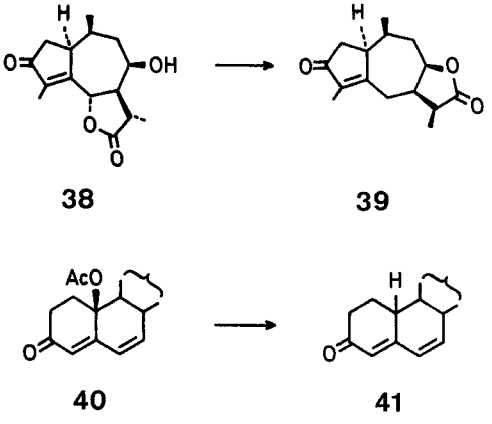
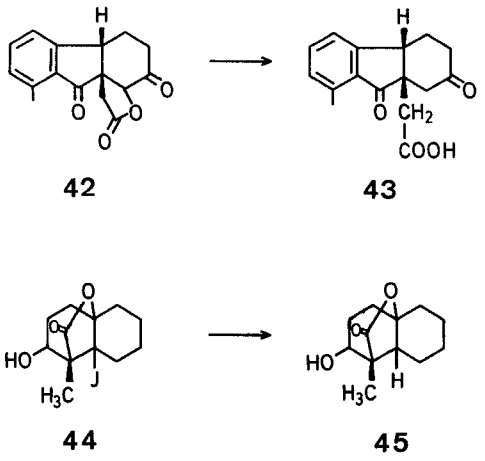


5. Reduction of Acyloxyketones

Chromium(II) salts will hydrogenolyse acetoxyl and lactone functions that are α- to a carbonyl group or allylic to a double bond. Thus the derivatives (e.g. **38**) in the geigerin series bearing such groups in the γ-position to an α,β-unsaturated ketone were reduced by chromium(II) chloride to the unsubstituted α,β-unsaturated ketones (e.g. **39**)[45].

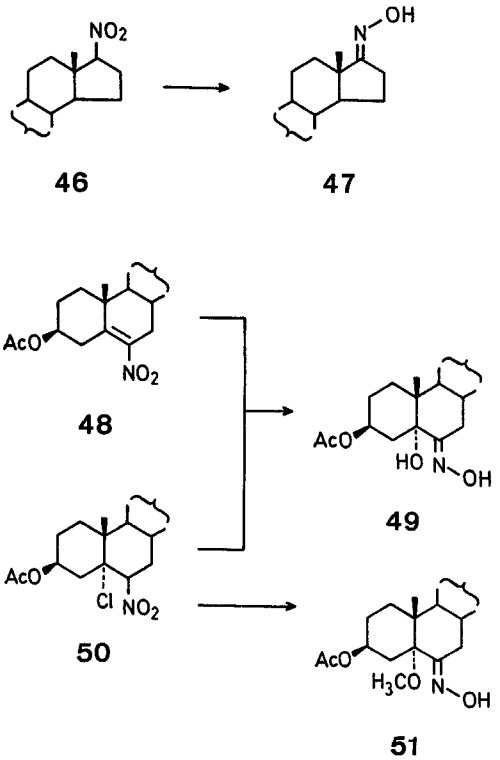


A similar reaction provided[46] an efficient synthesis of a 3-keto-$\Delta^{4,6}$-19-norsteroid in which the 10-acetoxyl group of (**40**) was hydrogenolysed with chromium(II) chloride to give (**41**). The lactone (**42**) is an intermediate in the synthesis of compounds related to gibberellic acid. Here the lactone was hydrogenolysed to give the keto-acid (**43**)[47]. In the synthesis of the ring A/B fragment of gibberellic acid the deiodination of the iodo-lactone (**45**) was achieved[48] using chromium(II) acetate in dimethyl sulphoxide containing ethanethiol.



6. Reduction of Nitro Compounds

The reduction of steroidal nitro compounds with chromium(II) chloride gives the corresponding oximes[49]. Thus reduction of 3β-acetoxy-17β-nitroandrost-5-ene (**46**) afforded the corresponding 17-oxime (**47**) in 70% yield. Similarly the α-nitroketone, 3β-hydroxy-16-nitroandrost-5-en-17-one afforded the corresponding α-oximinoketone. A nitro-olefin such as 6-nitrocholesteryl acetate (**48**) was reduced to the 5α-hydroxy-6-oxime (**49**)[50]. The reduction of 6β-nitro-5α-chlorocholestan-3β-yl acetate (**50**) afforded the 5α-hydroxy-6-oxime (**49**) with aqueous chromium(II) chloride and the corresponding 5α-methoxysteroid (**51**) in methanolic solution[51]. Both 6α- and 6β-nitrocholest-4-en-3-one gave 5α-cholestan-3,6-dione on reduction with chromium(II) chloride[49].



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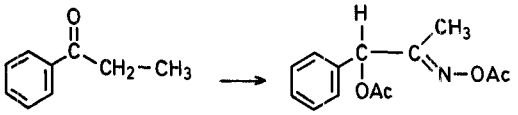
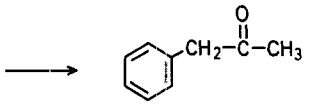
The 2,4-dinitrophenylhydrazones of some 3-keto-steroids can be cleaved[52] under relatively mild conditions by chromium(II) chloride reduction of the aromatic nitro groups to amines. The cleavage of oxime-*O*-acetates to form the parent ketones with chromium(II) acetate is a mild method of regenerating a carbonyl function particularly with conjugated ketones[53]. Furthermore ketoximes are available from other functions. Thus the method forms a useful way of transposing a ketone from one position to the adjacent position. For example oximation of propiophenone (**52**) followed by reduction with sodium borohydride and acetylation gave the α-acetoxy-acetoxime (**53**). Treatment of this with excess chromium(II) acetate afforded phenylacetone (**54**).



52 **53**



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Titanium(III) chloride will carry out a similar deoximation reaction.

Chromium(II) chloride promotes the addition of *N*-chlorocarbamates to olefins and enol-ethers and this leads to a potentially useful series of β-chloroamine derivatives[54].

In this review we have attempted to show that chromium(II) salts are easily prepared, versatile reducing agents. The scope of their reactivity complements that of other reducing agents such as the hydrides and indeed it is possible to achieve a selectivity with chromium(II) salts in which for example, halide and nitro groups are reduced and carbonyl functions remain unaffected.

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