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Review Article

Oxidation of some organic compounds with selective catalysis – Review

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ABSTRACT

The review surveys the development of kinetics and various oxidizing agents which can be used during the study of chemical kinetics along with oxidation of some organic substrates by hexacyanoferrate (III) /HCF (III). Since HCF (III) is acting as relatively poor oxidant, it acts as a selective outer-sphere reagent applicable for most of the easily oxidizable substrates and normally it is used as free radical interceptor; because of which it converts into a species acting as an efficient one electron oxidant mainly for the octahedral complexes in comparative study.

Keywords: Oxidation; organic compounds; metal, catalyst; selective

1. Introduction

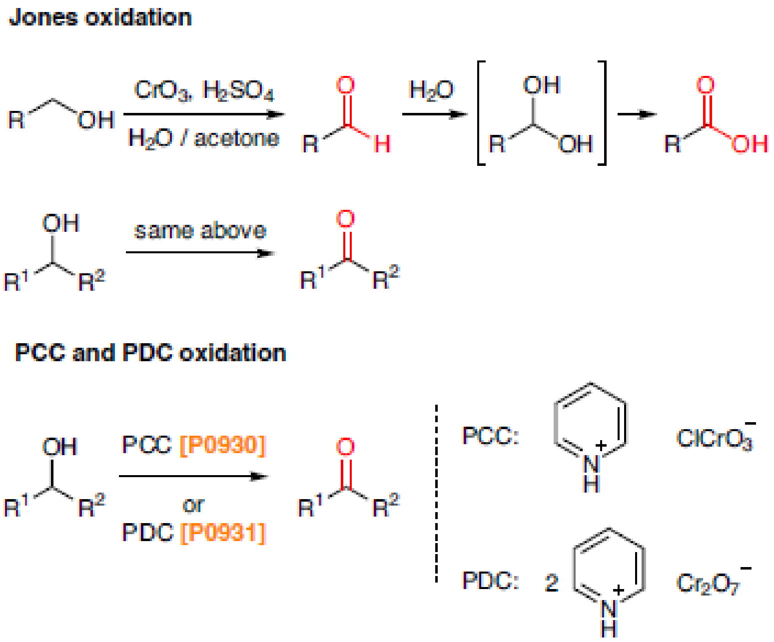
An oxidation–reduction or redox reaction is a reaction that involves the transfer of electrons between chemical species (the atoms, ions, or molecules involved in the reaction). Redox reactions are all around us: the burning of fuels, the corrosion of metals, and even the processes of photosynthesis and cellular respiration involve oxidation and reduction.

Oxidation is the reaction caused by contact between substances and oxygen molecules. Such substances may be metals or non-metals, such as living tissues. More technically, oxidation can be defined as the loss of one electron during the phase where two or more elements interact. In this, the elements do not necessarily include oxygen. In short, it can be described as an atom’s enhanced oxidation state via a chemical reaction. It's exact opposite is called reduction, which exhibits a decrease in its oxidation state. Both reactions entail formal electron transfers. Net loss involves oxidation while net gain is the state of reduction.

Oxidation, which makes its target substance lose electrons, is one of the most basic reactions in organic chemistry and is exemplified by the combination with oxygen or a dehydrogenation reaction. In particular, oxidizing agents have often been used for the transformation of alcohols to the corresponding aldehydes, ketones or carboxylic acids. Heavy metal compounds, such as chromium(VI) oxide and potassium permanganate, have been exploited for many years. Later, less harmful oxidizing agents without heavy metals were developed, such as Dess-Martin periodinane, the Mukaiyama oxidizing agent and oxoammonium salts. Moreover, oxidation reactions employing inexpensive cooxidants have been reported in the presence of oxidation catalysts like tetrapropylammonium perruthenate (TPAP) and TEMPO. In this way, oxidation reactions involving organic compounds have great diversity, and many books on oxidation have been published. [1] This report introduces a variety of oxidizing agents and catalysts for oxidation. We hope that it will be useful for your research in organic synthesis.

Chromate Salts Jones et al. reported that a mixture of chromium oxide (VI) and diluted sulfuric acid was useful for the oxidation of alcohols, and this reaction is called Jones oxidation.) It can convert primary and secondary alcohols into carboxylic acids and ketones, respectively. Since this report, chromium oxidants have been improved to develop the Sarett-Collins oxidation [2,3] process using complex chromium(VI) oxide-2py, pyridinium chlorochromate (PCC) [P0930] [4] and pyridinium dichromate (PDC) [P0931]. [5] These reagents can oxidize primary alcohols to aldehydes without overreaction. Caution: Chromium(VI) compounds and the chromium residue after the reaction are highly toxic, so they should be handled or discarded with consideration to the environment.

Transition metal complexes are effective and selective catalysts in a variety of organic reactions. Although these catalysts offered interesting results such as low influence of diffusion mechanisms on reaction performance, they become more useful if the separation process is tagged to recover them at the end of reaction especially for precious and strategic metal catalysts. However, the inclusion of separation process in some cases might be very difficult and challenging. The current developments in catalysis are mainly focused on immobilization of metal ions complexes either on inert materials, or on functionalized solid supports [6–9]. These heterogenized catalysts combine the advantages of homogeneous and heterogeneous catalysts and are capable of minimizing the drawbacks of both types of catalyst. They offered numerous advantages over solution phase catalysts such as, ease of separation from reaction mixture, significant reduction in problems of waste disposal, and re-use applications by recycling [10-12]. Early transition metal compounds (e.g., Mo, Ti, W, and V) in combination with hydrogen peroxide or alkylhydroperoxide are the most popular catalytic systems in the epoxidation of alkenes. In the industrial production of propylene oxide by Halcon process, the liquid phase epoxidation of propylene was carried out successfully using Mo(VI) catalyst in the presence of alkyl hydroperoxide. During the last decade, studies on the epoxidation of alkenes using heterogenized Mo(VI) catalysts have been carried out in the presence of *tert*butylhydroperoxide (TBHP). Carreiro et al. used boronic acid group containing resins as a support for Mo(VI) catalyst in the epoxidation of alkenes by TBHP [13]. Sherrington group has developed a wide range of polymer-supported Mo(IV) catalysts for epoxidation of alkenes. Among these heterogenized Mo(IV) systems, the polybenzimidazole and polysiloxane-supported systems are stable and offered significant technological applications in catalysis [14,15].

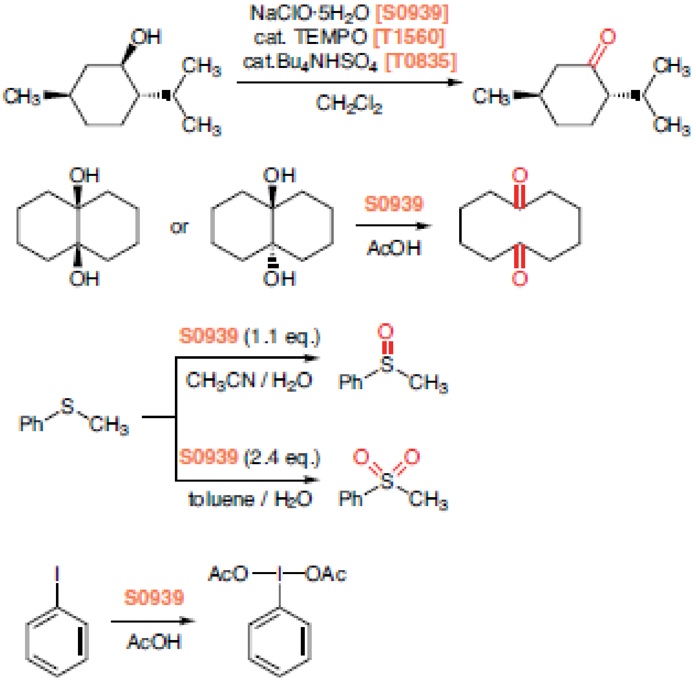


Scheme 1. Jones and PCC/PDC oxidation

2. Experimental

Sodium Hypochlorite

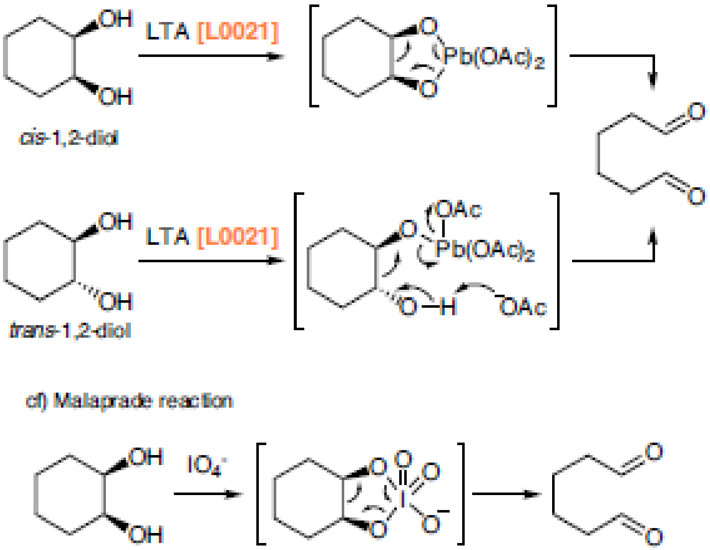
Sodium hypochlorite pentahydrate ($NaClO·5H_2O$) [S0939] is a stable crystalline solid and effective for the oxidation of hydroxy and sulfide groups. For instance, S0939 can oxidize secondary alcohols into ketones in the presence of a catalytic amount of TEMPO [T1560]. [16] S0939 is also utilized in the oxidative cleavage of 1,2-diols [17] and oxidation of sulfides. [18]Sulfoxides and sulfones can be synthesized in high yields by adjusting the equivalents of S0939. Furthermore, it has recently been reported that S0939 is useful for the convenient synthesis of hypervalent iodine compounds. [19]



Scheme 2. Sodium hypochlorite pentahydrate oxidation

Criegee Oxidation

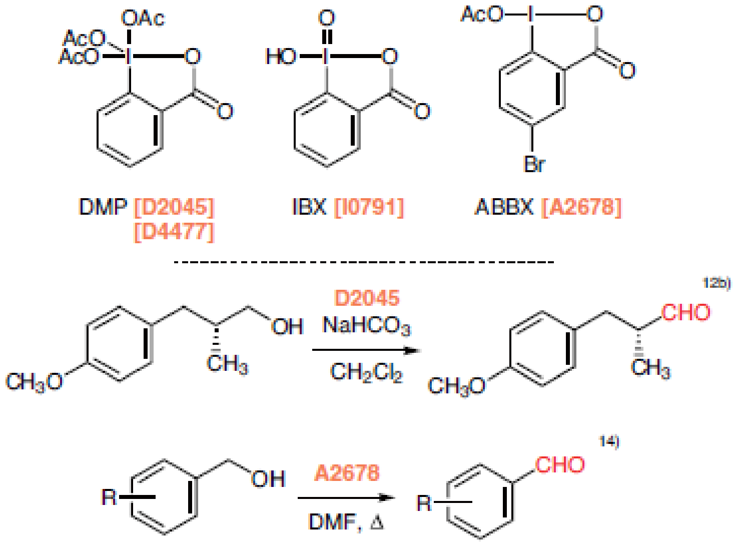
Criegee oxidation gives two ketones or aldehydes from 1,2-diols by using lead(IV) tetraacetate (LTA) [L0021] as an oxidant. [20] This reaction is different from the oxidative cleavage reaction using periodate salt (= Malprade reaction) [21]and proceeds when applied to *trans*-1,2-diols, which would be difficult to pass through the fivemembered intermediate. This indicates another reaction mechanism that does not pass through the cyclic transition state.



Scheme 3. Criegee oxidation

Oxidation using Hypervalent Iodine Compounds

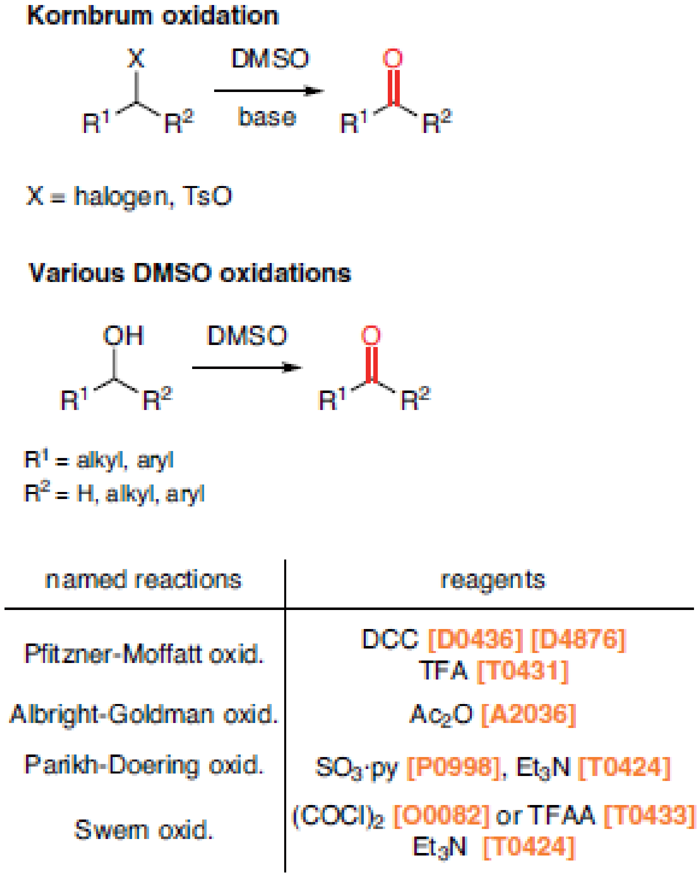
Dess-Martin periodinane (DMP) [22] [D2045] [D4477] can oxidize primary and secondary alcohols into aldehydes and ketones, respectively. DMP has some advantages compared with chromate (VI) compounds: the reaction using DMP proceeds under mild conditions; the generality of reactive substrates is wide; the environmental impact is lower; and the treatment after the reaction is easy. 2-Iodoxybenzoic acid (IBX) [23] [I0791] and 1-acetoxy-5- bromo-1,2-benziodoxol-3(1*H*)-one (ABBX) [24] [A2678], which was developed by Togo, are also utilized as oxidants of alcohols as well as other hypervalent iodine compounds. [25] These compounds are introduced in our brochure “Hypervalent Iodine Compounds”.



Scheme 4. Hypervalent Iodine oxidation

DMSO Oxidations and Odorless Swern Oxidants

Kornblum *et al*. found that the carbonyl group was produced from benzyl halides and tosylates by the treatment of DMSO [D0798] in the presence of a base. [26] After this report, various types of oxidations using DMSO have been reported as follows: Pfitzner- Moffatt oxidation [27] using DCC [D0436] or DCC (granulated) [D4876]; Albright-Goldman oxidation [28] using acetic anhydride [A2036]; Parikh-Doering oxidation [29] using SO_3-pyridine complex [P0998]; and Swern oxidation [30] using oxalyl chloride [O0082]. These reactions are utilized widely from the laboratory scale to the industrial scale.



named reactions	reagents
Pfitzner-Moffatt oxid.	DCC [D0436] [D4876] TFA [T0431]
Albright-Goldman oxid.	Ac_2O [A2036]
Parikh-Doering oxid.	SO_3·py [P0998], Et_3N [T0424]
Swern oxid.	$(COCl)_2$ [O0082] or TFAA [T0433] Et_3N [T0424]

Scheme 5. Swern Oxidants oxidation

One problem with DMSO oxidation is the odor of the byproduct dimethyl sulfide. To solve this problem, Togo *et al*. developed the odorless and recyclable imidazolium salts [M2274] and [M2321] for use in Swern oxidation [31] and Corey-Kim oxidation, respectively

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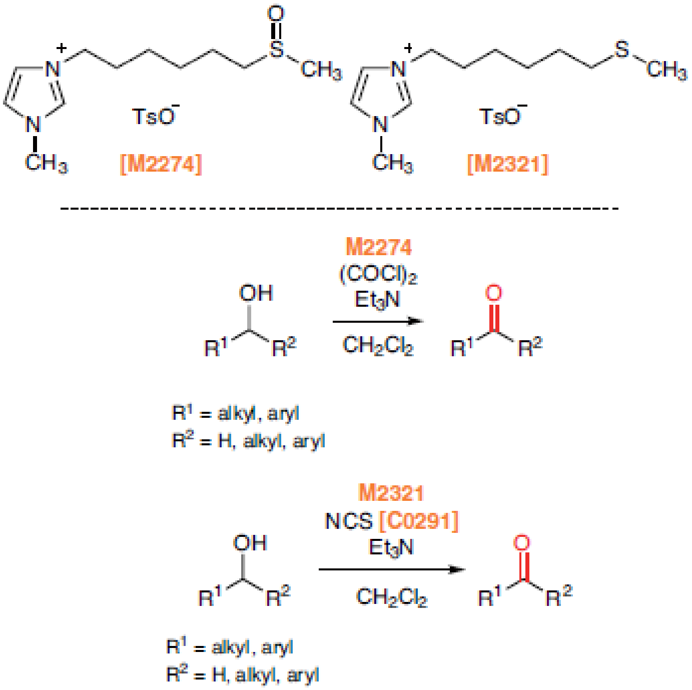
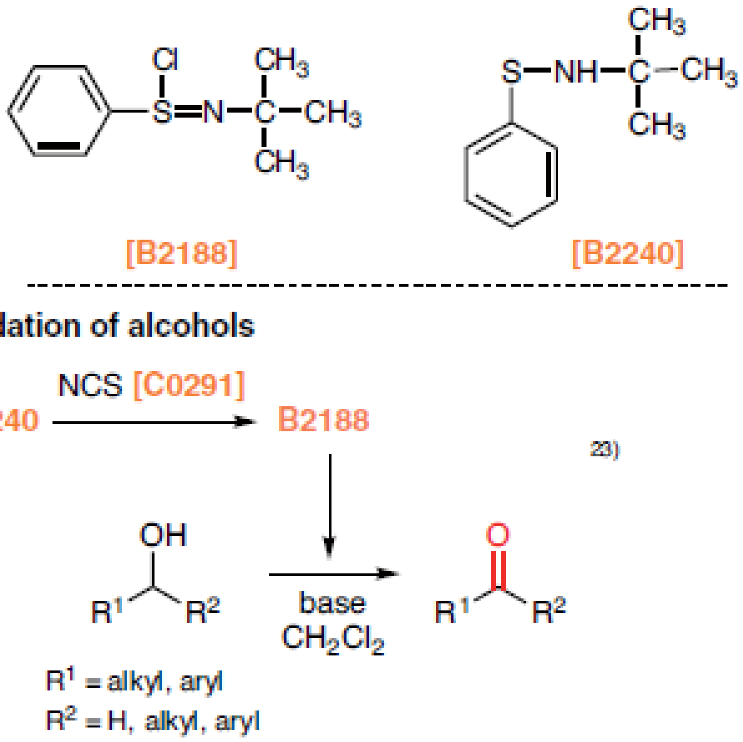
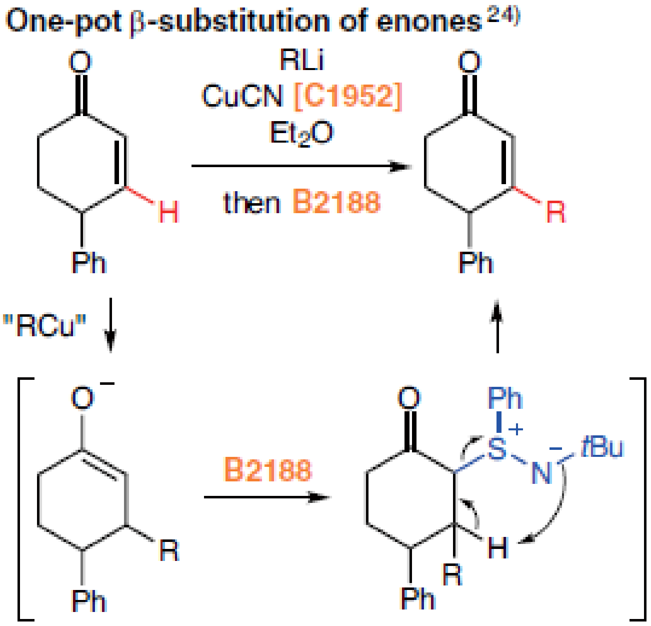


Mukaiyama Oxidation Reaction

Mukaiyama's group reported two new oxidation reactions using *N-tert*-butylbenzenesulfinimidoyl chloride [B2188], [32] and catalytic amounts of *N-tert*-butylbenzenesulfenamide [B2240] and NCS [C0291], [33] respectively. It is considered that B2188 is generated *in situ* by the reaction of B2240 and NCS, and turns into B2240 after the reaction; thus B2240 works as a catalyst. B2188 is a stable solid and can give a,b-unsaturated ketones from an enolate by deprotonation at the a-position or 1,4-addition. [34] In addition, the new method has been reported to afford a ketone from an aldehyde, an alkyllithium and B2188 in one pot. [35]

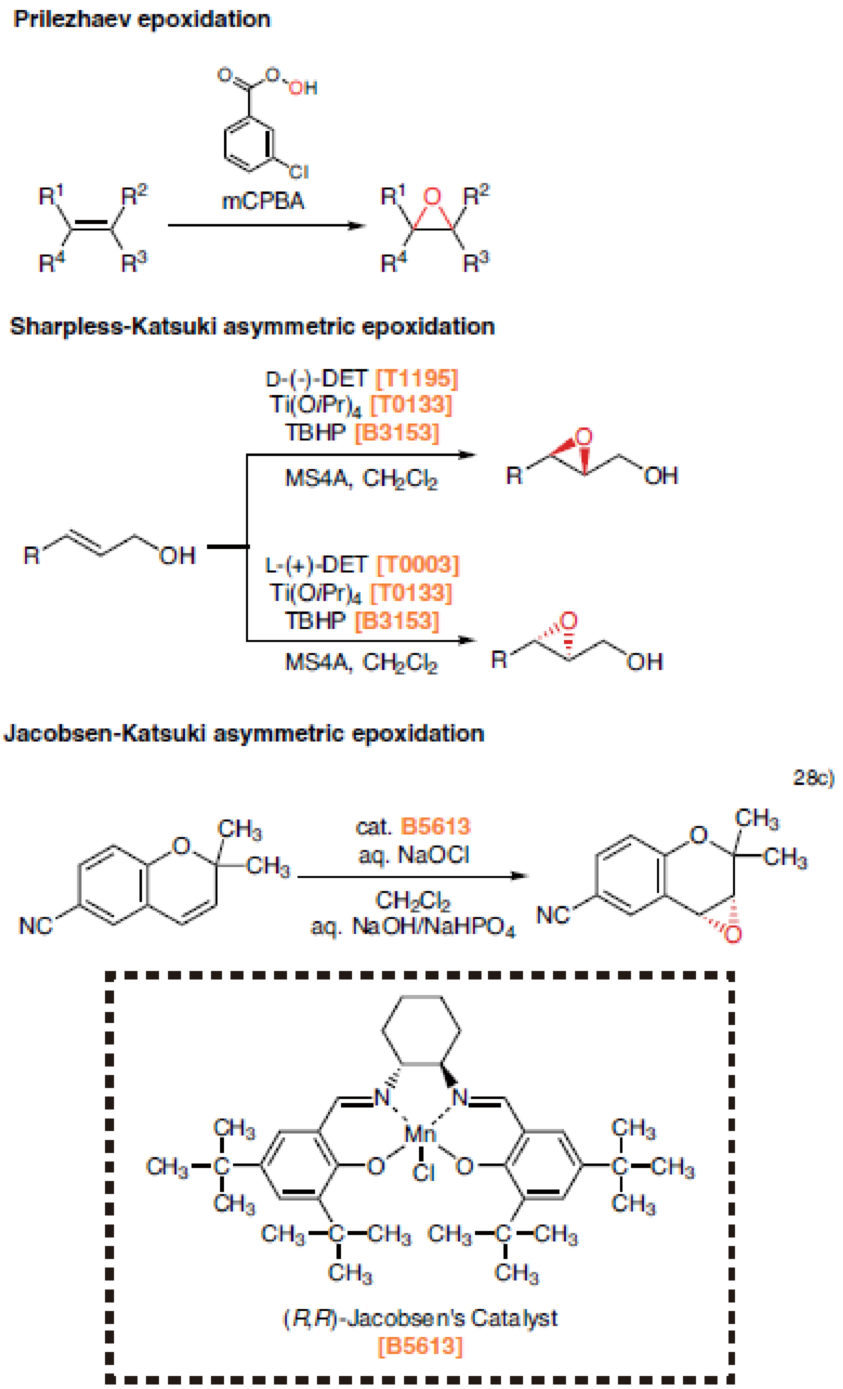




Scheme 6. Mukaiyama oxidation

Epoxidation Reaction

Epoxidation is also an oxidation reaction and the Prilezhaev(Prileschajew) reaction [36] with mCPBA is regarded as a representative epoxidation. Furthermore, asymmetric epoxidation reactions have been reported such as Sharpless-Katsuki asymmetric epoxidation [37] for allyl alcohols and Jacobsen- Katsuki asymmetric epoxidation [38] of *cis*-olefins. Sharpless-Katsuki asymmetric epoxidation is often used in the total syntheses of natural products.

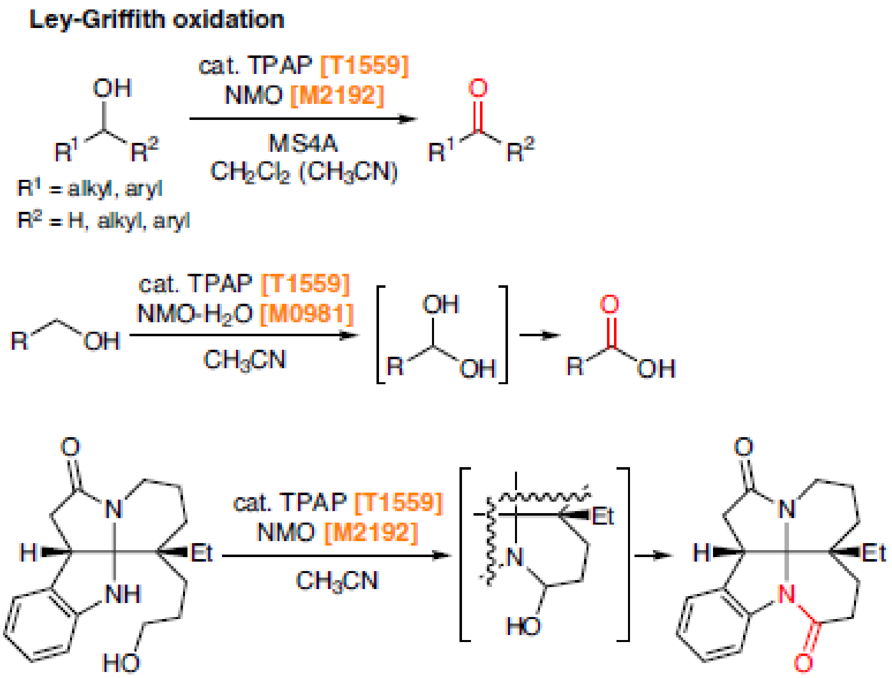


Scheme 7. Epoxidation oxidation

Catalytic Oxidation Reactions

Oxidation with TPAP Catalyst

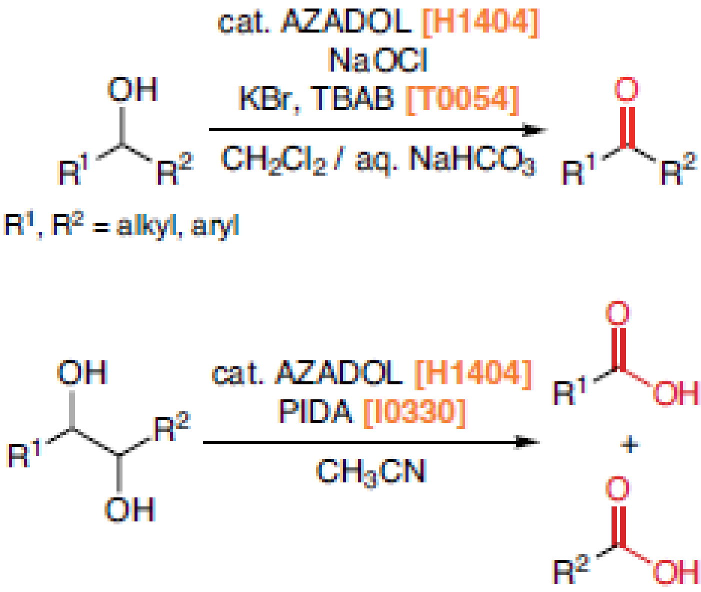
Tetrapropylammonium perruthenate (TPAP) [T1559] catalyst can oxidize alcohols into aldehydes and ketones by the addition of 4-methylmorpholine *N*-oxide (= NMO) [M2192] as a cooxidant (Ley-Griffith oxidation). [39] This reaction proceeds under very mild conditions to give the corresponding product in high yield even when applied to unstable substances. Moreover, this reaction can oxidize primary alcohols to carboxylic acids in the presence of water by hydration of the aldehyde to form a *gem*-diol and subsequent reoxidation. [40] TPAP and NMO are often applied in the syntheses of natural products. Gaich's group, for instance, have reported the total synthesis of (-)-leuconoxine by ingeniously applying this reaction at the last step. [41]



Scheme 8. Tetrapropylammonium perruthenate (TPAP) oxidation

Oxidation Using AZADOL®

AZADOL® [H1404], known as the precursor of an oxidation catalyst, is a hydroxyamine developed by Iwabuchi *et al*. [42] The oxidizing ability of H1404 is superior to that of TEMPO [T1560], particularly for secondary alcohols. In addition, 1,2-diols are oxidatively cleaved by the treatment of a catalytic amount of PIDA [I0330] to afford two carboxylic acids. H1404 is anticipated as a green catalyst for oxidation since sodium hypochlorite, sodium chlorite and even oxygen in air can be utilized as cooxidants. [43]

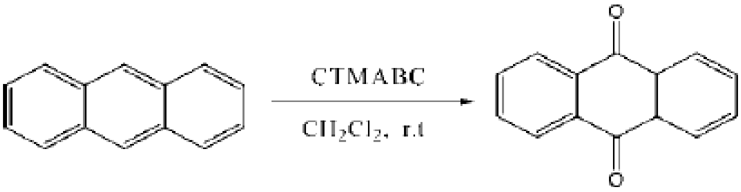


Scheme 9. AZADOL® oxidation

Cetyltrimethylammonium Bromochromate

synthetic potential of cetyltrimethylammonium bromochromate, $C_{19}H_{42}NCrO_3Br$ (CTMABC), and we have found that this reagent has certain advantages over similar oxidizing agents in terms of amounts of oxidant and solvent required, easier workup, and higher yields. Further, CTMABC does not react with acetonitrile, which is a suitable medium for studing kinetics and mechanism. The results obtained with CTMABC are very satisfactory and show the new reagent as a valuable addition to the existing oxidizing agents.

CTMABC in dichloromethan also oxidizes anthracene and phenanthrene to anthraquinone and phenanthraquinone in 98% and93% yields, respectively. These yields are higher than those obtained by other oxidizing agents under mild conditions. This reagent works as efficiently as activated manganese dioxide or Collins reagent.



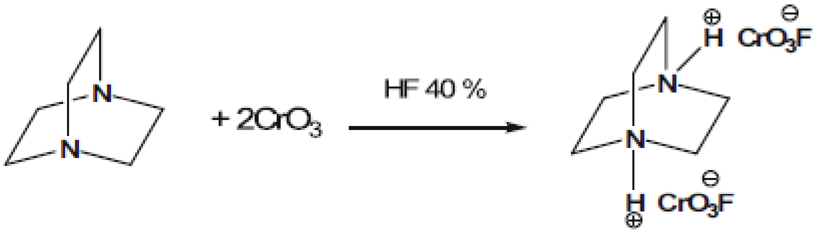
Scheme 10. CTMABC oxidation

CTMABC has also been used for oxidation of carbohydrates such as1,2:5,6-di-O-isopropylidine-a-D-glucofuranose to its relative ketosugare , like pyridinium chlorochromate, but in 97% yield (mp 105–1078C; lit.[14] 1068C) in 105 min. [44]

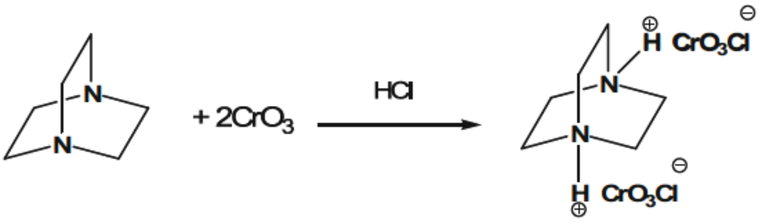
Inside a glove box purged by argon, a measured amount of chromium(VI) oxide (CrO3: 1.07 g, 10.7 mmol) is dissolved in dry acetonitrile (25 ml) in a polyethylene beaker and a stoichiometric amount of cetyltrimethylammonium bromide, $CH_3(CH_2)_{15}(CH_3)_3$ N Br_2 (3.89 g, 10.7 mmol) is added with stirring at room temperature. Within 5 min, a clear orange solution results. Upon refrigerating, solid CTMABC forms, which is isolated by filtration, washed with dry isopropanol and diethyl ether, pressed between the folds of a filter paper, and dried in vacuum for 1 h. Slow evaporation of the concentrated solution of $CH_3(CH_2)_{15}$ $N(CH_3)_3$ $[CrO_3Br]_2$ in acetonitrile gives suitable crystals after 1 week. Yield: 4.71 g (95%); mp 1048 C. $C_{19}H_{42}BrCrNO_3$: calc. C, 49.14; H, 9.05; N, 3.01. Found: C, 48.76; H, 9.19; N, 2.95. This procedure can be performed on a 250-g scale without any difficulty.

Dabco Ammonium Halochromates

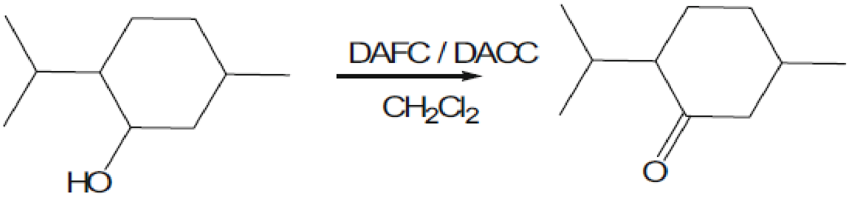
dabco ammonium fluorochromate (VI) (DAFC) and dabco ammonium chlorochromate (VI) (DACC) synthesized for the mild and efficient oxidation of organic substrates. A 0.2 g, 2 mmol sample of chromium(VI) oxide, CrO_3, and 3 mmol, 15 ml of 40% hydrofluoric acid were added to10 ml of water in a 100 ml polyethylene beaker with stirring. After 5–7 min, the homogeneous solution was cooled to 1–2 _C and 0.323 g, 1 mmol of pure dabco, was added in small portions, to this solution with stirring over a period of 2–4 h and stirring was continued for 0.5 h at ^{0}C. The precipitated orange solid was isolated by filtration on a polyethylene funnel, and washed with petroleum ether (3 9 20 ml) and dried in vacuum for 2 h at room temperature. Yield: 90%; mp 176 ^{0}C (electrical conductivity: 505 ms, pH 0.01 Mol: 2.5) [45]



Scheme 10. Synthesis of DAFC



Scheme 11. Synthesis of DAFC



Scheme 12. Menthol oxidation with DAFC/DACC

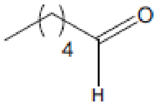
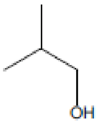
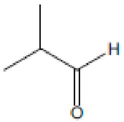
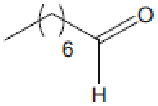
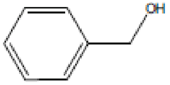
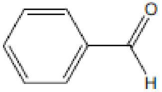
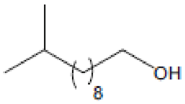
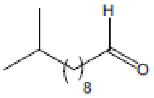
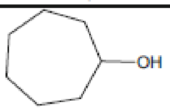
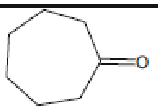
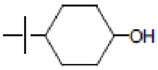
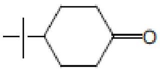
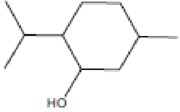
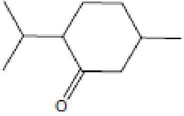
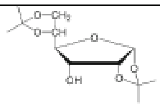
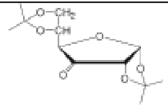
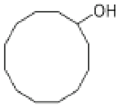
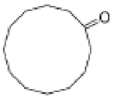
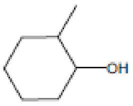
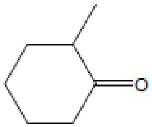
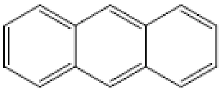
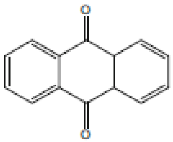
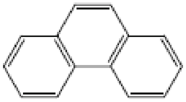
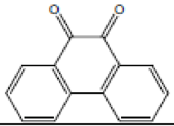
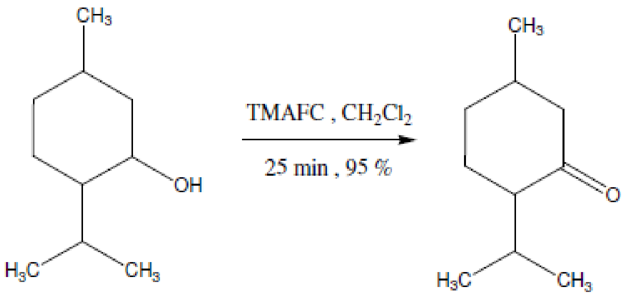
entry	Substrate	Time (min)	Product	Yield (%)	M.P.(°C)	B.P. (°C)
1		54(DAFC) 60(DACC)		85(DAFC) 82(DACC)		102
2		47(DAFC) 49(DACC)		78(DAFC) 80(DACC)		63-64
3		52(DAFC) 58(DACC)		77(DAFC) 80(DACC)		170- 172
4		35(DAFC) 38(DACC)		75(DAFC) 75(DACC)		177- 179
5		42(DAFC) 40(DACC)		78(DAFC) 80(DACC)		230- 234
6		58(DAFC) 55(DACC)		78(DAFC) 68(DACC)		179- 181
7		75(DAFC) 88(DACC)		72(DAFC) 75(DACC)	47-50	
8		70(DAFC) 75(DACC)		80(DAFC) 81(DACC)		83 81-
9		80(DAFC) 73(DACC)		63(DAFC) 60(DACC)	111-113	
10		64(DAFC) 60(DACC)		78(DAFC) 80(DACC)	50-61	
11		80(DAFC) 88(DACC)		72(DAFC) 67(DACC)		162- 163
12		55(DAFC) 62(DACC)		81(DAFC) 80(DACC)	284-285	
13		66(DAFC) 58(DACC)		75(DAFC) 72(DACC)		

Table 1. Oxidation of organic substrates with DAFC and DACC

dabco ammonium fluorochromate(VI) DAFC and dabco ammonium chlorochromate(VI) DACC are easily synthesized. They have proven to be low cost, readily available oxidizing reagents for a variety of organic compounds. Their advantages include higher yields, shorter reaction time, lower substrates/oxidant molar ratios, and ease of separation of products. Moreover, during the reaction, the color of the oxidants change from orange to brown, thus providing a visual means for ascertaining the progress of the oxidation. This reaction is easily applicable for producing a small to large amount of carbonyl compounds in a simple and efficient procedure. Because of phase transfer properties of reagents, availability, versatility and high oxidant interaction, these reagents are suitable for oxidation of organic compounds.

Tetramethyl ammonium Fluorochromate

The oxidation of alcohols to carbonyl compounds is a fundamental transformation in organic chemistry since carbonyl compounds are widely used as intermediates both in manufacturing and research. A fast and facile microwave accelerated oxidation of primary alcohols to aldehydes and secondary alcohols to ketones (Scheme 1).



Scheme 13. Menthol oxidation with TMAFC

Experiments were carried out in closed vessel multi-mode Microsynth Milstone laboratory microwave oven using a 900 Watts Westpointe microwave operating at 3.67 GHz with an internal volume of 0.9 m. All the experiments had good reproducibility by repeating the experiments in same conditions.

Tetramethylammonium fluorochromate (TMAFC) was prepared by the reported method [8]. In a small-scale experiment TMAFC (1 mmol) was suspended in dichloromethane (ca. 2 mL) and an alcohol (l mmol in 0.5 to 1.5 mL of CH2Cl2) was rapidly added at room temperature and the resulting mixture stirred vigorously for the appropriate time. The mixture was irradiated for the time indicated in Table 1 by microwave radiation (3.67 GHz, 300 W). The molar ratio of substrate to oxidant was 1:1 in the case of alcohols and 1:2 in the case of polycyclic arenes (antracene and phenantrene). The solution became homogeneous briefly before the black-brown reduced reagent precipitated. The progresses of the reactions were monitored by TLC and UV/Visible spectrophotometer (at 352 nm). Analysis of the reaction mixture for the corresponding carbonyl compound was accomplished by the procedure reported in earlier papers. The above procedure may be carried out on 1-100 g scales without any problem. [46]

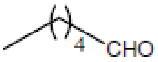
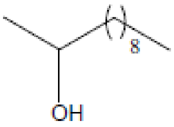
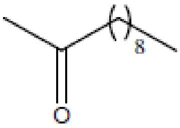
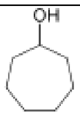
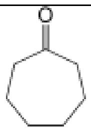
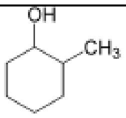
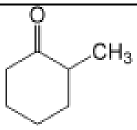
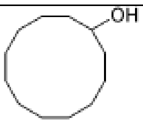
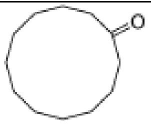
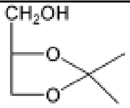
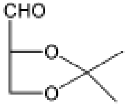
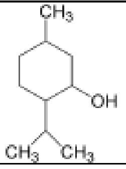
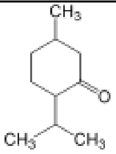
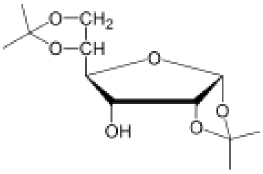
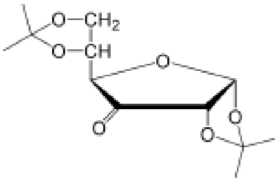
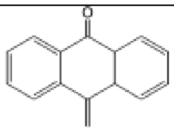
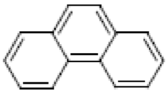
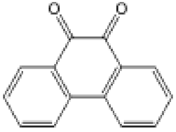
Substrate	Time (min)	Product	Yield%
	6		95
	11		95
	13		92
	17		92
	15		90
	16		98
	15		89
	25		95
	13		92
	20		98
	23		90

Table 2. Oxidation of some alcohols and polyarenes with tetramethylammonium fluorochromate: TMAFC

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