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Chromium(VI) oxidants having quaternary ammonium ions: studies on synthetic applications and oxidation kinetics

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Abbreviations: BIBC, benzimidazolium bromochromate; BIDC, benzimidazolium dichromate; BIFC, benzimidazolium fluorochromate; BPCC, 2,2-bipyridinium chlorochromate; BTPPCC, benzyltriphenylphosphonium chlorochromate; BTPPD, butyltriphenylphosphonium dichromate; ChOX, cholesterol oxidase; CPCC, 3-carboxypyridinium chlorochromate; CTAB, cetyltrimethylammonium bromide; CTACN, cetyltrimethylammonium ceric nitrate; CTADC, cetyltrimethylammonium dichromate; CTAP, cetyltrimethylammonium permanganate; DCM, dichloromethane; DCPCC, 2,6-dicarboxypyridinium chlorochromate; DCPFC, 2,6-dicarboxypyridinium fluorochromate; DMA, dimethyl acetamide; DMAPCC, dimethylaminopyridinium chlorochromate; DMF, dimethyl formamide; DMSO, dimethylsulfoxide; DMT, dimethoxytrityl; DNA, deoxyribonucleic acid; DTA, differential thermal analysis; DTG, differential thermogravimetric; FABMS, fast atom bombardment mass spectroscopy; FAD, flavin adenosine dinucleotide; ICC, imidazolium chlorochromate; IDC, imidazolium dichromate; IFC, imidazolium fluorochromate; IR, infrared; LAH, lithium aluminum hydride; MCC, 1-methylimidazolium chlorochromate; MOM, methoxymethyl; MPM, methoxyphenylmethyl; MS, molecular sieves; NDC, nicotinium dichromate; NMR, nuclear magnetic resonance; PBC, pyridinium bromochromate; PCC, pyridinium chlorochromate; PDC, pyridinium dichromate; PFC, pyridinium fluorochromate; QBC, quinolinium bromochromate; QCC, quinolinium chlorochromate; QDC, quinolinium dichromate; QFC, quinolinium fluorochromate; RT, room temperature; SET, single-electron transfer; TBDMS, *tert*-butyldimethylsilyl; TBS, tributylsilyl; TCA, trichloroacetic acid; TG, thermogravimetric; THF, tetrahydrofuran; THP, tetrahydropyranyl; TIPS, triisopropylsilyl; TMS, trimethylsilyl; TsOH, *p*-toluenesulfonic acid.

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1. Introduction

Chromium(VI) is established as a versatile oxidant for many types of substrates varying from metal ions to naturally occurring organic compounds, and has a wide range of applications spanning the synthesis of sulfur nanoparticles[1] and the determination of biological oxygen demand in organic polluted water. In nature, chromium mostly exists in the Cr(VI) and Cr(III) forms, which differ widely in their physicochemical properties and biological reactivities.[2] Cr(VI) as chromate or dichromate is highly soluble in water, while Cr(III) as hydroxide is insoluble, and Cr(VI) is reported to be highly toxic,[3] while Cr(III) is an essential nutrient and is used as a dietary supplement.[4] The reduction of Cr(VI) in the presence of suitable biomolecules, leading to the formation of Cr(V), is believed to be responsible for the mutagenicity and carcinogenicity of Cr(VI).[5–8]

Cr(V) and Cr(IV) are formed as intermediates during oxidation by Cr(VI) when it comes into contact with any reductant. Two units of Cr(V), at neutral pH in aqueous solution, rapidly disproportionate through a bimolecular mechanism producing one Cr(VI) species and a reactive Cr(IV) intermediate, which ultimately leads to the final redox proportions of two Cr(VI) and one Cr(III) ions (Scheme 1).

$$2\,\mathrm{Cr(V)} \rightarrow \mathrm{Cr(IV)} + \mathrm{Cr(VI)}$$
$$\mathrm{Cr(IV)} + \mathrm{Cr(V)} \rightarrow \mathrm{Cr(VI)} + \mathrm{Cr(III)}$$
$$\overline{3\,\mathrm{Cr(V)} \rightarrow 2\,\mathrm{Cr(VI)} + \mathrm{Cr(III)}}$$

Scheme 1.

At more acidic pH values, disproportionation of the Cr(V) species is minimal and decomposition is slow.[9] Among the one-electron oxidants, Cr(V) and Cr(IV), the latter is found to have a reduction potential E^0=1.35 V and is therefore a stronger oxidant than the former with a redox potential of 1.29 V.[10] Using a bidentate ligand, 2-ethyl-2-hydroxybutanoate, the redox potentials for various Cr(V)/Cr(IV) couples were determined by Bose et al.[11] These complexes were reported to be responsible for carcinogenic activities due to oxidation of DNA.[12]

Chromium also exists in the oxidation states Cr(0), Cr(I), and Cr(II), but these are unable to act as oxidants.[13]

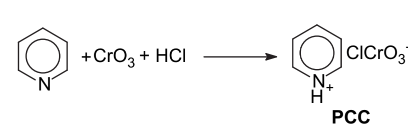
Before the discovery of onium chromates or dichromates, water-soluble potassium or sodium dichromates were in use with strong acids as oxidants and, in most cases, the products were non-specific. The first attempt to make the reagents mild was reported by Sarett and co-workers, who used pyridine to form a salt with CrO_3, a Lewis acid, in order to oxidize some steroidal alcohols.[14] This reagent was subsequently used by various workers without analyzing the structure of the oxidant.[15] Corey, in his novel attempt to establish pyridinium chlorochromate[16] as a versatile oxidant, revisited Sarett's reagent and discovered it to be pyridinium dichromate.[17] The present review deals with the synthetic applications and the kinetic studies of some non-conventional Cr(VI) oxidants having onium counterions.

2. Onium halochromates

2.1. Pyridinium chlorochromate

2.1.1. Synthetic applications.

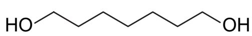
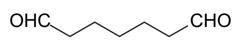
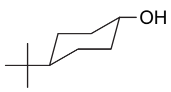
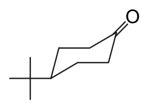
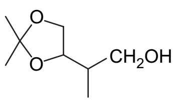
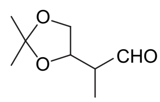
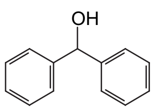
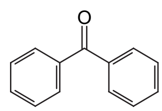
2.1.1.1. Reactions in solution. Pyridinium chlorochromate (PCC) was first prepared by the addition of pyridine to an equimolar mixture of hydrochloric acid and chromium trioxide at 0 °C (Scheme 2). The reagent is yellow-orange in color and is stable. It was applied to the oxidation of various primary and secondary alcohols to yield the corresponding carbonyl compounds (Table 1).[16]

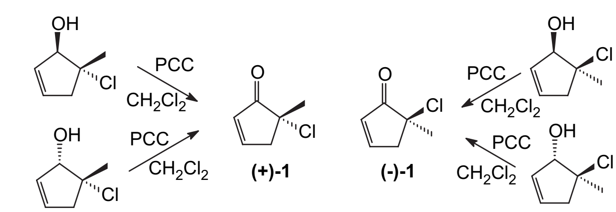


Scheme 2.

McMorris and Staake used PCC to oxidize the secondary hydroxy group of 5-chloro-5-methyl-2-cyclopenten-1-ol to the corresponding ketone (**1**) without affecting the stereochemistry of the adjacent carbon (Scheme 3).[18]

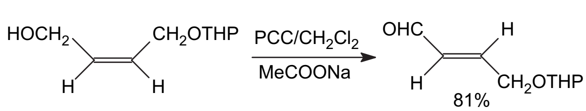
Table 1. Oxidation of primary and secondary alcohols with PCC (1.5 equiv; reaction time 1–2 h)

Substrate	Product	Yield (%)
Me−$(CH_2)_8$—CH_2OH	Me−$(CH_2)_8$—CHO	92
		68
		97
Me—$(CH_2)_4$—C≡C—CH_2OH	Me—$(CH_2)_4$—C≡C—CHO	84
		85
		100



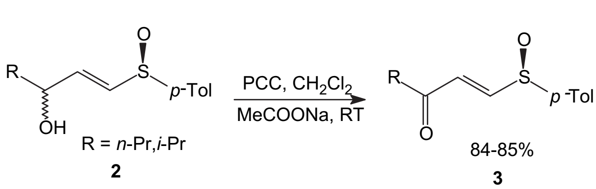
Scheme 3.

PCC is slightly acidic, the pH of 0.01 M solution being 1.75.[19] For the oxidation of compounds with acid-sensitive groups, e.g., tetrahydropyranyl ethers, the reaction mixture was buffered with powdered sodium acetate (Scheme 4).[16]

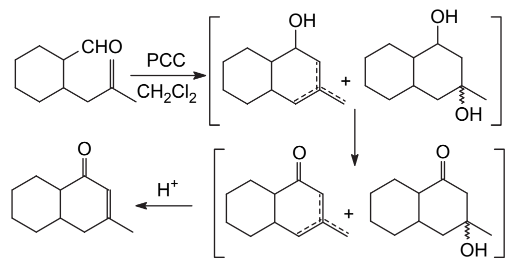


Scheme 4.

Recently, Ordonez et al. used a similar buffering methodology for oxidizing (*E*)-γ-hydroxysulfoxides (**2**) to the ketones (**3**) by PCC (Scheme 5).[20] Further, taking advantage of its mildly acidic nature, PCC was used in a one-pot synthesis of (−)-pulegone from (−)-citronellol in 70% yield.[21] The utility of PCC for the oxidative cationic ring fusion of some cyclic unsaturated alcohols or aldehydes was reported by Corey and Boger.[21] Efficient cyclization was observed only when the substrate was capable of affording a tertiary cation in the initial cyclic intermediate (Scheme 6).

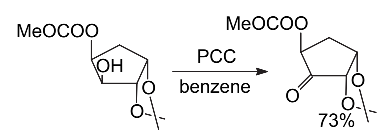


Scheme 5.

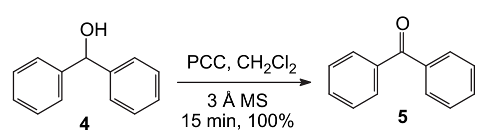


Scheme 6.

Oxidation of secondary hydroxy groups in sugars by using PCC in dichloromethane (DCM) was attempted by Hollemberg et al.[22] Substitution of benzene for DCM as the solvent improved the reactivity to a large extent and the corresponding ketones were obtained (Scheme 7). The reactivity of PCC in DCM for the oxidation of sugars was also improved by the addition of 3 Å molecular sieve (MS) powder.[23] By using this method, the oxidation of benzhydrol (**4**) afforded benzophenone (**5**) within 15 min, while the oxidation without MS took 90 min for completion (Scheme 8).

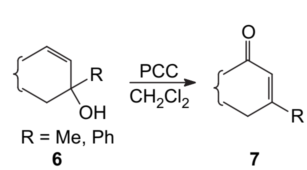


Scheme 7.

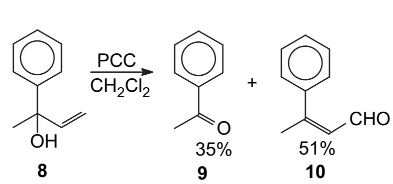


Scheme 8.

Generally, tertiary alcohols are inaccessible for oxidation by oxidants. With the appropriate substituents, however, PCC can transpose a tertiary alcohol, which is subsequently oxidized to the corresponding carbonyl compound. Dauben and Michno oxidized tertiary allyl alcohols (**6**) to the corresponding α,β-unsaturated ketones (**7**) (Scheme 9).[24] Oxidation of 2-phenyl-but-3-en-2-ol (**8**) by PCC also produced acetophenone (**9**) as a byproduct in addition to the usual transposed aldehyde (**10**) (Scheme 10).[25]

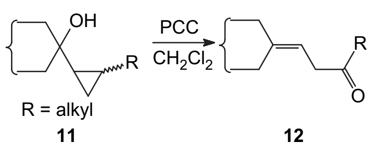


Scheme 9.



Scheme 10.

The similarity in reactivity of the cyclopropyl ring system to the allyl moiety has also led to a similar transposed mechanism for the oxidation by PCC. The tertiary alcohols (**11**) having a cyclopropane substituent were converted into the β,γ-unsaturated ketones (**12**) by using PCC in DCM (Scheme 11).[26] This mechanism prevailed in a reaction with epoxide ring systems having a tertiary α-hydroxy group. Ren et al. reported a facile one-pot synthesis of 1,3-diketones (**14**) with a stereogenic quaternary center at the C-2 position on the basis of an oxidative rearrangement of a series of α-hydroxy epoxides (**13**) in the presence of PCC (Scheme 12).[27,28]



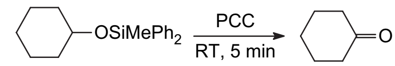
Scheme 11.

PCC was applied to an industrial preparation of some derivatives of cellulose aldehyde. Rui and Iguchi obtained the oxidized product by acetylating cellulose before oxidation by PCC.[29]

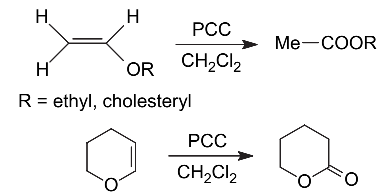
Selective oxidation of primary and secondary alcohols was achieved by PCC in the presence of trimethyl-, triethyl-, triisopropyl-, *tert*-butyldimethyl-, *tert*-butyldiphenyl, dimethyl-(1,1,2-trimethylpropyl)-, dimethyltrityl-, or *tert*-butylmethoxyphenyl-siloxy groups. Some of the reactions were carried out in the presence of sodium acetate, molecular sieves, Celite or neutral alumina.[30]

Alcohols with silyl protecting groups can be directly oxidized to the corresponding carbonyl groups by PCC. Trimethyl-,[31] triethyl-,[32] and methyldiphenylsilyl[33] ethers were rapidly oxidized to the aldehydes or ketones by PCC (Scheme 13). A primary trimethylsilyl ether showed preference over a secondary ether by PCC. This reaction is, however, less selective than that with a Collins reagent.[31] *tert*-Butyldimethyl,[32,34] *tert*-butylmethoxyphenyl-,[35] and *tert*-butoxydiphenyl-siloxy[36] groups were reported to be inert to PCC.

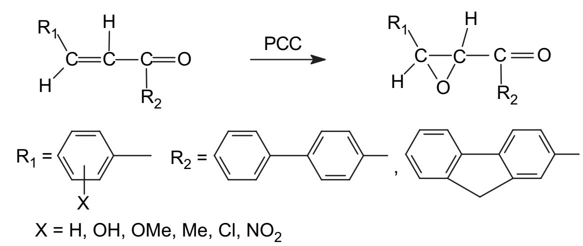
Cr(VI) oxidation of double bonds is limited to alkenes or their derivatives. Electron-rich enol ethers on allylic ketones were found to react with PCC to yield the esters and lactones (Scheme 14).[37] Oxidation of styryl biphenyl and styryl fluorenyl ketones by PCC in 90% acetic acid resulted in the formation of the corresponding epoxides (Scheme 15).[38]



Scheme 13.

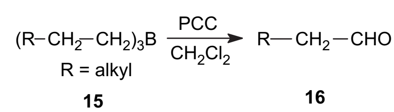


Scheme 14.



Scheme 15.

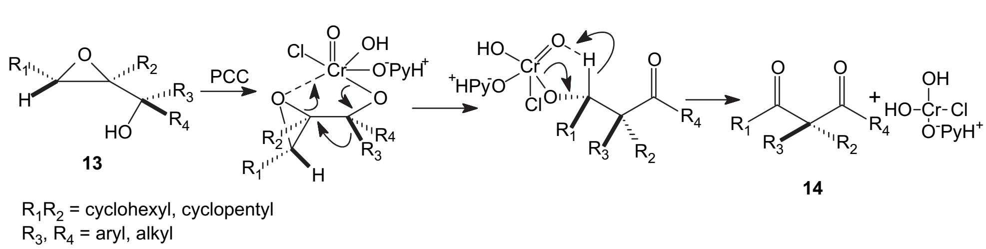
For the oxidation of organoboranes (**15**) to generate carbonyl compounds (**16**), PCC proved to be a superior reagent among the common oxidants (Scheme 16).[39]



Scheme 16.

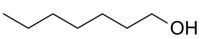
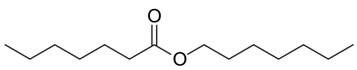
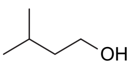
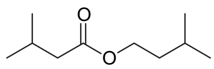
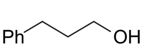
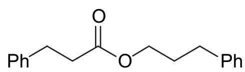
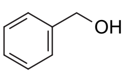
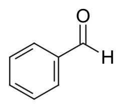
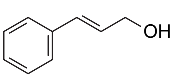
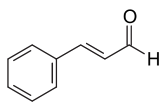
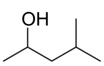
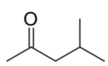
2.1.1.2. Reactions in solid phase. Solid-phase synthesis has emerged as a better technology in organic synthesis than synthesis in solution. It has contributed to green chemistry and, at the same time, it offers considerable advantages in terms of yield, selectivity, and simplicity in a reaction procedure.[40] PCC has been used in the solid phase by adsorption either on an alumina surface, a silica surface or a polymer surface. This modification of PCC has contributed to the catalysis of oxidation, moderating the acidity of PCC or simplifying the reaction workup.[41–43]

To decrease the acidic characteristics of PCC, Cheng et al. have used alumina for its adsorption.[42] PCC, adsorbed on a solid matrix, can efficiently oxidize primary and secondary alcohols to aldehydes and ketones, respectively. The oxidation of citronellol to citronellal without undergoing any



Scheme 12.

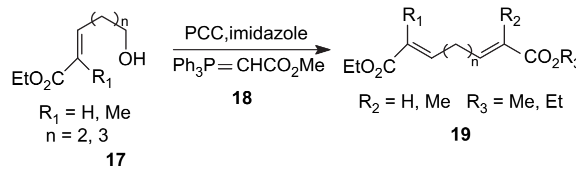
Table 2. Oxidation of primary alcohols using PCC on neutral alumina under solvent-free conditions

Substrate	Product	Yield (%)
		71
		65
		76
		82
		70
		83

cationic rearrangement is an additional advantage of using the reagent. PCC adsorbed on neutral alumina under solvent-free conditions was used to oxidize primary alcohols to alkyl alkanoates (Table 2).[44] Under these conditions, primary benzylic and allylic alcohols yielded the corresponding aldehydes, while secondary aliphatic and aromatic alcohols produced the ketones without isomerization and polymerization of the double bonds, over-oxidation and other side reactions. When both the alkyl and aryl alcoholic groups are present in the same molecule, the difference in reactivity of the alcohols gives rise to the formation of a cyclic product (Scheme 17).

PCC in conjunction with silica gel proved to be a better oxidant than in solution for organic substrates. Luzzio et al. demonstrated a classroom experiment for the oxidation of some primary alcohols on PCC-silica.[45] By activating PCC-silica using ultrasound waves, a remarkable increase in the yield of carbonyl compounds from the corresponding primary and secondary alcohols was observed.[46] For the synthesis of dienyl diesters (**19**), Phillips et al. oxidized α,β-unsaturated hydroxy esters (**17**) by silica-supported PCC and trapped the intermediate aldehydes with a Wittig reagent **18** ($Ph_3P{=}CHCO_2Me$) in a sequential one-pot procedure (Scheme 18).[47]

The allylic tertiary hydroxy group in 3-cyclohexene-1,2-diols (**20**) was oxidized by PCC-silica to yield the 1,4-dihydrobenzoquinones (**21**). The reaction followed a mechanism in which the secondary alcohol was initially oxidized to the corresponding ketone followed by subsequent transposition of the tertiary allylic alcohol and its oxidation and enolization that finally led to the product formation (Scheme 19).[48]



Scheme 18.

The aromatization of 1,4-dihydropyridines (**22**) to the corresponding pyridines (**23**) by PCC on various solid supports like alumina, silica gel, and montmorillonite (Scheme 20) was found to be more advantageous[49] than in solution. The solid matrix helps in the easy isolation of pure product from the gummy mass, which is mostly obtained in solution.[50]

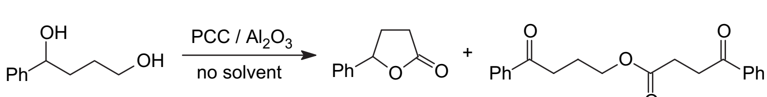
The oxidative transformations of alcohols (**24**), aldehydes (**25**), oximes (**26**), and cyclic acetals (**27**) afforded the corresponding oxidized products (**28–31**) using PCC under solvent-free conditions.[51] The oxidations of aromatic and cinnamylic aldehydes, which do not occur by PCC in solution, were found to produce the corresponding acids in solvent-free conditions (Scheme 21). The oxidative coupling of different types of mercaptans (**32**) to disulfides (**33**) by PCC was also undertaken in solvent-free conditions and the reactivity was compared with that in dichloromethane.[52] No appreciable differences in the yield was observed (Scheme 22).

Oxidative deprotection of the carbonyl group in oximes, phenyl hydrazones, and semicarbazones was attempted by using PCC in a catalytic amount (0.1 equiv) in the presence of *tert*-butyl hydroperoxide and on montmorillonite K-10 clay separately.[53] In the former conditions, the yield was found to be within 70–98% with a reaction time of more than hours, but, in the latter case, the reaction was completed within 6 min under microwave irradiation. The yield in the latter case was also appreciably high.

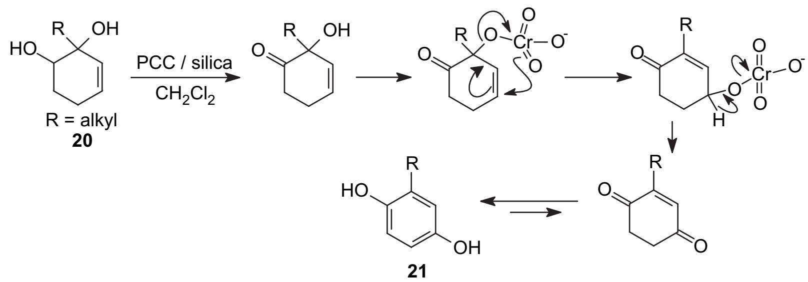
The use of PCC for the determination of some antibiotics containing multifunctional groups was reported recently by Dubey and Shukla. They claimed this method to be highly efficient with an error of 1%.[54]

2.1.2. Reaction kinetics. After the discovery of PCC as an oxidant to be used in a non-aqueous medium, Banerji made the first attempt to investigate the reaction mechanism of the oxidation of organic substrates by PCC.[55] From the first-order rate dependence of the substrate and the oxidant, and the kinetic isotope effect (for ethanol 5.71 at 303 K) in the oxidation of some primary alcohols by PCC, he proposed a hydride-ion transfer mechanism for the oxidation reaction (Scheme 23).

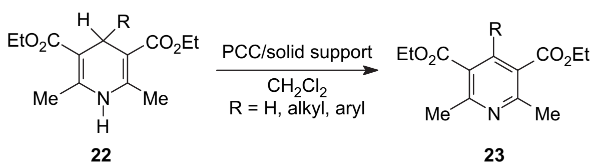
From the oxidation kinetics of substituted styryl phenyl ketones (**34**) and substituted styryl methyl ketones (**35**) by PCC in 90% acetic acid in the presence of perchloric acid, Nadar and co-workers proposed a mechanism involving a three-



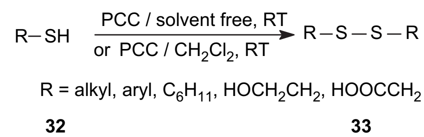
Scheme 17.



Scheme 19.



Scheme 20.



Scheme 22.

center-type addition of PCC and the styryl ketone, which, on rearrangement, forms the corresponding epoxide (**36**) (Scheme 24).[56] This work was extended to kinetic studies of the oxidation of substituted styryl-4-biphenyl ketones (**37**) and substituted styryl-2-fluorenyl ketones (**38**) using PCC.[38] In this case, the reaction mechanism involves a nucleophilic attack of PCC, leading to an unsymmetrical intermediate, from which the epoxides (**39**) are formed (Scheme 25).

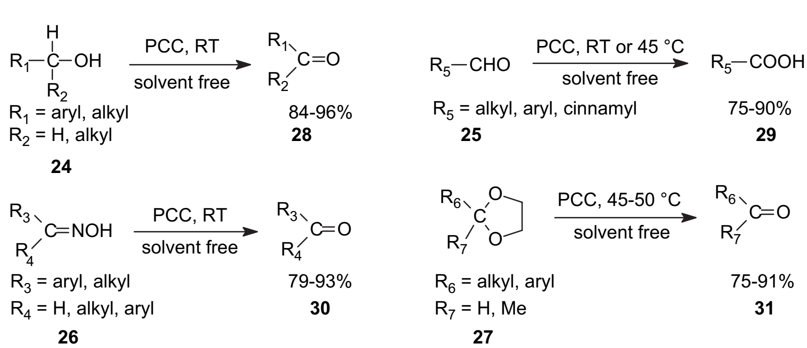
The rate of the oxidation reaction of aliphatic aldehydes (**40**) by PCC in dimethylsulfoxide (DMSO), producing the corresponding carboxylic acids (**41**), was found to be first order with respect to each of PCC, substrate, and added acid.[57] From the primary kinetic isotope effect (for MeCDO, k_H/k_D=6.12) and the solvent effect, the existence of an electron-deficient carbon center in the transition state was proposed. The reaction proceeds via a nucleophilic attack on the carbonyl group by PCC, forming a chromate ester, which subsequently undergoes decomposition through a five-membered cyclic transition state (Scheme 26).

Rajasekaran et al.[58] undertook kinetic studies of the oxidation of some *para*-substituted phenyl methyl sulfides such as **42** by using PCC in dipolar protic and aprotic solvents to yield the corresponding sulfoxides, e.g., **44**. From the Hammett reaction constant (ρ=−2.12) and other kinetic parameters, they proposed a reaction mechanism involving a three-membered electron-deficient cyclic transition state (**43**) (Scheme 27). In protic solvents, the reaction follows a second-order rate law, while, in aprotic solvents, the decomposition of the complex into the products follows Michaelis–Menten kinetics. The above observation indicates that the formation of the complex between the sulfide and PCC is the rate-limiting process in protic solvents, while the decomposition is the rate-determining process in aprotic solvents.

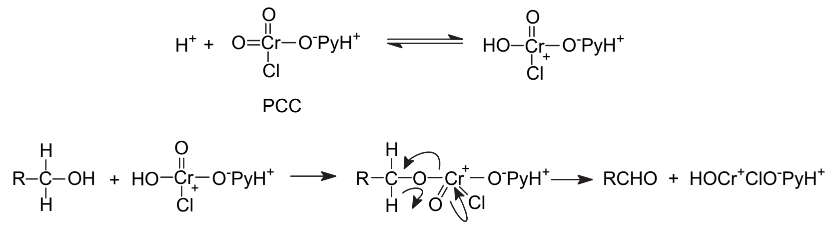
The regeneration of carbonyl compounds (**46**) from the respective oximes (**45**) can be achieved by PCC.[59] The kinetics of this reaction were followed in a DMSO solvent and it was found that the ketoximes are less reactive than aldoximes. A low positive value of the polar reaction constant indicates a nucleophilic attack by a chromate oxygen on the carbon. For the formation of the product, a mechanism involving a cyclic transition state was proposed (Scheme 28).

Inorganic species like thallium(I)[60] and tellurium (IV)[61] underwent oxidation by PCC to thallium(III) and tellurium(VI) exhibiting second-order kinetics involving Tl(II) and Te(V) as intermediates, respectively. The kinetics and mechanism of the oxidation of phosphite by PCC were investigated by Virkar and Gokavi.[62]

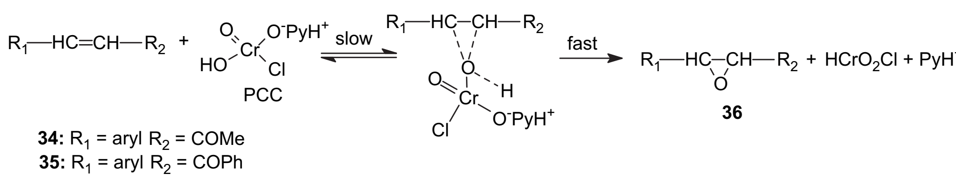
The mechanism of the co-oxidation of benzaldehyde and oxalic acid by PCC was investigated by running the kinetics in a 50% acetic acid medium.[63] The products were found to be benzoic acid and carbon dioxide, respectively. A cyclic



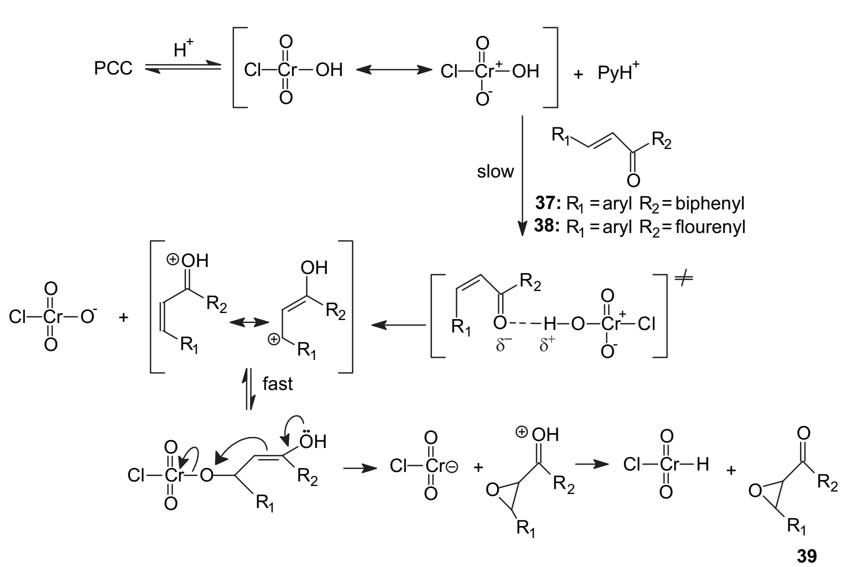
Scheme 21.



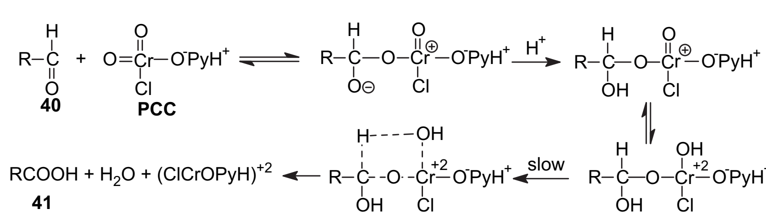
Scheme 23.



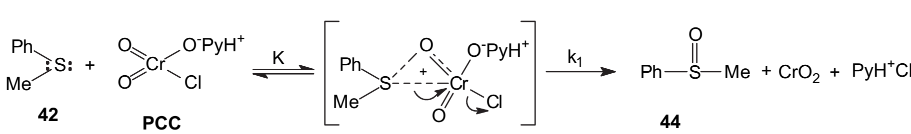
Scheme 24.



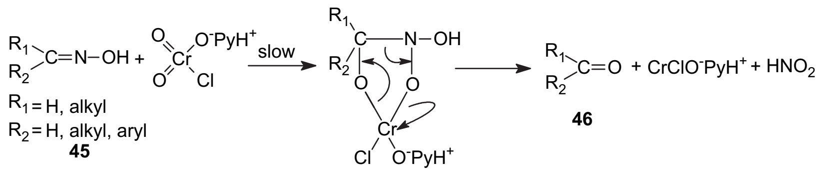
Scheme 25.



Scheme 26.



Scheme 27.

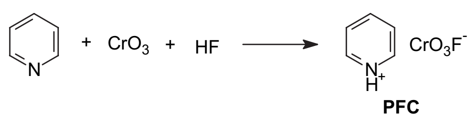


Scheme 28.

ternary complex was proposed to be involved in the rate-determining step.

2.2. Pyridinium fluorochromate

Pyridinium fluorochromate (PFC) was prepared from a solution of CrO_3 in HF and pyridine at an ice-cold temperature (Scheme 29).[19] With a 1:1:1 stoichiometry of the reactants, PFC was obtained in 99.2% yield.[64]



Scheme 29.

Pyridinium fluorochromate, $C_5H_5NH[CrO_3F]$, was also prepared by reacting CrO_3 with NH_4HF_2 in the presence of pyridine.[65] From X-ray diffraction studies, PFC crystals were found to be orthorhombic consisting of discrete pyridinium ($C_5H_5NH^+$) cations and fluorochromate $[CrO_3F]^-$ anions with a crystallographic mirror plane passing through the chromium, one oxygen, and a fluorine atom.

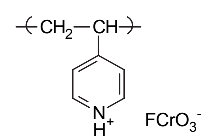
Pajak et al.[66] determined the crystal structure, molecular dynamics, and polar properties of pyridinium fluorochromate at 293, 240, and 150 K by X-ray diffraction and ^1H and ^{19}F nuclear magnetic resonance spectroscopy. The low-temperature phase was well ordered and the two high-temperature phases revealed molecular disorder of both pyridinium and fluorochromate ions.

Chaudhuri et al. used this reagent in the selective oxidation of secondary alcohols in the presence of primary alcohols and in the conversion of polycyclic hydrocarbons into cyclic ketones, benzoin into benzil, PPh_3 into $O{=}PPh_3$, methyl phenyl sulfide into the corresponding sulfoxide, cyclohexanone oxime into cyclohexanone and in the deprotection of dioxolanes and dithiolanes to aldehydes.[64] PFC was also applied to oxidize allylic Δ^5-steroids to α,β-unsaturated ketones.[67]

Pyridinium fluorochromate has been applied to a selective oxidation of secondary hydroxy groups in the presence of primary or secondary *tert*-butyldimethylsiloxy groups and the selectivity was found to be higher than that of PCC.[68] The selectivity was attributed to the lower acidity of PFC than PCC. Ho and Jana reported the desilylative oxidation of alkyl trimethylsilyl ethers to the corresponding carbonyl compounds with PFC.[69]

The oxidation of vasicine (**47**) with PFC in an acidic medium afforded vasicinone (**48**) as the major product, in which the 3-OH group was not oxidized, along with other minor oxidation products (**49**, **50**, and **51**) (Scheme 30). The formation of vasicinone (**48**) was explained by the authors on the basis of the distance between the two nitrogen atoms and the oxygen center forming an N–N–O triangle, leading to the ease of attack at position 9 of vasicine for oxidation.[70]

Similarly the oxidation of Δ^3-carnene (**52**) and α-pinene (**53**) with PFC afforded some novel oxidation products **54**–**56** and **57** and **58**, respectively, in an acidic medium (Scheme 31).[71]

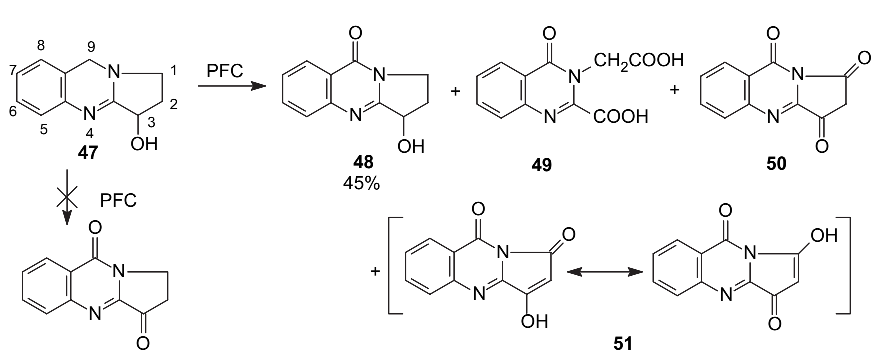


poly[vinyl(pyridinium)] fluorochromate

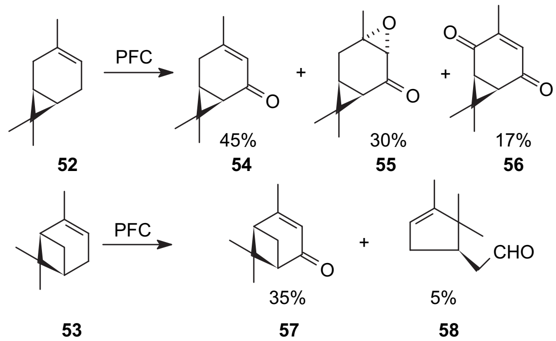
59

PFC, when attached to a polyvinyl system (**59**), can oxidize α,β-unsaturated alcohols efficiently.[72]

The kinetics and mechanism of the oxidation of alcohols by PFC have been investigated by several research groups[73,74] and the mechanism was found to be almost the same as that proposed for PCC.[74] While oxidizing some substituted oxanols by PFC, Mangalam et al. observed a conformational effect on the rate of oxidation.[75] The rate of oxidation of **60** having an axial hydroxy group was found to be faster than

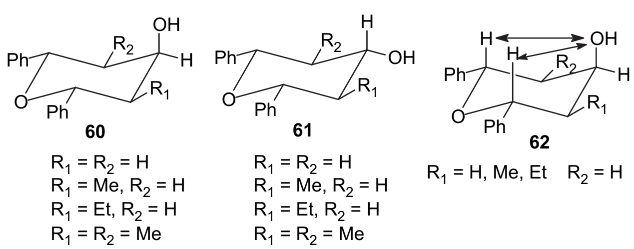


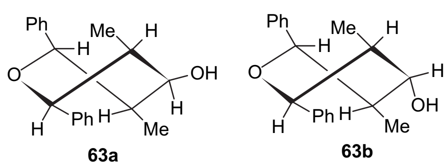
Scheme 30.



Scheme 31.

that of the corresponding equatorial epimer (**61**). A non-bonded steric interaction (**62**) was proposed to exist in the former compound. Further, to explain the reactivity for a strained system like 2,6-diphenyl 3,5-dimethyl-oxan-4-ol, the existence of a twist conformation (**63a**,**b**) was proposed.



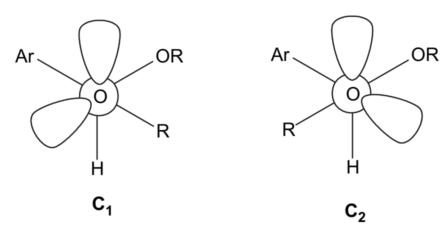


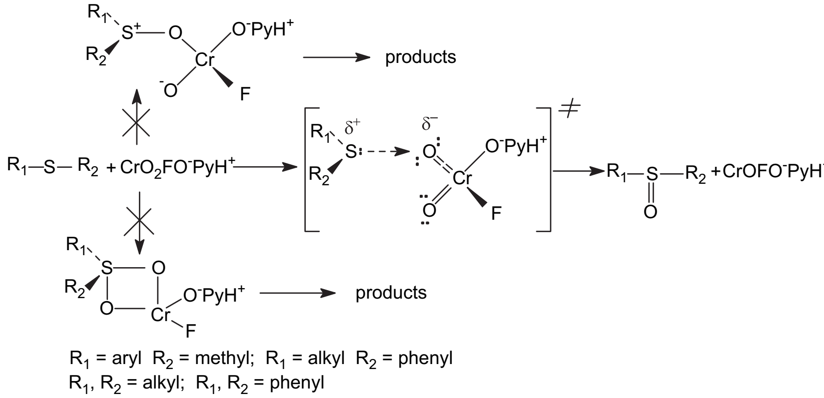
Banerji investigated the oxidation kinetics of organic sulfides by PFC in various solvents and proposed a mechanism involving a one-step electrophilic oxygen transfer from PFC to the sulfide, forming a polar transition state (Scheme 32).[76] He ruled out the formation of the charged and cyclic transition states, due to the highly polar structure and steric constraints. From the kinetic isotope effect and the solvent effect, a cyclic transition state was proposed for the oxidation of secondary alcohols.[77]

Investigations of the kinetics of oxidation of some cyclic ketones such as cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone, and various α-substituted cyclohexanones by PFC were conducted to evaluate the effect of the ring size on the rate of oxidation.[78] The oxidation yielded the corresponding 1,2-diketones. The relative reactivities of the cyclic ketones were rationalized on the basis of conformational differences and steric factors. For the oxidation of alicyclic ketoximes by PFC, the order of reactivity was cyclohexanone oxime>cyclopentanone oxime>cycloheptanone oxime, due to I-strain.[79]

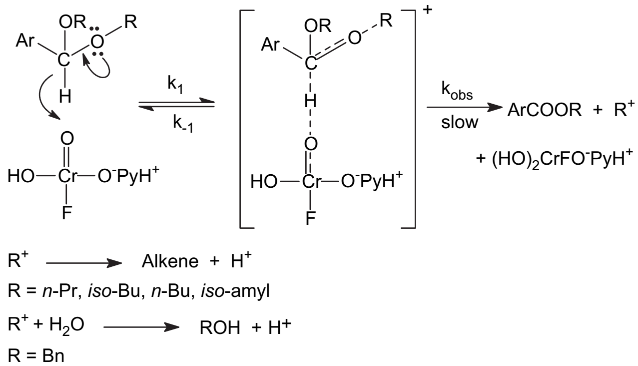
Bhandari et al.[80] investigated the oxidative regeneration of carbonyl groups from the corresponding oximes and proposed the involvement of a cyclic intermediate in the rate-determining step. In the presence of hydrogen peroxide[81] and wet alumina,[82] the yield was found to be improved. In a mechanistic study of the oxidation of phenols by PFC, Patil and Joshi[83] observed an increase in the rate, due to an increase in the solvent polarity, which suggests that the transition state is polar. PFC was also used for the oxidation of DL-methionine,[84] diphenyl nitrones,[85,86] salicylaldehyde,[87] β-benzoylpropionic acid,[88] and tetrahydrothiopyran-4-ones and their 1,1-dioxides.[89]

The kinetics of oxidation of aromatic acetals by PFC in an aqueous acetic acid medium were reported to be first order each in acetal and PFC.[90] From the substituent effect, the salt effect, and the solvent effect, a mechanism was proposed in which the transition state is less polar than the reactant (Scheme 33). The presence of electron-withdrawing substituents increases the rate of oxidation, while electron-donating substituents retard it. The order of reactivity was attributed to the stability of the carbocation formed during cleavage of the O–R bond and the conformation of the acetals (C_1 and C_2) with less torsional energy.





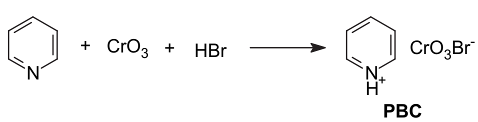
Scheme 32.



Scheme 33.

2.3. Pyridinium bromochromate

Pyridinium bromochromate (PBC) was synthesized by the addition of a solution of CrO_3 in HBr to pyridine, similar to the preparations of PCC and PFC (Scheme 34), and was used for various oxidation reactions.[91] PBC can also be used for the bromination of aromatic compounds.[91,92]

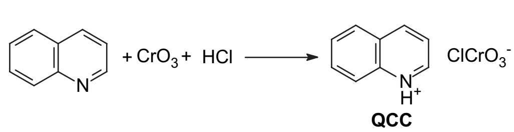


Scheme 34.

The kinetics of oxidation of benzhydrol,[93] methionine,[94] oxalic and formic acid,[95] aliphatic aldehydes,[96] benzyl alcohol,[97] aliphatic alcohols,[98] thioacids,[99] organic sulfides,[100] and amino acids[101] were carried out mostly in aqueous acetic acid. Recently, a study on the oxidative de-oximation of several ald- and ket-oximes by PBC in dimethylsulfoxide exhibited a first-order dependence on both the reductant (oxime) and the oxidant (PBC).[102] The oxidation of ketoximes was found to be slower than that of aldoximes. The rates of oxidation of aldoximes correlated well with the substituent parameters. The low positive values of the polar reaction constants indicated a nucleophilic attack by a chromate oxygen on the carbon.

2.4. Quinolinium chlorochromate

Quinolinium chlorochromate (QCC) is a mild and selective oxidant prepared by the treatment of chromium trioxide in HCl with quinoline (Scheme 35).[103] It was effectively used for the oxidation of alcohols to the corresponding carbonyl compounds.[104] A de-oximation reaction by using QCC under microwave irradiation was undertaken by Singh et al.[105] In most of the cases, the yield was higher than that using the conventional solution method. The time required for the oxidation was also remarkably less.



Scheme 35.

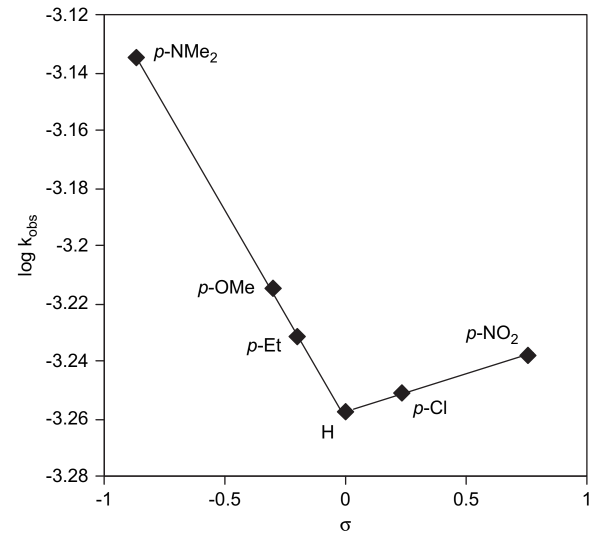


Figure 1. Hammett plot for the oxidation of substituted benzaldehydes by QCC in water–DMF mixtures at 25 °C (Ref. 107).

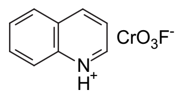
In the oxidation of benzyl alcohol in DMSO and DCM, the Hammett relationship between the rate and the substituent parameters led to a negative reaction constant, indicating a positively charged reaction center in the rate-limiting step. From the primary kinetic isotope effect, a cyclic hydride-transfer reaction involving a Huckel-type sigmatropic mechanism was proposed by Ozgun and Degirmenbasi.[106]

Jeyanthi et al.[107,108] investigated the effect of the solvent on the kinetics of oxidation of substituted benzaldehydes by QCC in aqueous–organic solvent media. They used both non-specific and specific solvent–solute interactions for analyzing the kinetic results and, from the nonlinear plot of log *k* versus substituent constant comprising two distinct lines, they proposed a dual mechanism (Fig. 1).[107] The electron-releasing groups in the benzaldehyde facilitate the formation of an oxidant–substrate complex, while the decomposition of the complex is accelerated by the presence of electron-withdrawing groups.

The kinetics of oxidation of furfural,[109] allyl alcohols,[110] 2,6-diphenyl-piperidin-4-ones,[111] D-fructose,[112] D-glucose,[113] D-mannose,[114] D-galactose,[115] methionine,[116] acrylic acid,[117] crotyl alcohol, crotonaldehyde, and maleic acid,[118,119] and some other unsaturated compounds[120] by QCC in aqueous acetic acid were investigated by various workers.

2.5. Quinolinium fluorochromate

The synthesis of quinolinium fluorochromate (QFC) (**64**) involves the treatment of quinoline with a solution of chromium trioxide in 40% aqueous hydrofluoric acid in a molar ratio of 1:1.5:1.[121,122] QFC is air stable and can be kept for a long period without decomposition. It is acidic (pH of 0.01 M solution: 2.65), but the acidity is less pronounced than that of PCC (pH of 0.01 M solution: 1.75). It is soluble in water and other polar organic solvents, sparingly soluble in dichloromethane and chloroform and insoluble in benzene, heptane, and ether. At a 1:1.5 M ratio of substrate:oxidant, alcohols can be oxidized to the corresponding aldehydes without over-oxidation or any side reactions.



64

Selective oxidation of certain aliphatic and aromatic alcohols and de-oximation of aromatic aldoximes and ketoximes to the corresponding carbonyl compounds were brought about by using QFC in dichloromethane.[123] Primary alcohols were found to be oxidized faster than secondary alcohols by this reagent. Oxidation of hydrazones by QFC in acetonitrile also afforded the corresponding carbonyl compounds.[124]

The chemoselectivity of QFC was found to be significant in the oxidation of various types of thioamides and thioureas to obtain corresponding oxo products. In a competitive deprotection reaction of thioamides, thioureas, thionoesters, and thioketones, the thioamide and thiourea moieties were selectively converted into the corresponding carbonyl groups in the presence of the other two functional groups (Scheme 36).[125]

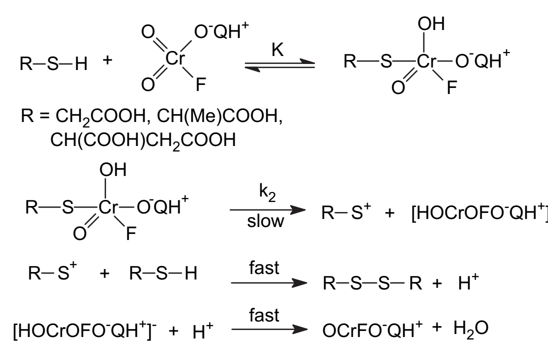
The oxidative cleavage of thiones was extended to thioacetals, which can be deprotected to the parent carbonyl compounds.[126] QFC supported on a solid support has proved to be a selective, stable, and versatile oxidant to oxidize alcohols and in the oxidative de-oximation of aldoximes and ketoximes.

Rajkumar et al. studied the oxidation behavior of QFC supported on alumina[127,128] and silica gel[129] on various substrates. A study on the stereochemical preference of QFC-silica gel in the oxidation of *cis*- and *trans*-*tert*-butylcyclohexanol indicates that the axial hydroxy group of the cis isomer is oxidized faster in higher yield than the equatorial hydroxy group of the trans isomer (Scheme 37).

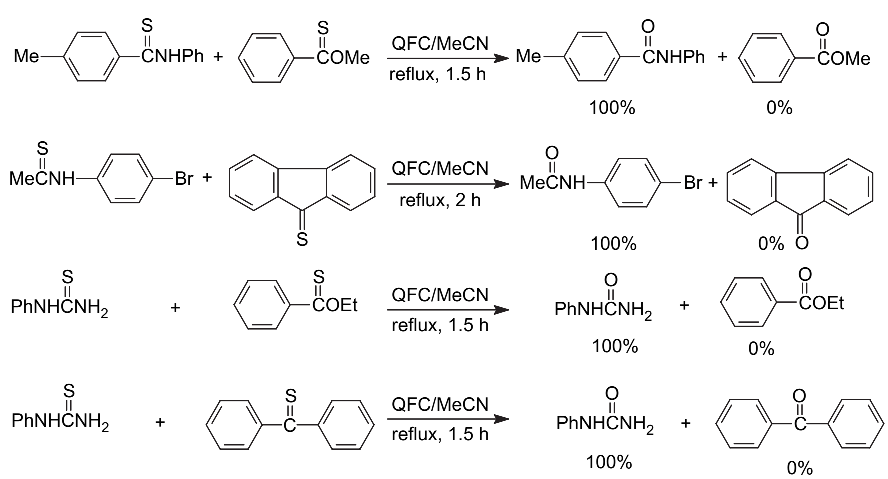
Studies on the oxidation kinetics of various substrates using QFC were initiated by Murugasen and Pandurangan.[130] From the relationship between the rate of oxidation of substituted benzyl alcohols with the Hammett substituent constants, the existence of an electron-deficient reaction center in the rate-determining step was proposed.[131] Further, the reaction was found to exhibit a steric acceleration due to *ortho* substituents.

The oxidation reaction of some vicinal and non-vicinal diols was found to be first order in QFC and the rate of the reaction obeys a Michaelis–Menten relationship with the substrate.[132] From the solvent effect on the reaction kinetics and the primary isotope effect, a symmetrical transition state in the rate-limiting step was proposed.

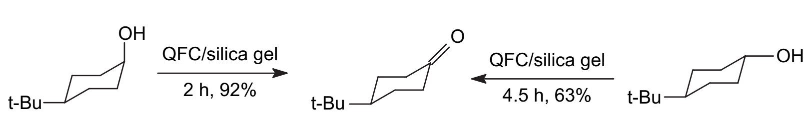
The oxidation of thioglycollic, thiolactic, and thiomalic acid by QFC in DMSO proceeds through a two-electron transfer mechanism to form the corresponding disulfides.[133] This reaction involves the formation of a thioester in the pre-equilibrium state and its subsequent decomposition to a sulfenium ion in the slow step (Scheme 38). The oxidation reactions of formic and oxalic acid in DMSO obey the Michaelis–Menten equation and exhibit a high primary



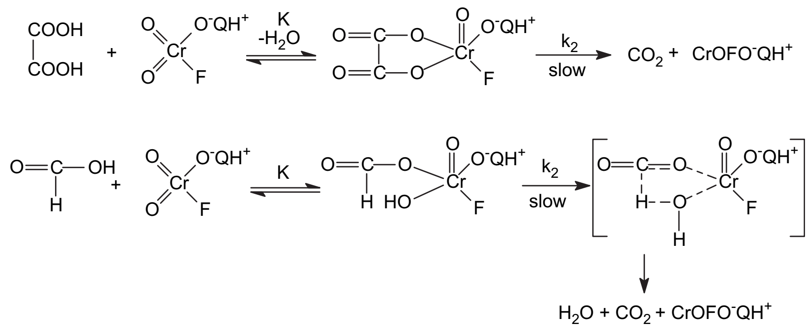
Scheme 38.



Scheme 36.



Scheme 37.



Scheme 39.

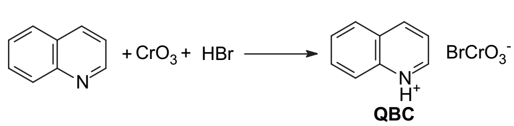
isotope effect (k_H/k_D=6.01). The kinetic parameters and the studies on the solvent effect support the formation of a five-membered cyclic transition state complex for oxalic acid (Scheme 39).[134]

The reaction kinetics of the oxidative generation of a carbonyl group from oximes by QFC was monitored in DMSO solvent by Dave et al.[135] The oxidations of ketoximes were found to be slower than those of aldoximes. A low positive value of the polar reaction constant indicated a nucleophilic attack by a chromate oxygen on the carbon.

The oxidation of methionine to the corresponding sulfoxide by QFC was investigated by various workers.[136,137] Bhuvaneshwari et al.[136] observed a contrasting solvent effect on the rate of oxidation by using two sets of solvent mixtures, i.e., water–acetic acid and water–DMSO. The reaction rate was found to increase with an increase in the mole fraction of acetic acid in the former, where a specific solvent–solvent–solute interaction was found to be dominant, while, in latter, the rate decreased with increasing mole fraction of DMSO, where the transition state was stabilized to a lesser extent by the solvation.

2.6. Quinolinium bromochromate

Quinolinium bromochromate (QBC), which was prepared using a similar method to that for QCC (Scheme 40), is a mild and a selective oxidizing agent.[138] It has also been found to be useful as an efficient brominating agent.[139]

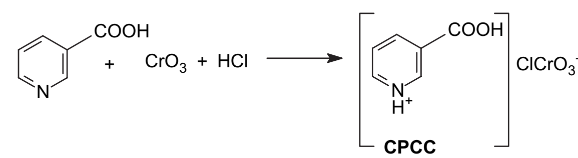


Scheme 40.

Saraswat et al.[140] investigated the oxidation kinetics of some primary alcohols by QBC in DMSO. From the effect of the solvents, isotope exchange, and other kinetic parameters, and by comparison with other halochromates, they proposed that the reactivity depends on the nature of the halogen present in the Cr(VI) and not significantly on the nature of the base. The kinetics and mechanism of the oxidation of substituted benzyl alcohols,[141] diols,[142] α-hydroxy acids,[143] secondary alcohols,[144] aliphatic aldehydes,[145] substituted benzaldehydes,[146] formic and oxalic acids,[147] unsaturated acids,[148] and amino acids[149] using QBC were investigated in DMSO or aqueous acetic acid. A mechanism involving the transfer of hydride ion from the substrate to the oxidant, via a chromate ester, was proposed in many cases.

2.7. 3-Carboxypyridinium chlorochromate

3-Carboxypyridinium chlorochromate (CPCC) was prepared from 3-carboxypyridine, chromium trioxide, and HCl (Scheme 41). With this reagent, oximes, phenyl hydrazones, *p*-nitrophenyl hydrazones, semicarbazones, and azines can be converted into the corresponding carbonyl compounds under non-aqueous conditions.[150]

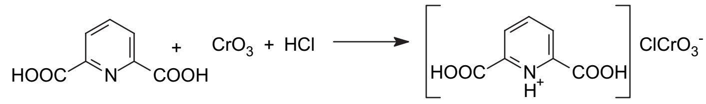


Scheme 41.

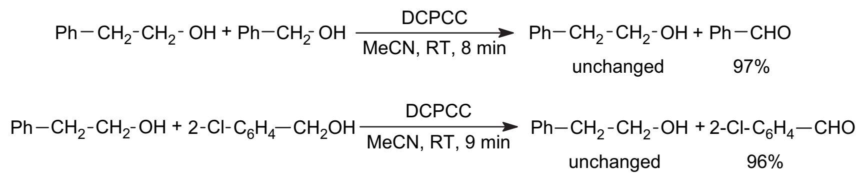
CPCC supported on alumina oxidize alcohols to the carbonyl compounds under solvent-free conditions and the reaction can be expedited by microwave irradiation.[151,152] In the oxidative deprotection of primary and secondary trimethylsilyl and tetrahydropyranyl (THP) ethers to their carbonyl compounds under non-aqueous conditions, the former were oxidized selectively in the presence of THP.[153] CPCC in the presence of aluminum chloride can selectively oxidize sulfides to sulfoxide and sulfones in solution and under microwave irradiation. It is noteworthy that different functional groups including carbon–carbon double bonds, ketones, oximes, aldehydes, ethers, and acetals are stable under these reaction conditions.[154] A variety of 1,4-dihydropyridines were oxidized to their corresponding pyridines in excellent yields by CPCC.[155] Different types of thioamides, thioureas, thionoesters, and thioketones were deprotected to their corresponding carbonyl compounds with this reagent in good to excellent yields. The reactions were carried out in solution, under solvent-free conditions and under microwave irradiation. The results showed that the rates of the reactions and the yields were usually highest under microwave irradiation.[156]

2.8. 2,6-Dicarboxypyridinium chlorochromate

2,6-Dicarboxypyridinium chlorochromate (DCPCC) can be prepared by the reaction of pyridine-2,6-dicarboxylic acid with chromium trioxide in 6 N hydrochloric acid (Scheme



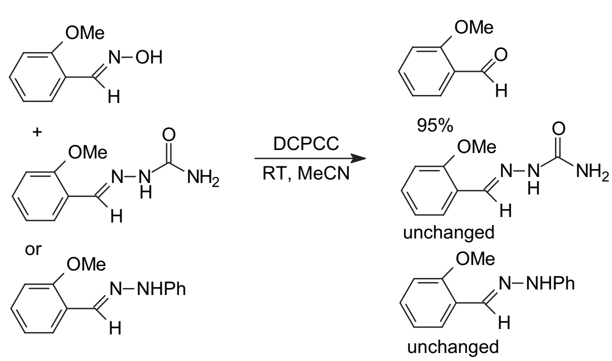
Scheme 42.



Scheme 43.

42).[157,158] DCPCC is soluble in polar solvents, slightly soluble in chloroform and dichloromethane and insoluble in benzene, hexane, and carbon tetrachloride. The compound is stable at room temperature and can be kept for a long period without losing its oxidation activity. The pH of a 0.01 M aqueous solution of this compound is 2.3, which is less acidic than that reported for 3-carboxypyridinium chlorochromate (2.02)[150] and pyridinium chlorochromate (1.75).[19]

DCPCC was used for the oxidation of semicarbazones, hydrazones, and oximes to the corresponding carbonyl compounds,[157] alcohols, silyl ethers, and tetrahydropyran ethers to the carbonyl compounds,[158] thiols to disulfides, disulfides to sulfoxides,[159] and for the oxidative deprotection of acetals, thioacetals, and 1,1-diacetates to the carbonyl compounds.[160] Selective deprotection of acetals or 1,1-diacetates in the presence of thioacetals at room temperature was also undertaken with this reagent. The reagent was able to selectively oxidize the hydroxy group in the presence of other oxidizable functional groups and benzylic alcohols in the presence of other primary or secondary hydroxy groups (Scheme 43).[158]

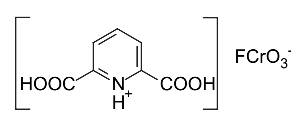


Scheme 44.

Another noteworthy advantage of this reagent is the exclusive oxidation of oximes, irrespective of the presence of semicarbazones or phenyl hydrazones (Scheme 44). Oxidation of semicarbazones or phenyl hydrazones requires a higher molar ratio of oxidant, a much longer reaction time, a reflux temperature in acetonitrile and gives low yields.[158]

2.9. 2,6-Dicarboxypyridinium fluorochromate

2,6-Dicarboxypyridinium fluorochromate (DCPFC: **65**) was prepared by using HF instead of HCl in the corresponding chlorochromate and was used for the oxidation of alcohols, phenols, and hydroquinones,[161] for the oxidative deprotection of trimethylsilyl ethers to their corresponding carbonyl compounds[162] and for the oxidative deprotection of oximes, phenyl hydrazones, and semicarbazones to their corresponding carbonyl compounds under solvent-free conditions.[163]

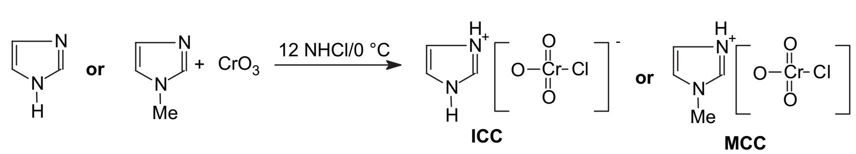


DCPFC

65

2.10. Imidazolium and 1-methylimidazolium chlorochromate

Imidazolium chlorochromate (ICC: **66**) and 1-methylimidazolium chlorochromate (MCC: **67**) were prepared by adding 12 N hydrochloric acid dropwise to the corresponding bases and chromium trioxide with constant stirring at 0 °C (Scheme 45).[164] These reagents show a similar selectivity and mechanism for the oxidation of alcohols to those of PCC. From the deuterium kinetic isotope effect, Agarwal et al.[164] suggested that the mechanism of oxidation of



Scheme 45.

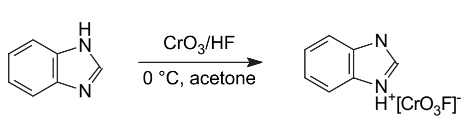
alcohols by PCC, ICC or MCC is not a simple one-step process as reported earlier by Banerji,[55] but it is a series reaction. The initial step involves the transfer of a hydrogen atom from the OH group of the alcohol to the oxidant in order to form the oxidant–substrate ester, which follows transfer of two electrons in a cyclic system.

2.11. Imidazolium fluorochromate

Imidazolium fluorochromate (IFC) was prepared and utilized in the oxidation of primary and secondary alcohols and in the oxidative de-oximation of ketoximes to the corresponding carbonyl compounds at room temperature.[165] The oxidation of methionine by IFC was studied in the presence of chloroacetic acid in water–acetic acid mixtures of varying molar compositions. The reaction rate was found to increase with increasing mole fraction of acetic acid in the mixture and specific solvent–solvent–solute interactions were found to predominate (86%), for which a solvation model was proposed.[166] The dependence of the reactivity on solute–solvent interactions was further supported by the kinetic data of the oxidation of *meta*- and *para*-substituted anilines by IFC in the presence of *p*-toluenesulfonic acid (TsOH).[167] The reaction was first order in IFC and TsOH and zero order with respect to the substrate. From a correlation of the rate data with the Kamlet–Taft solvatochromic parameters (α, β, π^*),[168] it was suggested that specific solute–solvent interactions play a major role in governing the reactivity.

2.12. Benzimidazolium fluorochromate and bromochromate

Benzimidazolium fluorochromate (BIFC) was prepared from benzimidazole, 40% hydrofluoric acid, and chromium trioxide in a molar ratio of 1:1.3:1 at 0 °C (Scheme 46).[169] The reagent was used for the oxidation of a wide range of alcohols such as primary, secondary, aromatic, aliphatic, and alicyclic alcohols under solvent-free conditions. In the oxidation of substituted benzaldehydes, electron-donating substituents afforded higher yields within shorter reaction times than electron-withdrawing substituents. Further, the lower acidic character of BIFC (pH of 0.01 M solution= 3.68), compared to PCC (pH of 0.01 M solution=1.75), increases the mildness of the reagent, which prevents the formation of pulegone by oxidative cyclization in the oxidation of citronellal.

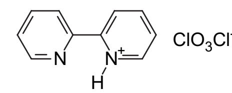


Scheme 46.

Benzimidazolium bromochromate (BIBC) was also prepared in the same way from benzimidazole, hydrobromic acid, and chromium trioxide by Ozgun et al. and was used for the oxidation of various organic substrates.[170]

2.13. 2,2-Bipyridinium chlorochromate

2,2-Bipyridinium chlorochromate (BPCC: **68**) was first prepared by Guziec and Luzzio from 2,2-bipyridine, chromium trioxide, and hydrochloric acid.[171] The oxidation kinetics by using BPCC were investigated for secondary alcohols,[172] aliphatic aldehydes,[173] α-hydroxy acids,[174] unsaturated acids,[175] and organic sulfides.[176]



68

2.14. Other onium halochromates

With the availability of a wide number of bases, there is scope for the proliferation of the onium halochromates with the objective of finding a more chemoselective and milder reagent. Some further examples of onium halochromates are presented in Table 3.

3. Onium dichromates

3.1. Pyridinium dichromate

3.1.1. Synthetic applications. Pyridinium dichromate (PDC) was synthesized by the gradual addition of pyridine to a cooled solution of chromium trioxide in water, maintaining the temperature under 30 °C (Scheme 47).[17] After dilution with acetone and cooling to −20 °C, PDC was collected as orange crystals with a good yield.

This reagent can also be prepared in situ from an alkali metal or ammonium dichromate and pyridine hydrochloride.[208] The high solubility in water, DMF, DMSO, and DMA contributes to the versatility of the reagent for organic substrates. It is sparingly soluble in dichloromethane, chloroform, and acetone. The insolubility in hexane, toluene, ether, and ethyl acetate indicates the compound to have ionic characteristics. PDC is unstable in acetonitrile solution.

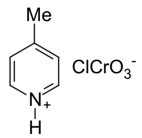
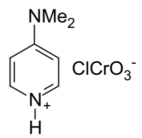
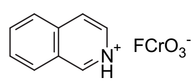
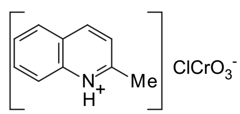
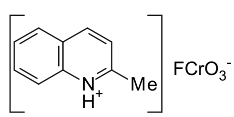
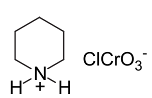
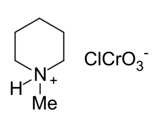
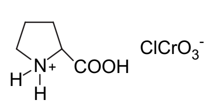
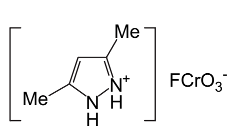
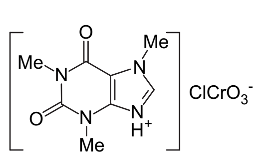
Before the structural characterization of the reagent, it was applied to the oxidation of alcohols by Cornforth et al.[209] These workers oxidized 2,4-dimethyl-4-(3-hydroxy-4-methyl pentyl)-1,3-dioxane (**69**) to the corresponding ketone (**70**) with a yield of 88% (Scheme 48).

Wuonola and Woodward[210] have applied the same procedure to oxidize a polyfunctional molecule (**71**) to obtain a precursor of the alkaloid, isolongistrobine (**72**), with a yield of 52% (Scheme 49).

After its characterization, PDC has been widely used for the oxidation of alcohols to aldehydes, ketones, and carboxylic acids. The reagent is mostly used in DMF and DCM.

One of the pioneering works by Corey and Schmidt on the oxidation of primary and secondary allylic alcohols and secondary saturated alcohols by PDC in DMF required 1.25 equiv of the oxidant to yield the corresponding carbonyl compounds with yields of around 90% (Table 4). No appreciable side products or over-oxidation or *E* to *Z* isomerization was obtained then.[17] The applications of PDC to the oxidation of alcohols[211–214] by some other workers are reported in Table 4.

Table 3. Other onium halochromates and their applications

Oxidant	Application	Ref.
 γ-Picolinium chlorochromate	Oxidation of secondary and benzylic/allylic alcohols to corresponding carbonyl compounds	177
	Oxidative deprotection of cyclic acetals and trimethylsilyl ethers	178
	Oxidation of alcohols and oximes to carbonyl compounds on silica support	179
	Oxidation of thiols to disulfides in solvent and solvent-free conditions on silica support	180
 4-Dimethylaminopyridinium chlorochromate	 Chemoselective oxidation of alcohols	181
 Isoquinolinium fluorochromate	Oxidation of alcohols to corresponding carbonyl compounds	182
 Quinaldinium chlorochromate	Oxidation of alcohols to corresponding carbonyl compounds and anthracene to anthraquinone on alumina	183
 Quinaldinium fluorochromate	Oxidation of alcohols to corresponding carbonyl compounds and anthracene to anthraquinone	184
 Piperidinium chlorochromate	Kinetic studies on oxidation of alcohols to carbonyl compounds	185
 *N*-Methylpiperidinium chlorochromate	Selective oxidation of benzyl alcohol on alumina	186
 Prolinium chlorochromate	Oxidation of benzyl and non-benzyl alcohols to corresponding carbonyl compounds	187
 3,5-Dimethylpyrazolium fluorochromate	Oxidation of alcohols to aldehydes, anthracene to 9,10-anthraquinone, phenanthrene to phenathrene-9,10-quinone and 3-acetoxy cholesterol to corresponding 7-keto derivative	188
 Caffeinilium chlorochromate	Oxidation of alcohols, oximes, and phenyl hydrazones to carbonyl compounds	189

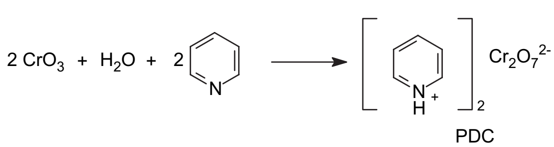
(*continued*)

Table 3. (*continued*)

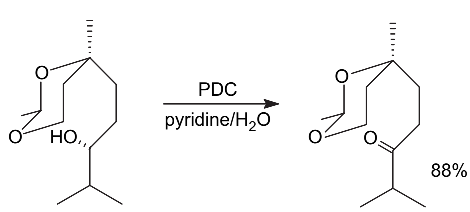
Oxidant	Application	Ref.
$[Me-NH_3]^+ClCrO_3^-$ Methylammonium chlorochromate	Oxidation of hydroxy groups on silica	190
	Regeneration of carbonyl compounds from the nitrogen containing-derivatives under mild and non-aqueous conditions	191
$[Me_2NH_2]^+ClCrO_3^-$ Dimethylammonium chlorochromate	Oxidation of alcohols to carbonyl compounds chemisorbed on alumina.	192
	Oxidation of alcohols and benzoins on alumina	193
	Oxidative cleavage of C=N under non-aqueous conditions	194,195
$[Me_3NH]^+FCrO_3^-$ Trimethylammonium fluorochromate	Selective oxidation of alcohols	196
$[Me_4N]^+ClCrO_3^-$ Tetramethylammonium chlorochromate	Oxidation of thiols to disulfides under non-aqueous conditions	197
$[Me_4N]^+FCrO_3^-$ Tetramethylammonium fluorochromate	Oxidation of alcohols	198,199
$[Et_3NH]^+FCrO_3^-$ Triethylammonium fluorochromate	Oxidation of alcohols to corresponding carbonyl compounds	200
$[Pr_3NH]^+FCrO_3^-$ Tripropylammonium fluorochromate	Oxidation of alcohols to aldehydes or ketones, anthracene and phenanthrene to anthraquinone and phenanthraquinone, respectively	201
$[Bu_3NH]^+ClCrO_3^-$ Tributylammonium chlorochromate	Oxidation of alcohols to corresponding carbonyl compounds, anthracene and phenanthrene to corresponding anthraquinone and phenanthraquinone	202
$[Bu_4N]^+ClCrO_3^-$ Tetrabutylammonium chlorochromate	Oxidation of alcohols to corresponding carbonyl compounds	203
$[(Bn)(Me)NH_2]FCrO_3^-$ *N*-Methylbenzylammonium fluorochromate	Oxidation of aryl alcohols to corresponding aldehydes and ketones	204
$[(Bn)(Et_3)N]ClCrO_3^-$ Benzyltriethyl ammonium chlorochromate	Oxidation of benzylic alcohols to corresponding carbonyl compounds	205
	Oxidation of formic acid and oxalic acid to yield CO_2	206
	Oxidation of aliphatic aldehydes to carboxylic acids	207

With 3.5 equiv of PDC in DMF, however, saturated primary alcohols are readily converted into carboxylic acids in good yields at room temperature (Table 5). Aldehydes are found to be the isolable intermediates in the reactions.[215]

This direct conversion of primary alcohols into carboxylic acids by PDC is convenient and is also possible in alcohols having acid- and base-sensitive functionalities (Table 6).[217–219]

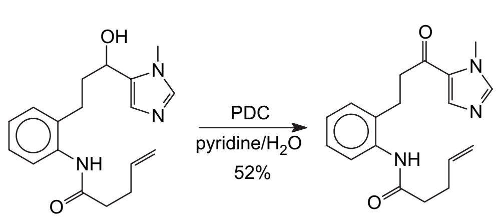


Scheme 47.



69 70

Scheme 48.



71 72

Scheme 49.

In the presence of a sensitive thioacetal group, PDC proved to be an efficient reagent to oxidize the secondary hydroxy group of **73** to yield the corresponding cyclic carbonyl compound **74** (Scheme 50). The reaction required 7 equiv of PDC in DMF at 0 °C. For **73**, PCC and the Jones reagent were found to be non-specific and the thioacetal unit was also affected by these reagents.[17]

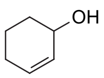
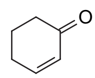
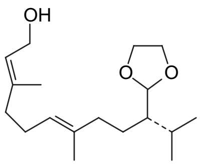
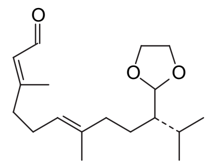
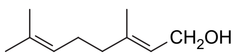
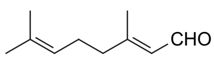
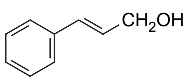
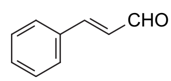
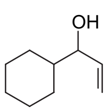
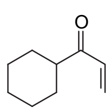
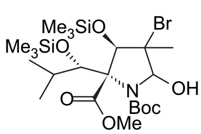
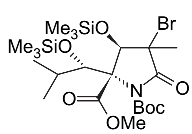
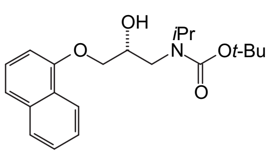
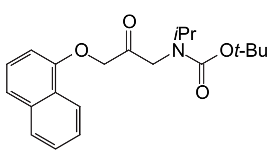
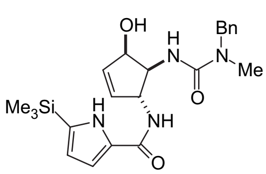
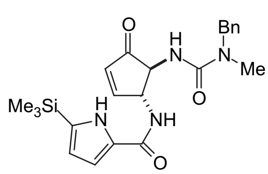
The oxidation of citronellol (**75**) to the corresponding acid (**76**) is another example of the mildness of the reagent. Under acidic conditions, the intermediate aldehyde (**77**) of citronellol undergoes cationic cyclization to form pulegone (**78**) (Scheme 51).[16,220]

In dichloromethane, PDC oxidizes primary alcohols slowly (24 h) to the aldehydes at 25 °C.[17] Some examples are illustrated in Table 7.

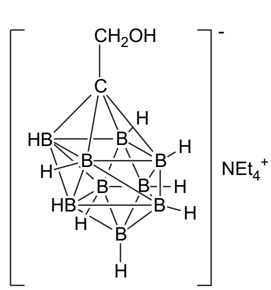
Addition of pyridinium trifluoroacetate increased the rate of oxidation of alcohols by PDC. In the presence of 0.4 equiv of pyridinium trifluoroacetate, 4-*tert*-butylcyclohexanone was produced in 97% yield from 4-*tert*-butylcyclohexanol with 1.5 equiv of PDC in methylene chloride at 25 °C for 3 h. Allylic alcohols react faster than their saturated analogs. The relative rates of oxidation of 2-cyclohexen-1-ol and cyclohexanol by PDC in DCM at 25 °C were 10:1, the yields of ketones being high in both cases. PDC is therefore particularly useful for the preparation of α,β-unsaturated carbonyl compounds.[17]

PDC was found to be effective for the selective oxidation of alcoholic groups in the presence of a reactive borane

Table 4. Oxidation of alcohols with PDC in DMF to yield carbonyl compounds

Alcohol	Product	Yield (%)	Ref.
		86	17
		75	211
		92	17
		97	17
		95	17
		67	212
		82	213
		73–76	214

system.[231] Treatment of [*closo*-1-CB_9H_9-1-(CH_2OH)]$^-$[NEt_4]$^+$ (**79**) with pyridinium dichromate in CH_2Cl_2 (2 equiv, 18 h, rt) afforded the colorless salt, [*closo*-1-CB_9H_9-1-(CHO)]$^-$[NEt_4]$^+$ in 72% yield. In a similar manner, the anion, [*closo*-1-CB_9H_9-1-(C_6H_4-*para*-CH_2OH)]$^-$, with PDC in CH_2Cl_2 engendered the aldehydic [*closo*-1-CB_9H_9-1-(C_6H_4-*para*-CHO)]$^-$ anion, which was isolated in 74% yield.



79

Arnone et al. reported a selective oxidation of a secondary alcohol over a primary alcohol by PDC.[225] At room

Table 5. Oxidation of alcohols to acids with PDC in DMF

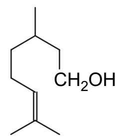
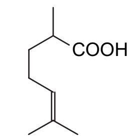
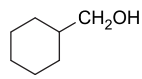
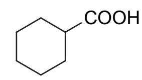
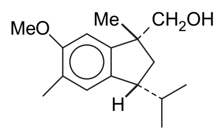
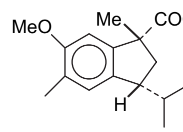
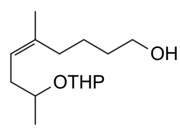
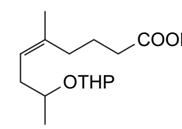
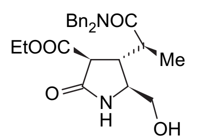
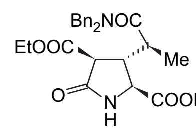
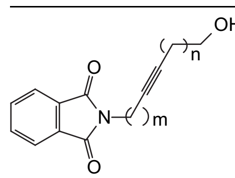
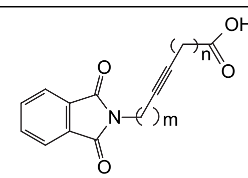
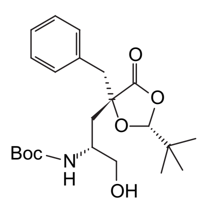
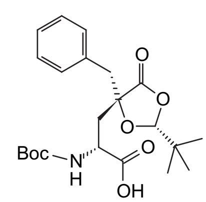
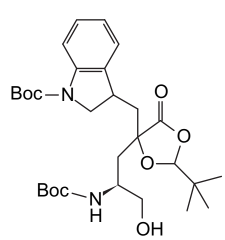
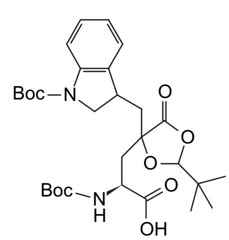
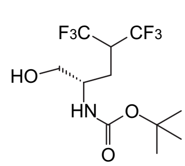
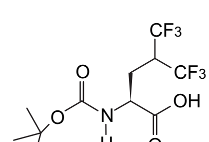
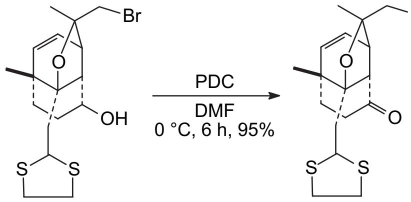
Substrate	Product	Yield (%)	Ref.
		83	17
		84	17
		85	17
		76	215
		54	216

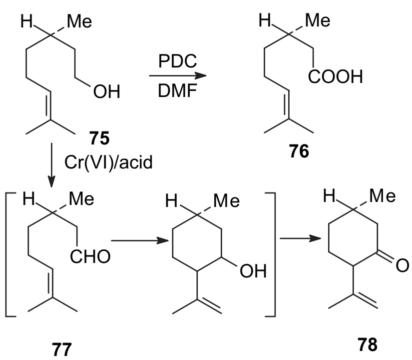
Table 6. Oxidation of alcohols with acid-sensitive functional groups by PDC (6 equiv) in DMF at room temperature

Substrate	Product	Yield (%)	Ref.
 m = 4, 6, 10 n = 2, 3	 m = 4, 6, 10 n = 2,3	72–80	217
		78	218
		76	218
		75	219



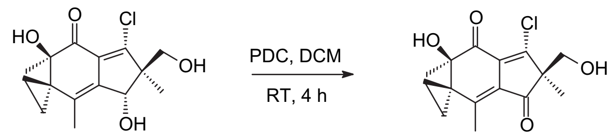
73 74

Scheme 50.



Scheme 51.

temperature, when treated with PDC for 4 h, **80** yielded **81** (Scheme 52).



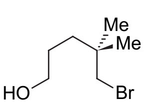
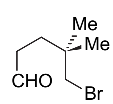
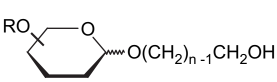
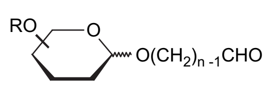
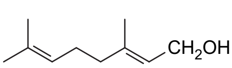
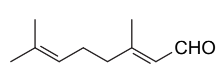
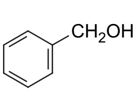
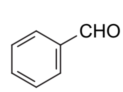
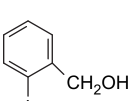
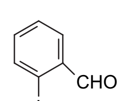
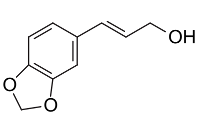
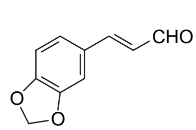
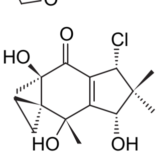
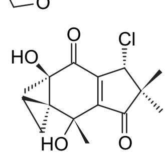
80 81

Scheme 52.

Pyridinium dichromate in DMF oxidized carbinols of the type **82a–e** and produced the corresponding *trans*-enediones (**84**) in good yields (Scheme 53). The conversion proceeds through a two-step sequence consisting of the oxidation of alcohol (**82**) to the 2-alkynyl ketone (**83**) and further oxidation of **83** to the enedione.[232] The intermediate ketone can, in some cases, be isolated after a short reaction time. Some of the substrates and the reaction conditions are listed in Table 8.

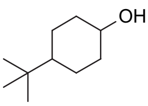
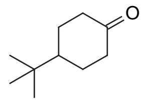
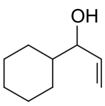
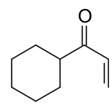
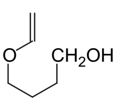
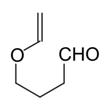
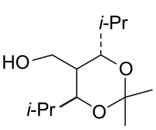
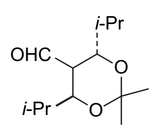
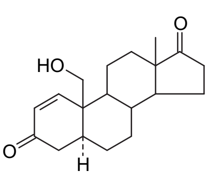
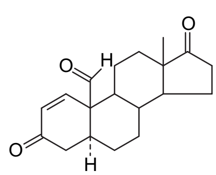
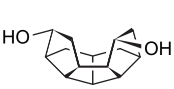
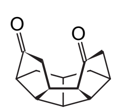
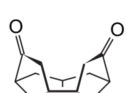
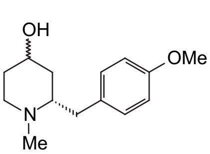
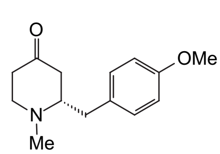
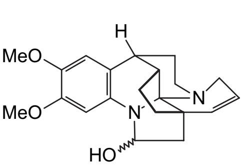
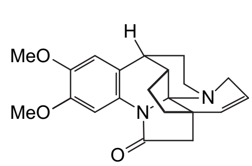
One disadvantage of this method is its failure to oxidize alcohols of the type **85**, which it essentially oxidizes to produce the 2-propynyl ketones (**86**). Prolonged reaction times

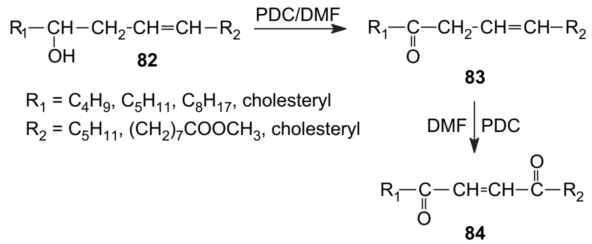
Table 7. Oxidation of alcohols with PDC in DCM

Substrate	Product	Yield (%)	Ref.
$Me(CH_2)_8CH_2OH$	$Me(CH_2)_8CHO$	98	17
$Me(CH_2)_{14}CH_2OH$	$Me(CH_2)_{14}CHO$	94	17
		75	221
 n = 3-16		63–76	222
		92	17
		82	17
		62	223
		55	224
		75	225

(*continued*)

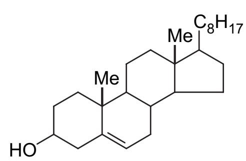
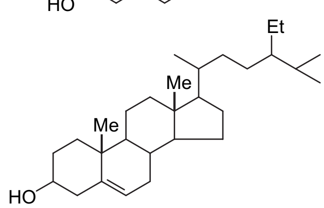
Table 7. (*continued*)

Substrate	Product	Yield (%)	Ref.
		94	17
		80	17
$C_5H_{11}C\equiv CCH_2OH$	$C_5H_{11}C\equiv CCHO$	70	17
$C_5H_{11}CH(OH)C\equiv CC_5H_{11}$	$C_5H_{11}C(=O)C\equiv CC_5H_{11}$	85	17
$C_5H_{11}CH(OH)—CH=CH_2$	$C_5H_{11}C(=O)—CH=CH_2$	80	17
		85	17
			226
		82	227
		79	228
		79	228
		79	228
		63	229
		27	230

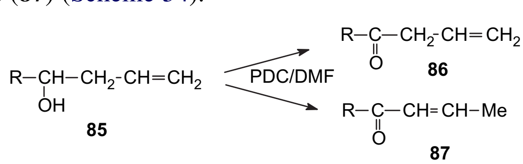


Scheme 53.

Table 8. Oxidation of homoallylic alcohols (**82**) with PDC in DMF[232]

	Alcohol	Reaction time (h)/temp (°C)	Yield (%)
82a	nC_5H_{11}-CH(OH)–CH_2-CH=CH–$(CH_2)_7$–COOMe	24/40	53
82b	nC_8H_{17}–CH(OH)–CH_2–CH=CH–nC_5H_{11}	24/40	56
82c	nBu-CH(OH)–CH_2–CH=CH–nC_5H_{11}	24/40	57
82d		15/70	75
82e		15/70	70

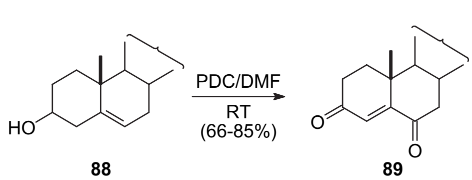
lead only to the formation of the isomeric 1-propynyl ketones (**87**) (Scheme 54).



Scheme 54.

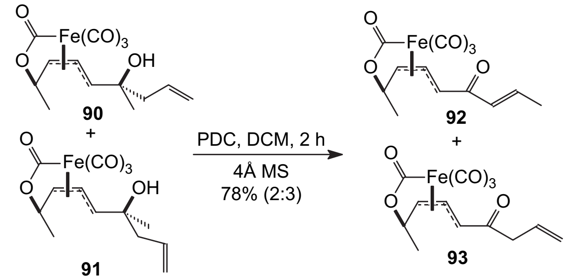
This one-step oxidation procedure is particularly useful for the oxidation of steroidal homoallylic alcohols (Table 8, **82d** and **82e**). Other methods for the synthesis of the corresponding enediones require strictly controlled conditions and tedious workups or follow more complex routes.

Hector et al.[233] also used PDC in DMF at room temperature for the oxidation of various substituted steroidal Δ^5-3β-alcohols (**88**) to the corresponding Δ^4-3,6-diketones (**89**) in good yield (66–85%) (Scheme 55).



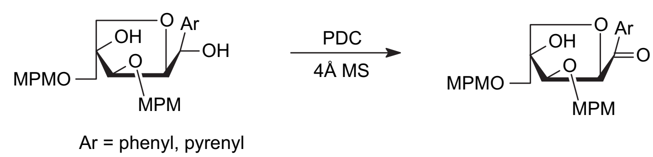
Scheme 55.

Ley et al., in a similar reaction, added molecular sieves of 4 Å in the oxidation of **90** and **91** in CH_2Cl_2 and obtained the corresponding eneones **92** and **93** in a 2:3 ratio within a shorter time period (Scheme 56).[234]



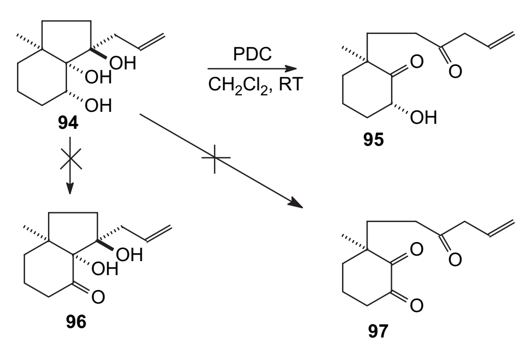
Scheme 56.

A benzylic hydroxy group attached to a lactone was oxidized by PDC in the presence of molecular sieves of 4 Å by blocking the other hydroxy groups (Scheme 57).[235]



Scheme 57.

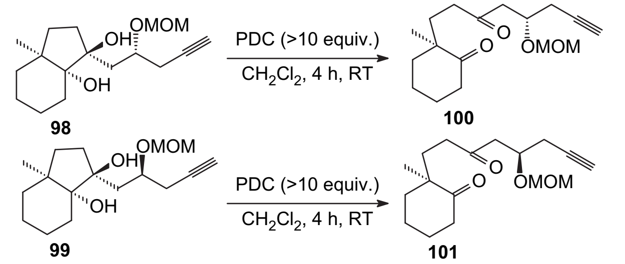
Oxidation of triol (**94**) with excess PDC (10 equiv) gave diketone (**95**) instead of the expected ketone (**96**) as the sole product in 93% yield. The stereochemistry of the secondary OH group in **95** was confirmed from its ^{1}H NMR coupling constant. Even though the reaction time was increased to 19 h using 10 equiv of PDC, the corresponding triketone (**97**) was not produced (Scheme 58).[236]



Scheme 58.

Similarly MOM (methoxymethyl) ethers **98** and **99**, bearing vicinal diaxial tertiary hydroxyl groups, were converted into the corresponding diketones **100** and **101** in quantitative yields (Scheme 59).

When the triols **102** and **103** were subjected to oxidation with PDC, interestingly a single product **104** was formed (Scheme 60). A probable reaction mechanism was proposed (Scheme 61) in which the selective oxidative cleavage of the vicinal tertiary diols is accompanied by remote asymmetric induction and the stereochemistry of the secondary hydroxyl group is controlled. This is achieved by an initial oxidation of secondary alcohol to corresponding carbonyl compound



Scheme 59.

(**A**) followed by formation of a chromate ester (**B**). The triketone (**105**) might not be produced, due to the stabilized conformation **C** with a sterically hindered hydroxyl group.

In a five-step synthetic process for β-acariolal, an analog of β-acaridial, the active principle of sex, alarm, and aggregation pheromones amongst astigmatid mites, PDC was used for the oxidation of an intermediate, 1,2,4-butanetriol, to yield the corresponding β-acaridiol with 63% yield, which was further oxidized to form β-acaridial.[237]

While oxidizing the hydroxy group of an *N*-aryl-*N*-methyl-β-amino alcohol (**106**) with PDC in CH_2Cl_2 to its corresponding ketone (**108**), the 1,3-oxazolidine (**107**) was obtained as the unexpected major product following a single-electron-transfer (SET) mechanism (Scheme 62).[238]

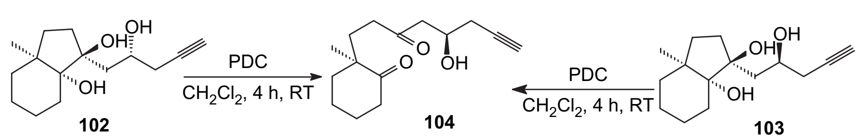
To investigate the generality of this new transformation, a variety of *N*-aryl-*N*-methyl-β-amino alcohols (**106**) were treated with PDC and the results are summarized in Table 9. The chiral cyclic 1,3-oxazolidines, which can be derived from enantiomerically pure β-amino alcohols, have been widely used as chiral auxiliaries.

Table 9. Oxidation of *N*-aryl-*N*-methyl-β-amino alcohols (**106**) with PDC in CH_2Cl_2

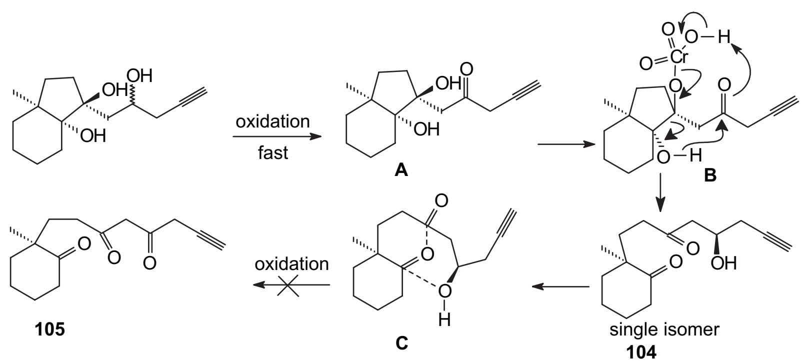
R_1	R_2	R_3	Yield (%)	
			1,3-Oxazolidine	Ketone
4-$MeOC_6H_4CH_2$	Ph	H	93	4
$PhCH_2$	4-MeC_6H_4	H	51	26
$PhCH_2$	Ph	H	68	17
$PhCH_2$	4-$MeOC_6H_4$	H	89	3
$PhCH_2$	4-ClC_6H_4	H	72	4
$PhCH_2$	Ph	Me	—	13
Me	Ph	H	46	—
$CH_2CHCH_2CH_2$	Ph	H	46	—
$CH_2CHCH_2CH_2$	$PhCH_2$	H	—	13
$PhCH_2$	Me	H	—	—
$PhCH_2$	Et	H	—	—

Pyridinium dichromate in benzene in the presence of *tert*-butyl hydroperoxide and Celite oxidizes alkyl-substituted aromatics at the benzylic carbon–hydrogen bond to furnish the corresponding ketones (Table 10).[239–42]

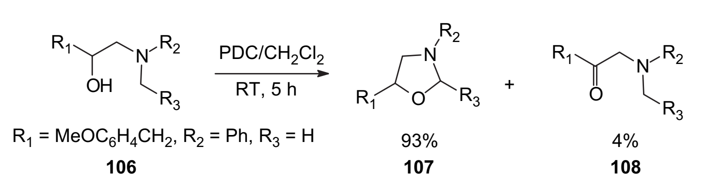
In chemical reactions, an alcohol group can be protected by transforming it into the corresponding silyl ether, which can be deprotected by various reagents, among which Cr(VI) has attracted the most attention from chemists. During the deprotection process, it can be oxidized to the corresponding carbonyl group. The selectivity of the silyl ether formed during protection toward PDC has generated a tool for the regioselective oxidation of alcohols. PDC in DCM selectively oxidized a primary trimethylsilyl ether in the presence of



Scheme 60.



Scheme 61.



Scheme 62.

Table 10. Reactions on methylene carbons by PDC in presence of *tert*-butyl hydroperoxide

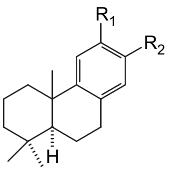
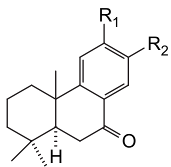
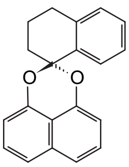
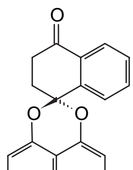
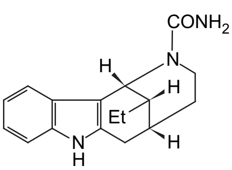
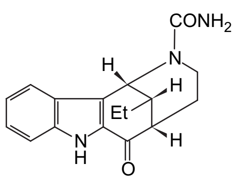
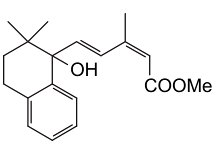
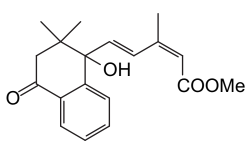
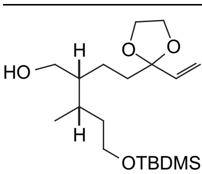
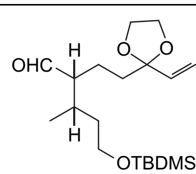
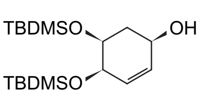
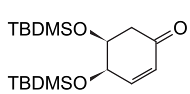
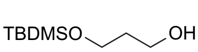
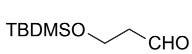
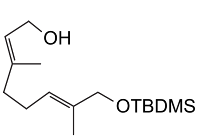
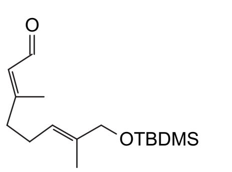
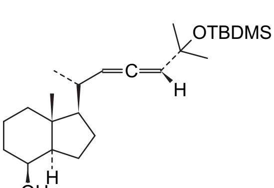
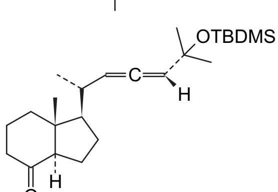
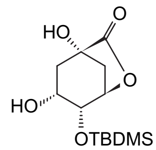
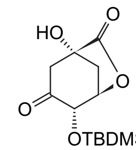
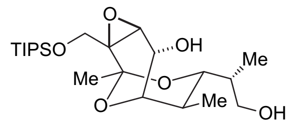
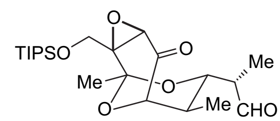
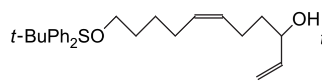
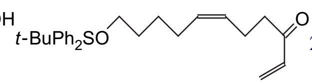
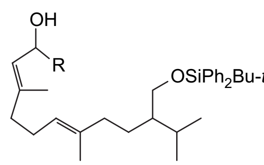
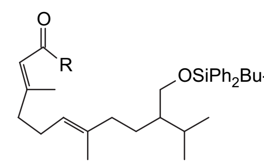
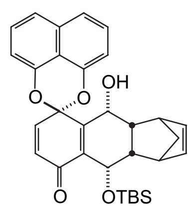
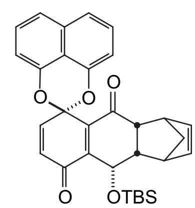
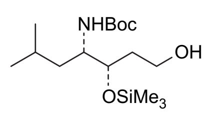
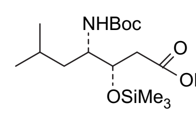
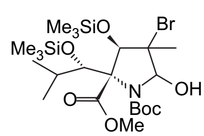
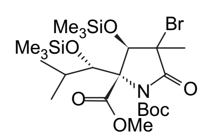
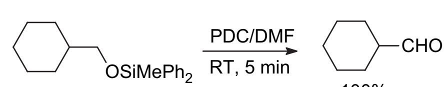
Substrate	Product	Yield (%)	Ref.
 R_1 = Me, R_2 = CO_2Me; R_1 = CO_2Me, R_2 = Me; R_1 = OAc, R_2 = Me		74–78	239
		42	240
		54	241
		78	242

Table 11. Selective oxidation of polyols using PDC by protecting one hydroxy group

Substrate	Product	Ref.
		244
		247
		248
		212
		250
		251
		253
		255
 R = H, CH_2CO_2Et		212
		256
		257
		213

a secondary trimethylsilyl ether.[243] *tert*-Butyldimethyl- and *tert*-butoxydiphenyl siloxy groups are found to be stable under these conditions. Thus, a primary alcohol[212,244–248] or a secondary alcohol[246,249–252] is selectively oxidized to an aldehyde or ketone, respectively, in the presence of *tert*-butyldimethylsiloxy groups. The reactions mostly occur in the presence of molecular sieves. Some of the applications of selective oxidation by this method are presented in Table 11. A similar selectivity has been observed in the presence of triisopropyl-,[253] *tert*-butyldiphenylsiloxy,[212,254,255] and tributylsiloxy[256] groups.

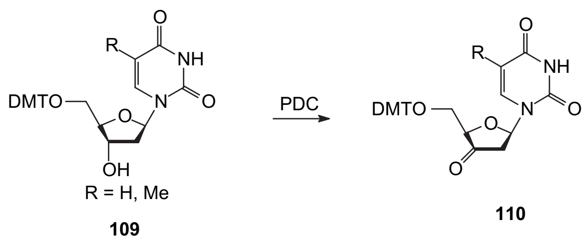
Pyridinium dichromate in DMF rapidly oxidized a primary methyldiphenylsilyl ether to the corresponding aldehyde (Scheme 63).[258] Although the trimethylsilyl ether is



Scheme 63.

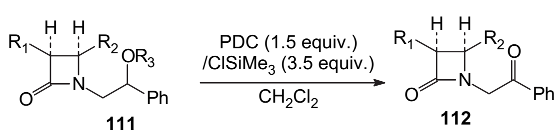
sensitive to PDC, Franciotti et al.[257] and Wardrop et al.[212] have separately reported the selective oxidation of the hydroxy group in the presence of the trimethylsilyl ether.

A dimethoxytrityl (DMT) group was also used for protecting OH from oxidation by PDC. To oxidize the 2-hydroxy group of thymidines (**109**), the 5-hydroxy group was blocked by a dimethoxytrityl group to obtain the corresponding ketones (**110**) (Scheme 64).[259]



Scheme 64.

The reactions of protected as well as unprotected β-lactams (**111**) with PDC in combination with chlorotrimethylsilane in DCM as solvent lead to a rapid, mild, and efficient method for the oxidation of these β-lactams to their corresponding carbonyl compounds (**112**) (Scheme 65).[260]



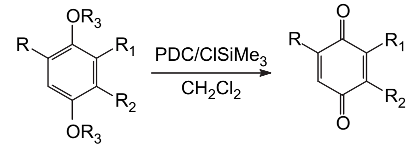
R_1 = C_6H_5O, TMS, TBDMS

R_2	R_3	Time	Yield
Ph	H	25 min	88%
	TMS	25 min	90%
	TBDMS	25 min	85%
4- $MeOC_6H_4$	H	30 min	85%
	TMS	30 min	85%
	TBDMS	1 h	95%
4- $NO_2C_6H_4$	H	30 min	80%
	TBDMS	4 h	40%

Scheme 65.

The utility of this method is the direct oxidative deprotection of the *tert*-butyldimethylsilyl lactam in good to excellent yield. Again, in the case of the oxidation of free hydroxy β-lactams **111** (R_3=H) with PDC in CH_2Cl_2, this requires a long reaction time, and suffers a low yield along with the formation of starting material and, in some cases, undesired products due to oxidative cleavage.

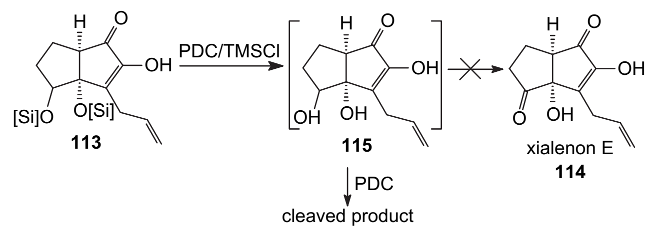
Oxidation of trimethylsilyl and *tert*-butyldimethylsilyl hydroquinones by means of the PDC–$ClSiMe_3$ system produced the corresponding quinones in excellent yields at room temperature in a very short time (Scheme 66).[260] In this reaction, it is interesting to note that, while the PCC and PDC oxidations were unsuccessful for compounds containing electron-withdrawing groups in the aromatic ring as well as for the non-activated bis(*tert*-butyldimethylsilyl)-ether, this procedure could give the corresponding quinones in good yields.



R: H, OMe, Me, Cl, t-Bu
R_1: H, Me R_2: H, Me, t-Bu
R_3: TMS, TBDMS, H

Scheme 66.

In an attempt to synthesize xialenon E (**114**) by the condition of Cossio et al.,[260] Hodgson[261] and co-workers used PDC–TMSCl for (double) desilylation of **113** followed by in situ oxidation of the liberated secondary alcohol (**115**), but failed to obtain the desired product. Instead, they observed complete decomposition of the reactant, which may be attributed to the oxidation of the diol produced in situ (Scheme 67).



Scheme 67.

Oxidation of alcohol **116** with pyridinium dichromate in DCM at 25 °C for 3 h afforded the corresponding aldehyde (85% yield), which cyclized to the lactol **117** after fluoride-mediated deprotection of the silyl ether in THF. Compound **117** was produced as a mixture of diastereomers, presumably from epimerization of the intermediate aldehyde under basic reaction conditions. Lactol to lactone oxidation by PDC in DCM at 25 °C for 2 h afforded a 1:3 mixture of **118** and its epimer **119** (Scheme 68).[262]

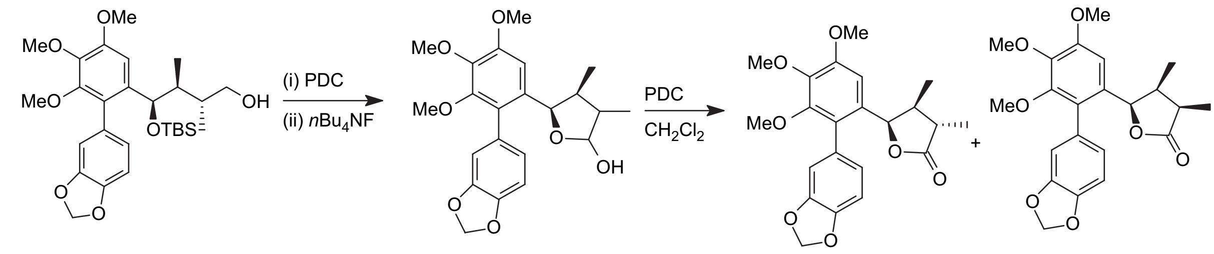
Cha and Chun[263] described the reductive oxidation of acid chlorides to aldehydes with lithium aluminum hydride (LAH) and PCC or PDC (Scheme 69). This procedure is broadly applicable, tolerating many substituents such as chloro, methoxy, nitro, and olefinic groups.

PDC is also useful for oxidizing aldehydes in aprotic media, giving rise to the corresponding acids,[17] e.g., cyclohexene-4-carboxaldehyde was converted into the corresponding carboxylic acid in DMF at room temperature with 90% yield (Scheme 70). PDC is, however, inert toward α,β-unsaturated aldehydes.[264]

During the synthesis of (±)-dihydronepetalactone, the precursor **121** was synthesized from the corresponding aldehyde (**120**) by using PDC in DMF (Scheme 71).[265]

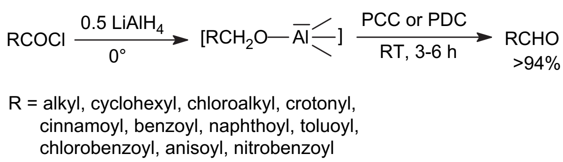
PDC was utilized for converting α-ynol-iodine complexes into α,β-unsaturated-α-iodoaldehydes in DCM at 25 °C (Scheme 72).[266] The conversion is regio- and stereo-specific, yielding only one of the two possible geometrical isomers.

On treatment of various non-electron-deficient carbocyclic and heterocyclic (η^3-allyl)molybdenum complexes with



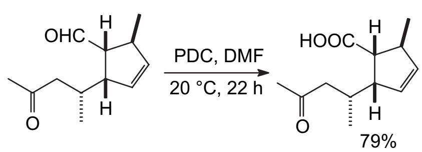
116 117 118 eupomatilone 6 119

Scheme 68.



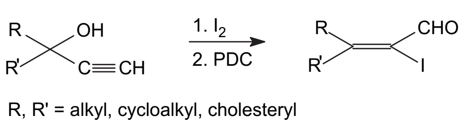
Scheme 69.

Scheme 70.



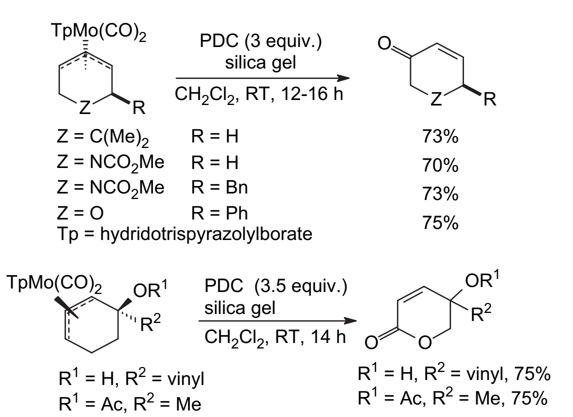
120 121

Scheme 71.



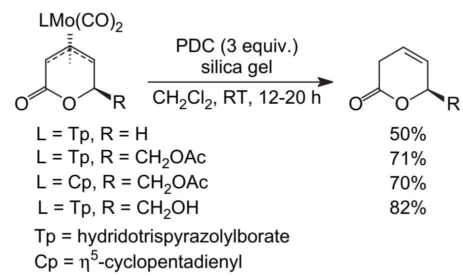
Scheme 72.

PDC–silica gel,[267] demetallation occurred with concurrent oxidation of a terminal position of the π-system in good yields and with high regiocontrol. This led to the preparation of unsaturated ketones and lactones of high enantiopurity (Scheme 73).



Scheme 73.

In contrast, treatment of electron-deficient (η^3-allyl)molybdenum complexes with PDC–silica gel (CH_2Cl_2, 24 h) followed a photodemetallation course (Scheme 74).[267]



Scheme 74.

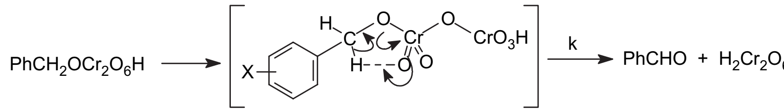
3.1.2. Reaction kinetics. The oxidation kinetics of various substrates such as alcohols, amines, and sulfides by PDC in a non-aqueous medium have been investigated by various research schools. Oxidation of some primary and secondary alcohols with PDC catalyzed by *p*-toluenesulfonic acid (TsOH) was found to show first-order dependence on PDC.[268] Michaelis–Menten dependence was observed on [alcohol]. The order dependence on TsOH was more than a first order and less than a second order. Pyridine was found to retard the rate of oxidation significantly, indicating the possibility of a parallel competitive reaction with TsOH.

Kabilan et al. used eight different substituents occupying *meta*, *para* or *ortho* positions on the benzyl alcohol to oxidize by PDC in anhydrous acetonitrile, acidified with trichloroacetic acid.[269] The results revealed the following: (i) the reaction is first order with respect to each of the reagents PDC, substrate, and TCA, (ii) benzaldehyde is the only product emerging from the oxidation of benzyl alcohol, (iii) no reaction is observed in the absence of TCA, pointing to a catalytic action by TCA, (iv) $[HCr_2O_7]^-$ is assumed to be the only oxidizing agent present in the reacting solution, and (v) the reaction mechanism involves a neutral ester intermediate (Scheme 75).

$$PhCH_2OH + HCr_2O_7^- + CCl_3COOH \overset{K}{\rightleftharpoons} PhCH_2OCr_2O_6H + H_2O + CCl_3COO^-$$

Scheme 75.

The oxidative rate-determining step is a concerted process triggered by the shrinkage of a pair of electrons from a σ-bond into a non-bonding chromium orbital, leading to the formation of benzaldehyde and an unstable Cr(IV)–O–Cr(VI) species, which involves the formation of planar



Scheme 76.

five-membered cyclic ground and transition states stabilized by intramolecular hydrogen bonds linking an oxygen atom from the inorganic moiety to an α-hydrogen in the organic counterpart, providing scope for an intramolecular proton transfer in the dichromate ester (Scheme 76).

The accelerating effect of dipolar electron-donor substituents in the *meta* and *para* positions is due to increased electric potential in the immediate vicinity of the chromium atoms undergoing reduction. The oxidation rates are slow in the presence of substituents at the *ortho* position. This retarding effect was ascribed to bulky groups, which partially hinder the stabilized formation of intramolecular hydrogen bonds in the ester and cause steric inhibition of solvation.

From the rate of oxidation by PDC using oxalic acid as the catalyst, the separation of steric and electronic effects on the rate was also investigated.[270,271]

The oxidation of aniline and *p*- and *m*-substituted anilines by PDC to afford the corresponding azobenzenes was studied in an aqueous acetic acid medium by Palaaniappan and Sekar.[272] With *p*-NO_2-, *m*-NO_2-, and *m*-Br-substituted anilines, the order is fractional and with the other anilines, the order is 1. Both electron-releasing and electron-withdrawing groups retard the reaction rate.

Oxidation of diethyl, diphenyl, and *meta*- and *para*-substituted phenyl methyl sulfides with PDC in an acetonitrile medium in the presence of *p*-toluenesulfonic acid (TsOH) in a 1:3 stoichiometry of PDC–substrate yielded the corresponding sulfoxides. The reaction kinetics studies exhibited a second-order dependence on TsOH and first-order each on the substrate and oxidant.[273]

Addition of acrylonitrile was found to retard the rate of diphenyl sulfide oxidation significantly. Electron transfer from sulfur to Cr(VI) resulting in a free-radical intermediate was assumed to be the rate-limiting step. Sulfur cation free radicals were proposed to be involved in the oxidation of sulfides and sulfoxides by various authors.[274,275] The reaction was found to have Michaelis–Menten dependence on [sulfide] in the oxidation of substituted phenyl methyl sulfides with PDC in an acetonitrile medium.[273] There was no significant oxidation in the absence of TsOH. The order dependence on [TsOH] is >1 and <2. Both electron-releasing and -withdrawing groups retard the reactivity of aryl methyl sulfides. The nonlinear concave downward- type Hammett plot (Fig. 2) was a composite of two straight lines, one with a positive ρ value and the other with a negative ρ value. A negative ρ value indicates that the nucleophilic sulfur atom is more positively charged in the transition state than in the reactant, while a positive ρ value indicates the dispersal of positive charge. These results were explained by invoking a mechanism having a shift in the rate-limiting step within the same overall reaction pathway (Scheme 77). Step (2) is slow and rate-limiting for electron-withdrawing groups

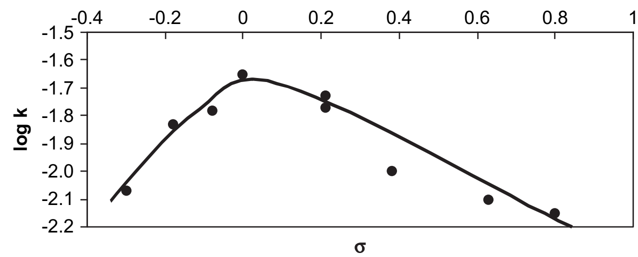
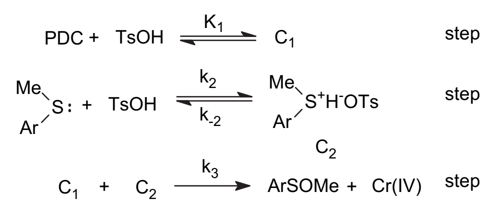


Figure 2. Hammett plot for the oxidation of substituted phenyl methyl sulfides by PDC in acetonitrile (Ref. 273).

while for electron-releasing groups, step (3) is the rate-limiting step.



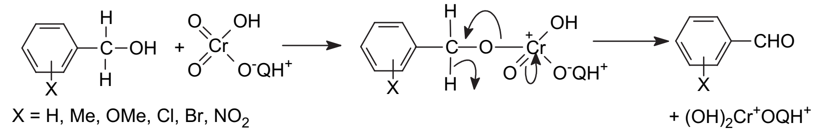
Scheme 77.

3.2. Quinolinium dichromate

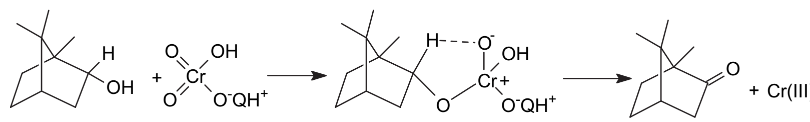
3.2.1. Synthetic applications. Quinolinium dichromate (QDC) is a stable orange solid, obtained by dissolving CrO_3 in water and adding quinoline at ice temperature.[276] It is soluble in water, DMF, and DMSO, sparingly soluble in methylene chloride and chloroform, and insoluble in heptane, toluene, and ethyl acetate. The reactions of QDC with alcohols in dichloromethane and DMF, with 1 and 1.5 equiv, respectively, yielded the corresponding carbonyl compounds. Oxidation of aldehyde led to the formation of the corresponding acids in DMF. QDC crystallizes in the monoclinic space group $p2_1/c$, with eight cations and four anions in the unit cell.[277] The quinolinium cations and a dichromate anion are connected through N–H···O and C–H···O intermolecular hydrogen bonds and by aromatic π–π stacking interactions. The dichromate geometry is normal, with a Cr–O–Cr angle of 135.1°. Although a literature study reveals not much application of QDC in synthetic processes, a lot of data have been reported on kinetic studies using QDC.

3.2.2. Reaction kinetics. The oxidation kinetics of primary, secondary, and allylic alcohols by QDC were investigated by Nongkynrin et al.[278] under acid-catalyzed condition. The reaction led to the formation of the corresponding carbonyl compounds involving the decomposition of a cyclic chromic ester in an electrocyclic ring-opening manner.

The reaction kinetics of the oxidation of substituted benzyl alcohols by QDC in DMF in the presence of hydrochloric acid were investigated by Dey and Mahanti.[279] Electron-releasing substituents accelerated the reaction and



Scheme 78.

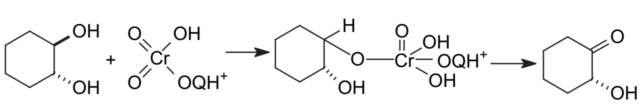


Scheme 79.

electron-withdrawing groups retarded the process. From the Hammett relationship, these workers obtained the reaction constant to be −1.67, thus proposing an electron-deficient transition state. The kinetic isotope effect (k_H/k_D) was determined by using $PhC(D)_2OH$ as the substrate and was found to be 5.89, suggesting a C–H bond cleavage from the alcohol carbon atom. In view of the above observation, they proposed a mechanism for the oxidation of alcohols as shown in Scheme 78.

To investigate the effect of the environment on the transition state of the oxidation of benzyl alcohol by QDC, Manikyamba[280] used different pure protic and aprotic solvents and proposed a solvation model for the stability of the transition state. Nongkynrih and Mahanti[281] oxidized borneol and isoborneol and obtained camphor as the oxidized product (Scheme 79). A Hückel-type cyclic transition state for the reaction involving hydrogen abstraction in the slow step was proposed by them.

The mildness of QDC can be demonstrated effectively in the oxidation of diols. Kuotsu et al.[282] could oxidize a single hydroxyl group of a diol to the corresponding hydroxy carbonyl compound. The reaction was found to be first-order dependent each on [diol], [QDC], and [H^+]. These workers obtained an inverse solvent isotope effect, $k(H_2O)/k(D_2O)$, of around 0.5. The experimental findings were correlated with a mechanistic pathway involving the formation of an acyclic chromate ester intermediate, which underwent decomposition to yield the product (Scheme 80).



Scheme 80.

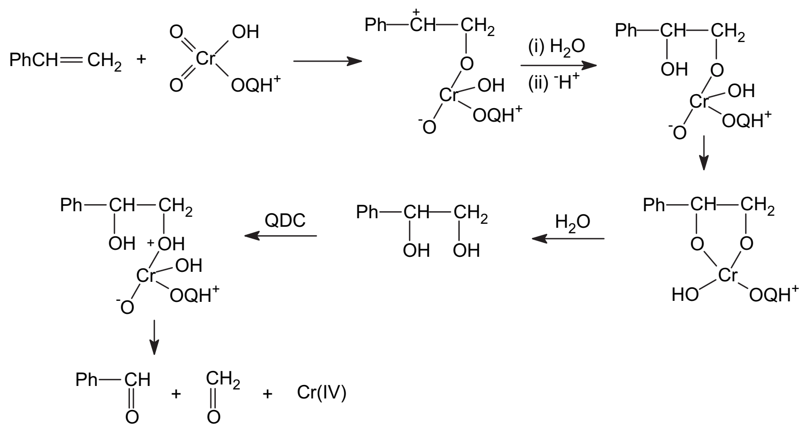
From the kinetic data of oxidation of allyl alcohols by QDC in aqueous perchloric acid, Chimatadar et al.[283] proposed a free-radical mechanism for the reaction. Oxidation of α-hydroxy acids, e.g., lactic acid, α-hydoxyphenylacetic acid and its 4-chloro derivative by QDC in 30% aqueous acetic acid resulted in the formation of the corresponding aldehydes. From the product formation, Aruna et al.[284] proposed a mechanism involving C–C bond cleavage. Similarly, QDC in DMF exhibits the unique feature of being able to oxidize hydroxy acids by both pathways, converting mandelic acid into benzaldehyde (process of decarboxylation), and tartaric acid into glyoxalic acid (absence of decarboxylation).[285] An increase in the polarity of the medium accelerates the rate of oxidation. From various kinetic parameters, the oxidation of α-hydroxy acids such as lactic acid and mandelic acid in aqueous acetic acid in the presence of perchloric acid was proposed to proceed through the formation of a cyclic chromic ester between protonated QDC and the α-hydroxy acid followed by decomposition to aldehydes and carbon dioxide.[286]

Chaubey and Mahanti investigated the oxidation kinetics of aliphatic aldehydes, e.g., valeraldehyde,[287] isovaleraldehyde, and isobutyraldehyde,[288] other long-chain aldehydes[289] and heterocyclic aldehydes[290] (pyridine 2- and 3-aldehyde) by QDC. A cyclic transition state having Hückel's aromatic stability was suggested by these workers. Hiran et al. studied the reaction kinetics of a series of aliphatic aldehydes and reached the same conclusion.[291]

While investigating the oxidation kinetics of benzaldehydes in a 50% aqueous acetic acid medium, Mediem observed that the rate decreases with an increase in the water content of the medium.[292] For α,β-unsaturated aldehydes, the kinetic results support a mechanistic pathway proceeding via a rate-determining oxidative decomposition of the chromate ester of the aldehyde hydrate.[293–298]

Oxidation of cyclohexanone by QDC in an aqueous acetic acid medium in the presence of sulfuric acid proceeds through enol formation followed by chromyl esterification and decomposition to adipic acid.[299] For 3-alkanones, the mechanism involves the attack of protonated QDC on the enol form of the ketone in the rate-determining step, forming a cyclic chromate ester, followed by a fast decomposition of the ester to give the product.[300] Studies on the oxidation kinetics of some acyclic ketones were also extended by Mahanti and co-workers.[301] β-Diketones are prone to oxidative cleavage by QDC in the presence of perchloric acid.[302] The kinetic data propose a mechanism in which the oxidant reacts with the enol tautomer of the β-diketone in the slow step, forming a cyclic chromate ester, which, being a Hückel-type system, undergoes subsequent cleavage of the C–C bond, yielding the product by oxidative decarboxylation. Manikyamba and Aruna reported the oxidation kinetics of chalcone by QDC and proposed a mechanism involving the slow attack of $(QDC)H_2^+$ on the chalcone to produce benzoic acid.[303]

Formic and oxalic acids were oxidized by QDC and the rate of reaction was monitored under various conditions.[304] The



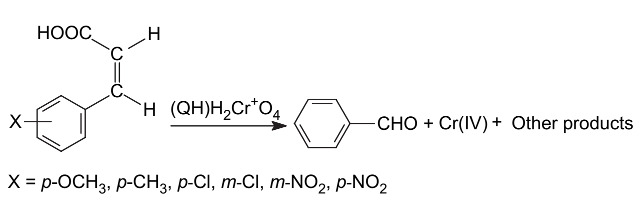
Scheme 81.

product in both cases was carbon dioxide. In the former case, C–H bond cleavage takes place, while, in the latter, the C–C bond cleaves in the rate-limiting step. The studies on the oxidation kinetics of dicarboxylic acids such as malonic,[304] succinic,[305] glutaric,[306] and adipic acids[307] by QDC were undertaken in sulfuric acid to yield the corresponding semialdehydes through oxidative decarboxylation. The effect of the dielectric constant of the medium on the reaction rate suggested the possibility of an ion–dipole interaction. The kinetic results and the nature of the products formed were interpreted by a mechanism involving C–C bond fission. The kinetic study was extended to the oxidation of unsaturated acids,[307,308] ketoacids,[309,310] and thioacids[311] by QDC.

Oxidations of aromatic acids by QDC were monitored for substituted benzoic acids,[312] pyridinecarboxylic acids,[313] and other heterocyclic acids.[314] The rate-determining step involves the formation of a cyclic chromate ester, which decomposes to give the corresponding hydroxy acids.

Styrene undergoes oxidative cleavage at the C═C bond to yield the corresponding carbonyl compounds by QDC.[315] The plot of Hammett substituent constant against rate led to a negative reaction constant value, suggesting the formation of a cationic intermediate in the rate-determining step. From the kinetic parameters and the inverse solvent effect of 0.80, a mechanism was proposed as shown in Scheme 81.

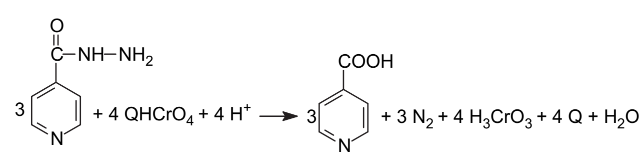
The oxidation of substituted cinnamates by QDC afforded the substituted benzaldehydes, indicating cleavage of the olefinic double bond during the reaction (Scheme 82).[316] The reaction was found to be acid catalyzed. Solvents with a low dielectric constant favored the reaction. From the studies of substituent effects, the Hammett reaction constant was found to be −0.53, indicating an electron-deficient transition state. The solvent isotope effect, $k(H_2O)/k(D_2O)$, was reported to be 1.90.



Scheme 82.

The oxidation of 2-naphthol by QDC afforded 1,2-napthaquinone and Cr(III) as the products.[317] Hydroxylation of heterocyclic acids by QDC was reported by Hauzachin and Mahanti,[318] who investigated the kinetics of the reaction in a sulfuric acid–acetic acid medium to elucidate the mechanism of hydroxylation.

Considering the advantage of mildness and effective oxidation by QDC, Kulkarni et al. used this reagent for the determination of isoniazid in the pure form and in pharmaceutical formulations.[319] Isoniazid is oxidized to the corresponding acid by consuming 4 equiv of QDC (Scheme 83).

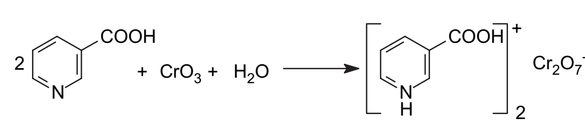


Scheme 83.

Oxidation of the methylene group of fluorene by QDC was monitored by Sarma and Mahanti.[320] From an ESR spectral analysis of the reaction mixture, they proposed the existence of Cr(V) as an intermediate. QDC was used for the oxidation of thallium(I) to Tl(II) in an aqueous acetic acid medium in the presence of HCl. Chimatadar et al. showed that the active species of QDC and Tl in the reaction are $ClCrO_3^-$ and $TlCl_2$, respectively.[321] Recently, they have extended their work to study the oxidation of arsenic(III) to As(V) by QDC.[322]

3.3. 3-Carboxypyridinium dichromate

3-Carboxypyridinium dichromate or [nicotinium dichromate (NDC)] was prepared by adding 2 equiv of chromium trioxide to a solution of nicotinic acid in water at 0–5 °C (Scheme 84).[323]

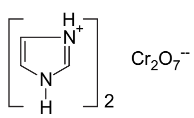


Scheme 84.

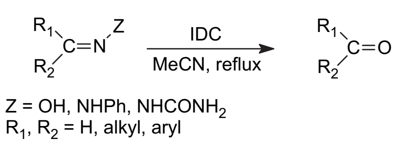
It is an efficient reagent for the oxidation of alcohols into carbonyl compounds in the presence of pyridine in an optimum molar ratio of 1:2.5:20 for substrate, reagent, and pyridine, respectively.[324] It allows selective oxidation between benzylic and aliphatic alcohols. It has been used for the oxidation of a variety of substrates, e.g., hydroquinones to quinones,[324] sugars to the corresponding carbonyl compounds,[325] 1,4-dihydropyridines to the corresponding pyridines[326] and conversion of thiocarbonyls into oxocarbonyls.[327] The kinetics of oxidation using NDC were investigated for substituted benzaldehydes,[328] anilines,[329] organic sulfides,[330,331] and 1,4-dihydropyridines.[332]

3.4. Imidazolium dichromate

Imidazolium dichromate (IDC: **122**) was synthesized from imidazole and chromium trioxide and was applied to the oxidation of alcohols to carbonyl compounds by Kim and Lhim.[333] De has reported the de-oximation of aldoximes and ketoximes to the corresponding carbonyl groups.[334] Acid-sensitive methoxy groups remained unaffected and the α,β-unsaturated cinnamaldoxime was de-oximated without any difficulty. Several phenyl hydrazones and semicarbazones were deprotected by using IDC to give the corresponding carbonyl compounds in excellent yields (Scheme 85).



122

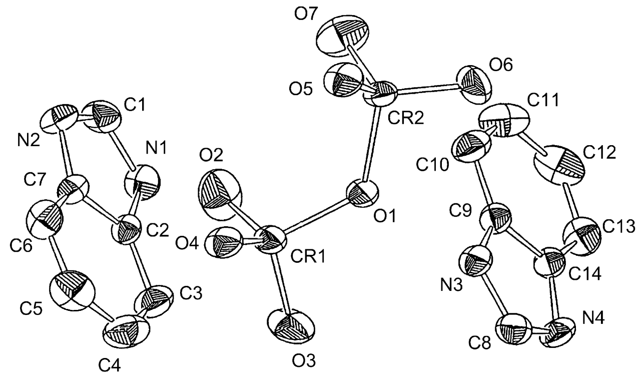


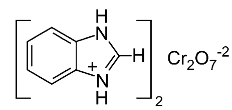
Scheme 85.

Kinetic studies of the oxidation of furfural[335] and aromatic aldehydes[336,337] by IDC in an aqueous acetic acid medium revealed that the oxidation reaction involves a two-electron-transfer process. Karunakaran and Chidambaram investigated the oxidation kinetics of organic sulfides by using IDC and observed a zero-order dependence of the rate on the substrate.[338] The oxidation kinetics of some more organic substrates such as alcohols,[339,340] α-hydroxy acids,[341,342] diphenyl sulfides,[343] and diphenacyl sulfides[344] by IDC have been investigated.

3.5. Benzimidazolium dichromate

Benzimidazolium dichromate (BIDC: **123**) was obtained from the reaction of benzimidazole and chromium trioxide in water[345] or in the presence of aqueous acetic acid.[346] BIDC was characterized by IR or NMR spectra and TG-DTG-DTA thermal analysis. The crystal structure of BIDC was analyzed by Ramaiah et al.[346] and Meng et al.[347] The analysis of the X-ray crystal structure reveals that a dichromate ion connects two benzimidazolium rings face to face in an intramolecular aromatic stacking (Fig. 3).





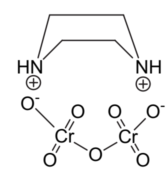
123

Figure 3. Crystal structure of benzimidazolium dichromate.

The major force in the crystal formation is suggested to be from hydrogen bonds and an intermolecular hydrogen bridge is formed to connect two neighboring dichromate ions. The oxidation of some alcohols by BIDC was reported by Ramaiah et al.[348] BIDC can selectively oxidize benzylic and allylic alcohols to the corresponding carbonyl compounds under microwave irradiation.[349]

3.6. Piperazinium dichromate

Piperazinium dichromate (**124**) was prepared by adding a solution of chromium oxide proportionately to piperazine in water at room temperature followed by stirring for a few minutes.[350]



124

The X-ray crystallographic study of **124** reveals that the compound consists of dichromate dianions, which are connected to the cyclic piperazinium dications via hydrogen bonding.[351] There are two crystallographically independent piperazinium dications, both located on centers of inversion. The oxidant was used for oxidative coupling of thiols to sulfides with the following stoichiometry (Scheme 86).[350]

$$2Cr(VI) + 6\ RSH \rightarrow 3\ RSSR + 6H^+ + 2\ Cr(IV)$$

R = alkyl, aryl

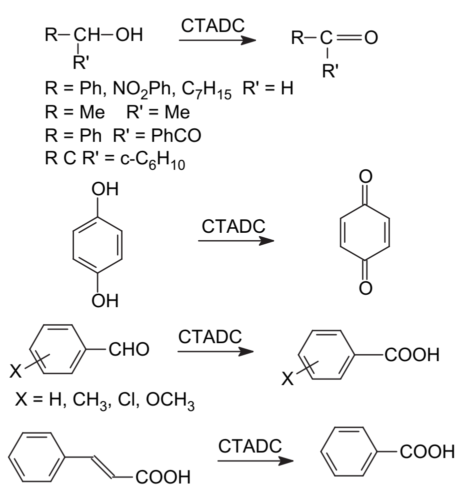
Scheme 86.

3.7. Cetyltrimethylammonium dichromate

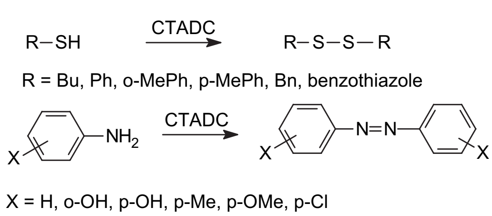
The cetyltrimethylammonium ion has already been used for converting Mn(VII)[352–355] and Ce(IV)[356] into lipopathic oxidants for application in organic solvents for organic substrates. The synthesis of cetyltrimethylammonium dichromate (CTADC) was carried out by a simple ion-exchange method. Addition of potassium dichromate with cetyltrimethylammonium bromide (CTAB) in aqueous solution afforded the water-insoluble yellowish-orange crystalline salt of CTADC (Scheme 87).[357] The elemental analysis clearly envisages the presence of two CTA units per molecule of dichromate. The spectral characteristics and solubility of other oxidants, e.g., permanganate and ceric nitrate, with a CTA carrier were compared with those of CTADC and the results suggest the existence of a tight ion pair of CTADC in organic media. CTADC is soluble in most organic solvents. In organic solvents, the compound absorbs at around 353–383 nm. CTADC is stable in these solvents at reflux temperature and for an appreciable time period. On a water surface, it assumes an area of 51 Å^2/molecule at a temperature of 298 K.[358]

$$\mathbf{2}\ C_{16}H_{33}N^{+}(Me_3)Br^{-} + K_2Cr_2O_7 \longrightarrow [(C_{16}H_{33}N^{+}(Me_3)]_2Cr_2O_7^{-} + \mathbf{2}\ KBr$$

Scheme 87.



Scheme 88.



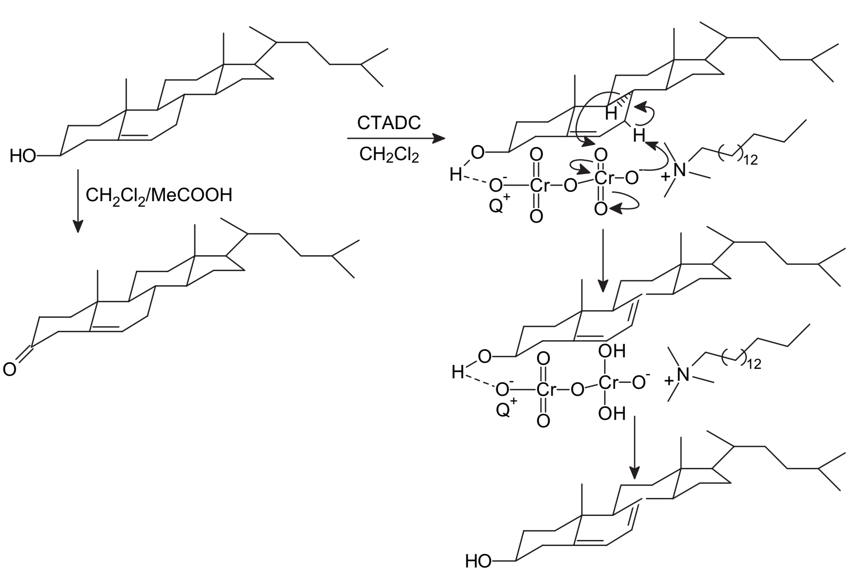
Scheme 89.

3.7.1. Synthetic applications. CTADC oxidizes various functional groups with a stoichiometric ratio of 3:1 of substrate and oxidant.[357] The organic products from alcohols and hydroxyquinones were found to be the corresponding carbonyl compounds and benzoquinones, respectively (Scheme 88). Similarly, oxidation of aromatic aldehydes led to the formation of substituted benzoic acids and cinnamic acid afforded benzoic acid (Scheme 88).

Thiols and aromatic amines on oxidation with CTADC produced disulfides and diazo compounds, respectively (Scheme 89).[359]

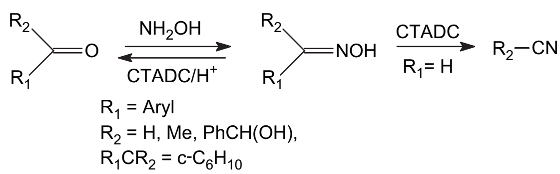
When cholesterol was refluxed with CTADC in DCM for 6 h, 7-dehydrocholesterol was obtained, which was characterized from its ^{13}C NMR, ^{1}H NMR, and FABMS spectral characteristics.[360] For the dehydrogenation, a remote-functionalization mechanism akin to that reported by Breslow et al.[361] was proposed. The reaction process may be initiated by an association of the 3-OH group with the chromate ion of CTADC and subsequent reaction takes place at an equidistant site of the active center of the reagent at the cholesterol nucleus (Scheme 90). The secondary overlap of π-orbitals of cholesterol at the C_5–C_6 position with that of Cr=O may assist the system to achieve proper orientation for the reaction. The dehydrogenation occurs through a seven-membered cyclic transition state involving a change of oxidation state of Cr(VI) to Cr(IV) (Scheme 90).

At reflux conditions, from a solution of CTADC and cholesterol in 20% acetic acid in DCM, 5-cholesten 3-one was isolated.



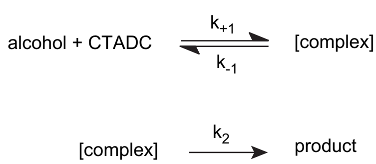
Scheme 90.

Oximes, on treatment with CTADC in the presence of a trace amount of acetic acid in dichloromethane, gave the corresponding carbonyl compounds (Scheme 91).[362] The color change of the reaction mixture from orange to green suggested the reduction of Cr(VI) to Cr(III). When the reaction was performed in the absence of acetic acid, however, the corresponding nitrile derivatives resulted. The ketoximes remained unreacted under these reaction conditions.



Scheme 91.

3.7.2. Reaction kinetics. The oxidation kinetics of a series of aliphatic primary and secondary alcohols and cyclohexanol were investigated in DCM.[363] The reaction kinetics were found to obey the Michaelis–Menten equation with respect to [alcohol], i.e., a complex is formed between the oxidant and substrate prior to the rate-determining step. The complex subsequently decomposes into the products (Scheme 92).



Scheme 92.

Further, the solvent kinetic isotope effect, $k(H_2O)/k(D_2O)$ was found to be 0.76. The reverse isotope effect was attributed to the involvement of a pre-equilibrium protonation in the reaction mechanism. This indicates that the hydroxyl group is not involved in the pre-equilibrium or in the rate-determining step, which precludes the possibility of breaking an O–H bond in the rate-determining step and supports the formation of a dichromate ester in the reaction process.

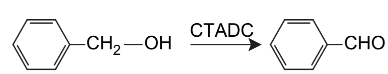
The kinetic isotope effect of 2.81 obtained by using methanol-d_4 as the substrate supports the involvement of α-C–H bond breaking in the rate-determining step. This small kinetic isotope effect may, however, be explained on the basis of the two-step mechanism (Scheme 92). The contribution of the ester formation toward the rate-determining step is also significant where there is no primary kinetic isotope effect, which diminishes the isotope effect.

To be consistent to the above observations, a mechanism was proposed where the dichromate ion forms an ester intermediate with the alcohol, which subsequently decomposes by α-hydrogen abstraction to the corresponding aldehyde or ketone (Scheme 93).

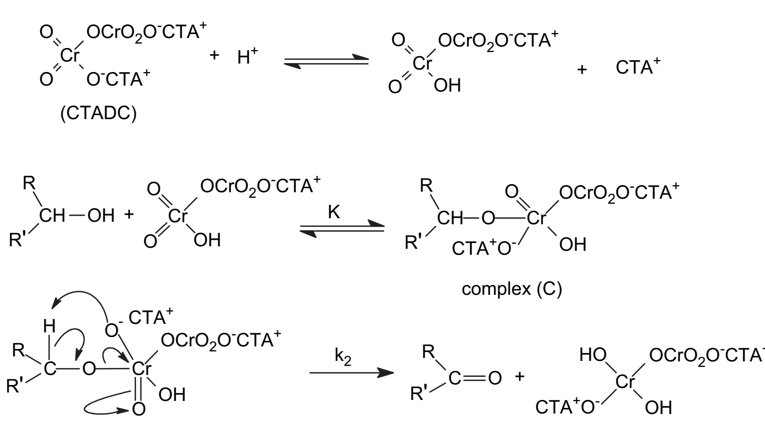
With increasing concentrations of CTADC, the rate constant was found to decrease nonlinearly with concavity. This decrease was attributed to the formation of a reversed micelle in which the dichromate ion is enveloped by CTA^+. CTAB forms reversed micelles in DCM providing a cationic interface and a suitable residing site for anions. At a cationic CTAB-reversed micellar interface, a proton may not be available for the dichromate and, thus, it leads to a decrease in the rate. With increasing [CTADC], there may be an increase in reverse micelle formation and, thus, a negative trend is inevitable. The asymptotic rate fall due to an increase in [CTAB] also supports the reversed micellization.

The rate constants obtained in a set of solvents with varying polarity were correlated with various solvent parameters and it was found that the rate constants largely depend on the chemical nature of the solvents. An increase in the dielectric constant on the higher side did not bring forth significant changes in the rate constant proposing less contribution of the electrostatic effect in the transition state.

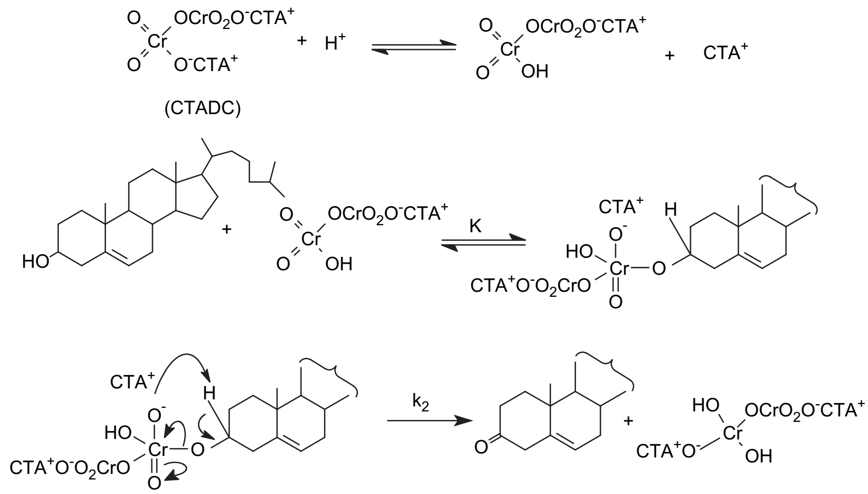
Similar oxidation kinetics of benzyl alcohol by CTADC were carried out in various organic solvents and in surfactant systems.[363] Benzaldehyde was found to be the only oxidation product (Scheme 94).



Scheme 94.



Scheme 93.



Scheme 95.

The variation in rate constants with change in [acid], [substrate], [oxidant], and [surfactant] led to the proposal that the reaction occurs in a reversed micellar system produced by the oxidant, akin to an enzymatic environment. The changes in the rate constant with variations in [surfactant] and solvent isotope effect suggest the path of the reaction to be through the formation of an ester complex, the decomposition of which is the rate-determining step.

The rate of oxidation of cholesterol by CTADC in DCM in the presence of acetic acid to 5-cholesten-3-one was found to obey Michaelis–Menten-type kinetics.[364] From the inverse solvent isotope effect ($k(D_2O)/k(H_2O)=0.72$) and other kinetic parameters, it was suggested that the reaction occurs in a reversed micellar system, and that the reaction path involves the intermediate formation of an ester complex, which undergoes decomposition to give the product (Scheme 95).

3.8. Other onium dichromates

Some further examples of dichromates with different onium ions are presented in Table 12.

The conventional Cr(VI) oxidants including potassium, sodium, and ammonium dichromates are now in use in solvent-free condition with various techniques. Lou and Xu oxidized some primary and secondary alcohols to the corresponding carbonyl compounds with potassium dichromate in solvent-free conditions with no over-oxidation.[379] They also experienced a difference between shaking and stirring the reaction mixture. On shaking sodium dichromate with various primary and secondary alcohols in solvent-free conditions they obtained the corresponding carbonyl compounds with good yield.[380] Similarly, ammonium dichromate was also used to oxidize aliphatic alcohols[381] and substituted benzyl alcohols[382] to the corresponding carbonyl compounds in dry state.

Comparative studies of the oxidation of diphenyl sulfide,[383] diethyl sulfide,[384] benzyl alcohol,[385] 2-propanol,[386] pentanol,[387] and mixture of pentanol with oxalic acid[388] by different Cr(VI) oxidants were carried out by different workers. From the kinetic results, it was proposed that the bases of the oxidants do not have an appreciable effect on the effectiveness of the oxidant and that all the oxidants behave similarly in the reaction mechanism.

4. Onium halochromates and dichromates containing phosphorus and tellurium

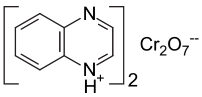
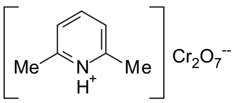
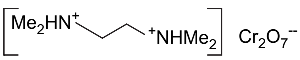
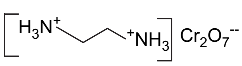
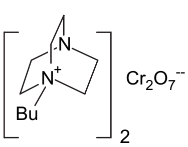
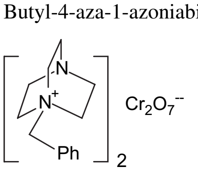
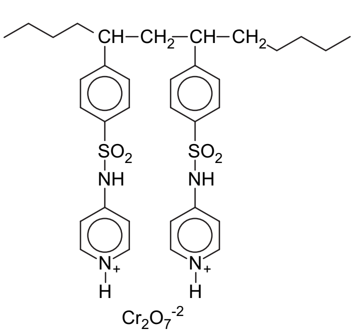
Some hetero-onium reagents such as phosphonium and telluronium chromates and dichromates have recently been synthesized for specific oxidation reactions.

Benzyltriphenylphosphonium chlorochromate (BTPPCC) was prepared from an aqueous solution of chromium trioxide in 6 N HCl and benzyltriphenylphosphonium chloride in quantitative yield at room temperature.[389] This reagent is found to be stable in the dark and can be kept for a long period without losing its activity. The reagent is soluble in acetonitrile, chloroform, and dichloromethane and sparingly soluble in carbon tetrachloride, ether, and hexane. This compound can selectively oxidize benzyl alcohol in the presence of phenyl ethanol, benzhydrol or methyl phenyl sulfide. The reactivity of this reagent in organic solvents and in microwave conditions was compared separately for the oxidation of alcohols to the corresponding aldehydes. Oxidation of sulfides to the corresponding sulfoxides was also reported by Hajipour and Ruoho.[390]

Similarly, butyltriphenylphosphonium chlorochromate was readily prepared from an aqueous solution of chromium trioxide in 6 N HCl and butyltriphenylphosphonium bromide in quantitative yield.[391] It was used for the transformation of alcohols into the corresponding carbonyl compounds in good yield.

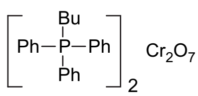
Mohammadpoor-Baltork et al. prepared butyltriphenylphosphonium dichromate (BTPPD) and reported its application for the oxidation of some hydroxy groups to the corresponding carbonyl compounds.[392] This reagent was also used for the transformation of thiones to the corresponding carbonyl compounds by microwave irradiation.[393] The reactions were found to be faster in the

Table 12. Examples of other onium dichromates and their investigations

Reagent	Investigation	Ref.
 Quinoxalinium dichromate	Reaction kinetics of oxidation of substituted benzyl alcohols	365
 Bis(2,6-dimethylpyridinium)dichromate	X-ray crystallographic study	366
 Tetramethyl-ethylenediammonium dichromate	Selective oxidation of benzylic and allylic alcohols	367
$[Me_4N^+]_2Cr_2O_7^{2-}$ Tetramethylammonium-dichromate (and trichromate)	X-ray diffraction study and differential scanning calorimetry; crystallizes in an orthorhombic form	368
$[Bu_4N^+]_2Cr_2O_7^{2-}$ Bis-tetrabutylammonium dichromate	Oxidation of naphthalene and 2-methylnaphthalene to corresponding naphthaquinones	369
	Synthesis of 1,4-diacylbenzenes	370
	Conversion of oximes into the corresponding carbonyl compounds under microwave irradiation	371
$[(C_8H_{17})Me_3N^+]_2Cr_2O_7^{2-}$ Bis-octyltrimethylammonium dichromate	Crystallographic study from X-ray diffraction data; structure consists of discrete dichromate anions stacking up in a layer, separated by a double layer of octyltrimethylammonium surfactant chains lying in parallel. The interlayer spacing of 43.4 Å, smaller than the expected value for the fully extended molecular model, is achieved through a tilting of the surfactant chains of about 37.5° from the normal to the $(Cr_2O_7)^{2-}$ plane	372
$[(C_{16}H_{33})Me_2N^+]_2Cr_2O_7^{2-}$ Bis-dihexadecyldimethyl-ammonium dichromate	X-ray diffraction study; the compound exhibits a lamellar structure	373
 Ethylenediammonium dichromate	X-ray crystallography studies	374
 Butyl-4-aza-1-azoniabicyclo[2.2.2]octane dichromate	Oxidation of sulfides to corresponding sulfoxides	375
 1-Benzyl-4-aza-1-azoniabicyclo[2.2.2]octane	Conversion of oximes and semicarbazones into the corresponding carbonyl compounds in solvent-free conditions in presence of a catalytic amount of aluminum chloride	376
 Poly[*N*-(4-pyridinium dichromate)-*p*-styrenesulfonate]	Oxidation of alcohols to corresponding alcohols in aprotic solvents	377
	Oxidation of oximes to carbonyl compounds	378

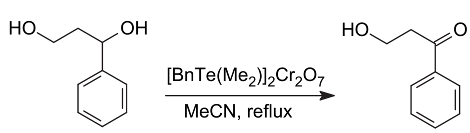
microwave method when carried out neat than refluxing in solution. Similarly, the oxidation of thiols by BTPPD under microwave irradiation afforded corresponding disulfides.[394]

The reaction kinetics of substituted benzyl alcohols and α-hydroxy acids by BTPPD were investigated by Banerji and co-workers.[395]

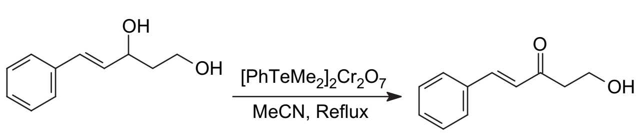


BTPPD

Recently Song[396] prepared benzyldimethyltelluronium dichromate by adding an aqueous solution of potassium dichromate to an aqueous solution of benzyldimethyltelluronium bromide at room temperature. The resulting orange-yellow solid is slightly soluble in acetonitrile or dimethylformamide, air stable, and effective after long storage times. Song reported the reactivity of the oxidizing agent with benzylic alcohols. The oxidation of benzyl alcohol with 2 equiv of benzyldimethyltelluronium dichromate in boiling acetonitrile gave benzaldehyde in 1 h in 95% yield. The chemoselective oxidation of diols was observed for benzyldimethyltelluronium dichromate. 1-Phenyl-1,3-propandiol (**125**) having a benzylic and a saturated primary hydroxyl group under the same reaction conditions was oxidized to 3-hydroxy-1-phenyl-1-propanone (**126**) in 4 h in 75% yield without affecting a saturated primary hydroxy group (Scheme 96). Similarly, compound **127** was also transformed into the corresponding hydroxy ketone (**128**) in 5 h in 67% yield (Scheme 97).



Scheme 96.



Scheme 97.

5. Conclusions

Albeit Cr(VI) is undisputedly a reagent with a caution tag for its carcinogenic characteristics, it is proliferated in the chemical world due its versatile applications. In redox reactions, Cr(VI) is reduced to Cr(V), which plays the vicious role of damaging DNA. With different nitrogen bases, chromium trioxide or dichromates, the conventional Cr(VI) oxidants, are recasted to mild halochromates or quaternary ammonium dichromates for the oxidation of organic substrates in both aqueous and non-aqueous media to selective products. The recasting technique has also been used for solid-state oxidation by Cr(VI) on various solid matrices. These techniques may help in removing the caution tag from Cr(VI) and, at the same time, may provide scope for generating new reagents with improved selectivity and for green chemistry. Further, the use of tailor-made onium reagents may be explored to produce biomimic systems like micelles, reversed micelles, microemulsions and vesicles with Cr(VI) at a specific site, i.e., the interface of organized assemblies or in the nano-domain of reversed micelles, which can have analogy with enzymes.

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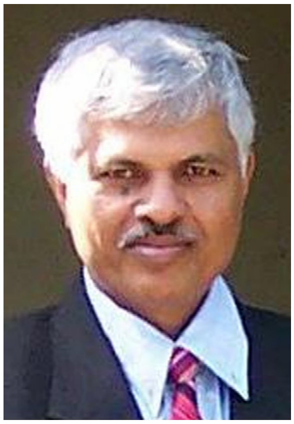
Biographical sketch



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