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Chromium-Catalyzed Oxidations in Organic Synthesis[‡]

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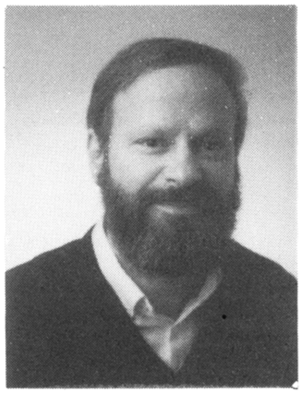
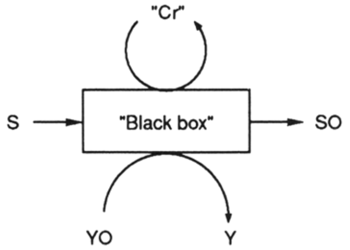


Jacques Muzart was born in 1946, in Vienne La Ville, a small village in the Argonne area, 200 km east of Paris. After his graduate work in organic photochemistry (Doctorat de 3ème cycle—1972, Doctorat d'Etat—1976) under direction of J. P. Pete at the Université de Champagne-Ardenne, Reims, he spent 15 months involved in natural product synthesis with E. J. Corey at Harvard University. On his return to Reims, he started the study of the photochemistry of η^3-allylpalladium complexes. He is now Directeur de Recherche at the Centre National de la Recherche Scientifique. His research interests are in organic chemistry, with currently particular reference to catalysis and photoinitiated asymmetric reactions.

I. Introduction

Chromium oxidations have been widely explored since the very beginning of organic chemistry, and the topic remains of current interest as exemplified by the extensive number of papers in which at least one step involves the use of an oxochromium(VI) reagent. This is primarily due to the wide variety of oxidizable functions by the proper choice of reagent. A plethora of chromium reagents and procedures have been proposed and they have been extensively described in reviews and books.[1,2] These methods, in which the oxidative ability and selectivity have now been in part evaluated by computer assistance,[3] imply either the use of stoichiometric quantities or large excesses of poisonous chromium reagents.[4] The metallic byproduct residues are also toxic, and furthermore, their presence often makes the workup difficult.

SCHEME 1



Considering cost and environmental factors, it would be advantageous to use catalytic methods. Such a system is illustrated in Scheme 1 where "Cr" is the catalyst (chromium salt or complex), YO the oxygen source, and S and SO the organic substrate, respectively, before and after oxidation. To be of interest, the process has to employ an inexpensive YO and the byproduct Y has to be easily disposable or recyclable. Furthermore, the synthetic organic chemist engaged in a laboratory scale experiment would prefer to test the feasibility and the efficiency of an oxidation step with a system which only requires a commercial or rapidly available catalyst.

For the last few years, we have been interested in chromium-catalyzed oxidations. Since there is no literature report reviewing this topic,[5] we decided to undertake this task. The present review will be exclusively concerned with chromium-catalyzed oxidations of organic compounds which lead to the formation of a new C—O or C=O bond. Hence, chromium-catalyzed dehydrogenations of hydrocarbons such as the aromatization of cyclohexane[34] or the dehydrocyclization of hexane[35] will not be included here. Oxidations carried out to achieve a complete decomposition of organic compounds[36] will also be discarded. This review will be organized around the formal oxidation state of the catalyst. Of course, such a classification may be arbitrary since the real catalyst could be a new species formed in situ with an oxidation state different from that of the starting chromium material. Throughout

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[‡] No reprints available.

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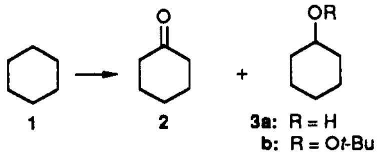
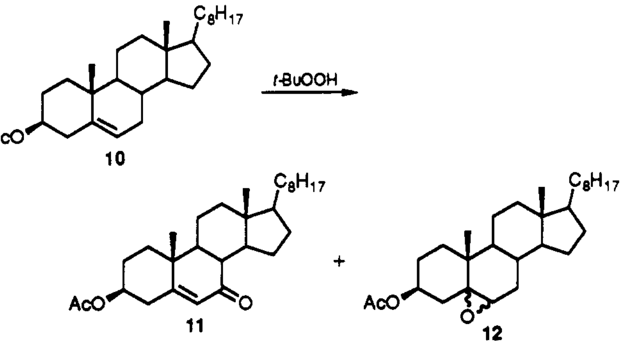
TABLE 1. Oxidation of Cyclohexane



reactants and conditions[a]	C		results		ref
			2	3	
ozone					
$Cr(CO)_6$	8.7	*S*	84–89		38
oxygen or air					
$Cr(TPP)I$ + propionaldehyde (5.6 eq.) [1/∞/0.2] PhH, 30 °C, 1.5 h		*T*	1	0.5 (R = H)	186
$[Ru_3O(OCOR)_6L_3]^+$ [37000/∞/1] MeCN, 75 °C, 12 h		*T*	3.2	14.8 (R = H)	165
As above + $CrCl_3$ (1 equiv/Ru_3)		*T*	45.7	150.3 (R = H)	165
$(Bu_4N)_2Cr_4O_{13}$ + $h\nu$[1/∞/0.01] MeCN, 7 h		*T*	3	1.5 (R = H)	265
$(Bu_4N)_2CrO_4$ + $h\nu$[1/∞/0.004] CH_2Cl_2, 16 °C, 3 h		*T*	1.5	1 (R = H)	266
$(Bu_4N)_2CrO_4$ + PhIO (0.02 equiv) + $h\nu$[1/∞/0.004] CH_2Cl_2, 16 °C, 6 h		*T*	5	6 (R = H)	266
hydrogen peroxide					
Cr(TTP)Cl [1/12/0.012] MeCN–CH_2Cl_2, 30 °C, 3 h		*Y*	3.6	1.6 (R = H)	184
Cr(TTP)Cl + 4-aminopyridine (0.13 equiv) [1/12/0.012] MeCN–CH_2Cl_2, 30 °C, 3 h		*Y*	9.0	4.5 (R = H)	184
CrO_3 [1/0.2/0.001] MeCN, 20 °C, 168 h		*T*	20	10 (R = H)	224
$(Bu_4N)_2CrO_4$ [1/0.2/0.001] MeCN, 20 °C, 168 h		*T*	1.4	2.2 (R = H)	224
$(Bu_4N)_2Cr_2O_7$ [1/0.2/0.001] MeCN, 20 °C, 168 h		*T*	18	13.6 (R = H)	224
$(Bu_4N)_2Cr_4O_{13}$ [1/0.2/0.001] MeCN, 20 °C, 168 h		*T*	19	11.2 (R = H)	224
$(Bu_3SnO)_2CrO_2$ [1/0.2/0.001] CH_2Cl_2, RT, 16 h		*T*	0.8	0.4 (R = H)	226
tert-butyl hydroperoxide					
$Cr(acac)_3$ [∞/100/1] C_6H_{12}, 90 °C		*Y/O*	5	48 (R = H) 28 (R = *t*-BuO)	82
$Cr(acac)_3$ + *t*-BuOH (0.5 equiv) [1/0.4/0.0005] neat, 108 °C, 2 h	13	*S*	42	22 (R = H)	83
1-methylcyclohexyl hydroperoxide					
$Cr(acac)_3$ [∞/300/1] C_6H_{12}, 125 °C, 20 h		*Y/O*	7.8	5.6 (R = H)	85
$Cr(st)_3$ [∞/300/1] C_6H_{12}, 125 °C, 20 h		*Y/O*	8.4	5.2 (R = H)	85
cumyl hydroperoxide					
Cr(TPP)Cl [∞/20/1] C_6H_{12}–PhH, RT, 24 h		*Y/O*	13	33 (R = H)	169
iodosylbenzene					
Cr(TPP)Cl [∞/20/1] C_6H_{12}–PhH, RT, 4–15 h		*Y/O*	4	4 (R = H)	169
CrO_3 [1/0.02/0.001] MeCN, 360 h		*T*	3		261
as above + α-picolinic acid (0.002 equiv)		*T*	8		261

[a] See section VIII for the definitions for the abbreviations and symbols.

TABLE 2. Oxidation of 3β-Acetoxy-5,6-cholestene



reactants and conditions[a]	C		results		ref
			11	12	
$Cr(CO)_6$ [1/3/0.5] MeCN, 80 °C, 15 h		*Y*	80		41
$C_5H_5NHCrO_2Cl$ [1/7/0.05] CH_2Cl_2, RT, 4 h	71	*Y*	21	1	78
$C_5H_5NHCrO_2F$ [1/7/0.05] CH_2Cl_2, RT, 4 h	74	*Y*	25	1	78
CrO_3 [1/7/0.05] CH_2Cl_2, RT, 5.5 h	85	*Y*	46	20	241
$(Bu_3SnO)_2CrO_2$ [1/7/0.05] PhH, 50 °C, 25 h	95	*Y*	49	6	227

[a] See section VIII for the definitions for the abbreviations and symbols.

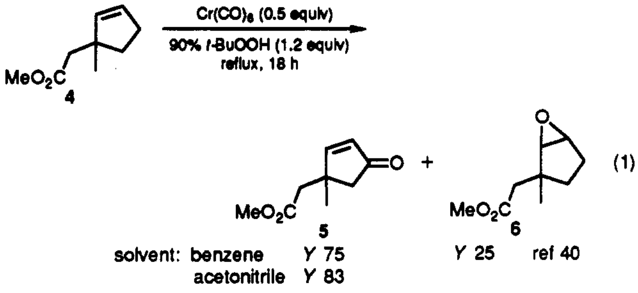
the review, we will try to provide some information concerning the "black box" of Scheme 1. In addition to specific examples, we will include collective tables which will allow comparisons between different procedures applied to the same starting compound or to the same kind of transformation.

II. Chromium(0) as Catalyst

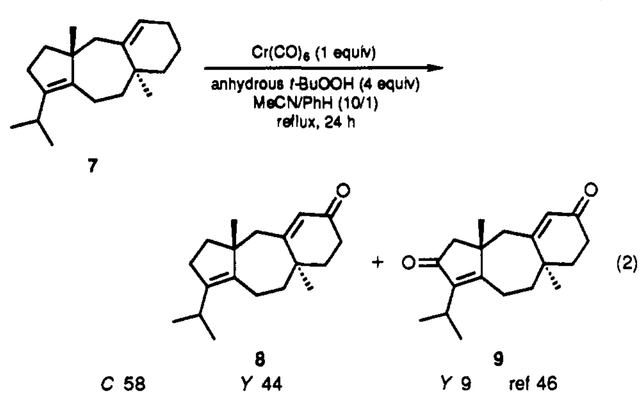
Only chromium carbonyl complexes have been used as chromium(0) catalysts to achieve the oxidation of organic compounds. Attempts have been reported solely during the last decade.

1. $Cr(CO)_6$

Although ozone[37,38] or oxygen[39] was used in the first reports of oxidation employing chromium hexacarbonyl as catalyst, the main papers described *tert*-butyl hydroperoxide as the oxygen source.[40-45] A fair selectivity was obtained at low conversion for oxidation of cyclohexane 1 to cyclohexanone 2 by O_3 in the presence of $Cr(CO)_6$ (Table 1).[37,38] Epoxidation and allylic oxidation of an alkene were achieved with $Cr(CO)_6$ and either O_2[39] or a benzenic solution of 90% *t*-BuOOH (containing 5% H_2O and 5% *t*-BuOH) (eq 1).[40] In contrast,



when using acetonitrile instead of benzene as solvent, the oxidation of 4 by the $Cr(CO)_6/t$-BuOOH mixture produced only the enone 5.[40,41] Therefore, this latter procedure has been employed in the course of natural product synthesis (eq 2 and Table 2).[44-46] The allylic oxidation of Δ-5 steroids such as 10 was accomplished,[41,44] while a Δ-7 steroid was reluctant to react.[47] It is worthwhile to note that the $Cr(CO)_6/t$-BuOOH/MeCN association can selectively oxidize an allylic methylene group of 13a which also bears a secondary hydroxy function (eq 3).[40,41] Alcohols can be oxidized in the absence of double bonds as well (eq 4).[41] Alkanes used as solvent have been oxidized by the $Cr(CO)_6/t$-BuOOH system with fair efficiency: 0.3–0.4 mol of isomeric alkanones per mole of t-BuOOH.[42] The regioselective benzylic oxidations of tetralin 17, 6-methoxytetralin 20, and estrone derivatives 23 have been easily achieved with this system in acetonitrile[43] (Tables 3 and 4 and eq 5). Recently, the oxidation of allyl ethers to α,β-enones under similar conditions has been briefly mentioned.[48]



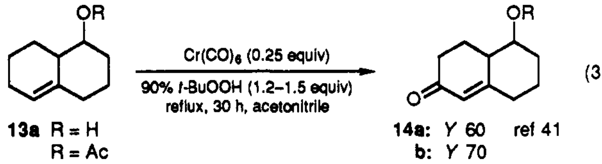
7

(2)

8 Y 44

9 Y 9 ref 46

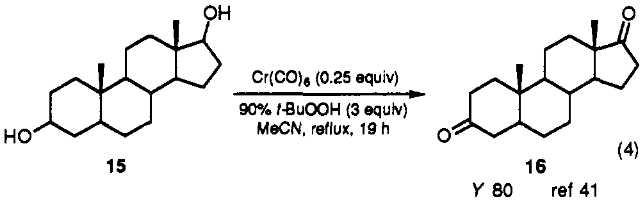
C 58



(3)

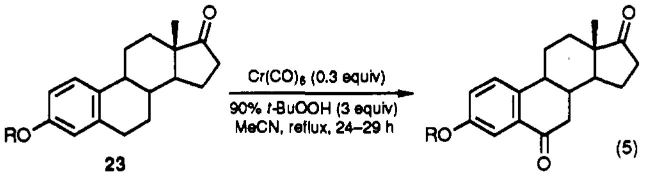
13a R = H
R = Ac

14a: Y 60 ref 41
b: Y 70



15

16 (4)
Y 80 ref 41



23

24 (5)

	C	S	
R = Me	63	85	ref 43
R = Ac	52	54	

Pearson et al. claimed that $Cr(CO)_6$, when associated with t-BuOOH, may be used in true catalytic amounts but they employed larger quantities (0.2–0.5 equiv) in order to shorten reaction times. However, a stoichiometric quantity of $Cr(CO)_6$ and an excess of t-BuOOH led only to 58% conversion of 7 after 1 day reaction time (eq 2).[45,46] The $Cr(CO)_3(MeCN)_3$ complex would be produced in situ in acetonitrile, and it was assumed that oxidation in this solvent involves catalysis only by Cr^0 species since firstly, the reaction medium remains almost colorless, secondly the chromium–carbonyl bands in the IR spectra are unchanged throughout the reaction, and thirdly, the original catalyst could be recovered almost quantitatively after completion of the oxidation.[40,41,43] In contrast, the oxidation of alkanes by the $Cr(CO)_6/t$-BuOOH system could involve complexation of t-BuOOH with about 10% of the $Cr(CO)_6$ followed by oxidation of Cr^0 within the complex to Cr^{VI} which is then the active species[42] (Scheme 2, path a). This Cr^{VI} complex would be an alkyl peroxychromate 25 which gives a Cr^{IV} compound 26 through oxidation of the alkane. 25 is then regenerated from 26 by t-BuOOH. When an alkane/$Cr(CO)_6/t$-BuOOH mixture was exposed to air for long periods, a polymeric Cr^{III} oxide was formed which presented catalytic activity far superior to $Cr(CO)_6$[42] (Scheme 2, path b). The decomposition of methyl oleate hydroperoxide formed by autooxidation of methyl oleate in the presence of $Cr(CO)_6$[39] could follow a similar pathway.

The in situ evolution of the catalyst was also reported in the course of oxidations with the $Cr(CO)_6/O_3$/air system since Cr^{III}, Cr^{IV}, and Cr^V were present in the reaction mixture.[38]

2. $Cr(CO)_5(MeCN)$

This complex has been mentioned exclusively as oxidation catalyst for benzylic oxidations with t-BuOOH.[43] It reacts instantly with t-BuOOH to give presumably an oxide of chromium and is much less selective than $Cr(CO)_6$.

III. Chromium(III) as Catalyst

A plethora of catalytic processes involve chromium in the formal oxidation state (III) as a starting catalyst. Chromium(III) oxide has been used since the beginning of chromium-catalyzed oxidations and has been associated almost exclusively with oxygen. Many experiments thereafter have been carried out with chromium acetylacetonate or chromium esters in conjunction with oxygen or hydroperoxide. Recently, chromium porphyrins and more generally, metalloporphyrins have been subjected to intensive investigation since they mimic the cytochrome P-450 monooxygenases. These studies provide a model to better understand the essential steps of these metalloenzymes.[19,21,24-26,49] A large variety of oxygen sources have been tested with the chromium porphyrins.

1. Cr_2O_3

In a few publications,[50-52] the catalyst used was chromia, which is probably best formulated as $Cr(OH)_3$.[52] Since it is used after or during heating, the catalyst is probably Cr_2O_3.[53] Thus, these publications will be referred to in this paragraph.

It seems that the first uses of chromium(III) oxide as a catalyst occurred more than a half century ago during screening of heavy metal oxides to attempt to accelerate oxidations of benzylic methylene and methyl groups to the corresponding ketones and acids, at high

SCHEME 2

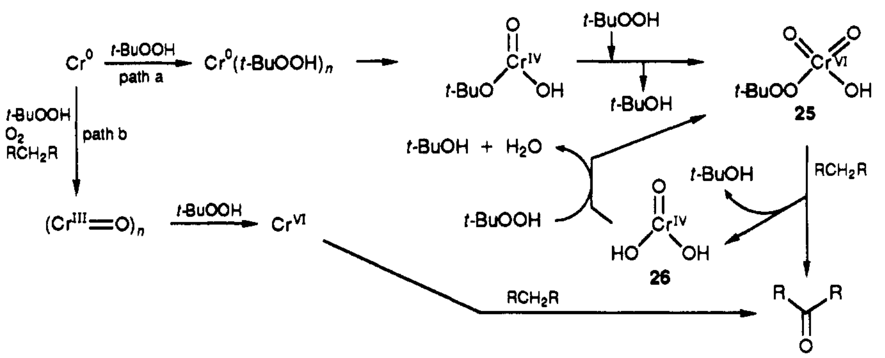
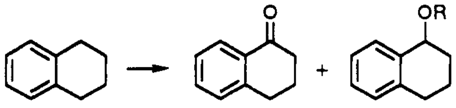


TABLE 3. Oxidation of Tetralin

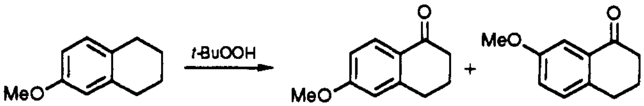


17 18 19a: R = H
b: R = OH
c: R = O*t*-Bu

reactants and conditions[a]	*C*		results		ref
			18	19	
oxygen or air					
Cr_2O_3 [1/∞/0.01] neat, 85–125 °C, 3–5 h		*Y*	30–35	trace (R = H)	55
$Cr(acac)_3$ [1/∞/0.012] AcOH, 72 °C, 66 min	20.3	*S*	30.9	9.4 (R = H) 50.1 (R = HO)	106
$Cr(OAc)_3$ [1/∞/0.012] AcOH, 72 °C, 59 min	18.9	*S*	32.6	2.7 (R = H) 55 (R = HO)	106
$Cr(naph)_3$ + $BuNH_2$ (0.0015 equiv) [1/∞/0.000 005] 80 °C, 3 h	3	*S*	97.2		108
CrO_3, DMF, 90 °C, 7 h	16.0	*S*	92.7	2.2 (R = H) 4.0 (R = HO)	229
CrO_3, DMA, 90 °C, 7 h	35.2	*S*	96.1	0.1 (R = H) 1.8 (R = HO)	229
QCC, DMA, 90 °C, 7 h	30.5	*S*	88.1	6.2 (R = H) 3.1 (R = HO)	229
QDC, DMA, 90 °C, 7 h	9.8	*S*	86.5	8.8 (R = H) 1.7 (R = HO)	229
PrCC, DMA, 90 °C, 7 h	32.7	*S*	77.9	12.4 (R = H) 2.2 (R = HO)	229
PrDC, DMA, 90 °C, 7 h	22.0	*S*	95.9	0.5 (R = H) 0.2 (R = HO)	229
PtCC, DMA, 90 °C, 7 h	28.5	*S*	88.7	6.3 (R = H) 3.0 (R = HO)	229
PtDC, DMA, 90 °C, 7 h	28.7	*S*	92.0	3.2 (R = H) 4.5 (R = HO)	229
tert-butyl hydroperoxide					
$Cr(CO)_6$ [1/3/0.3] MeCN, 80 °C, 23 h	100	*Y*	88		43
CrO_3 [1/7/0.05] CH_2Cl_2, 0 °C, 22 h	*b*	*Y*	64		240
CrO_3 [1/7/0.05] CH_2Cl_2, RT, 21 h	*c*	*Y*	43		240
PDC [1/4/0.1] CH_2Cl_2, RT, 4 h	85[d]	*Y*	74	1 (R = *t*-BuO)	225
$(OCMe_2CH_2CMe_2O)CrO_2$ [1/7/0.1] CH_2Cl_2, 0 °C, 8 h	84	*Y*	55		287

[a] See section VIII for the definitions for the abbreviations and symbols. [b–d] 1,4-Naphthoquinone was also obtained: *b*, 5%; *c*, 23%; *d*, 8%.

TABLE 4. Oxidation of 6-Methoxy-1,2,3,4-tetrahydronaphthalene

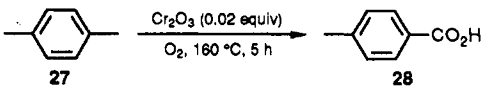


20 21 22

reactants and conditions[a]	*C*		results		ref
			21	22	
$Cr(CO)_6$ [1/3/0.3] MeCN, 80 °C, 23 h	72	*Y*	44		43
CrO_3 [1/7/0.05] CH_2Cl_2, RT, 9 h		*Y*	36	17	240
$(Bu_3SnO)_2CrO_2$ [1/7/0.05] CH_2Cl_2, 40 °C, 7.5 h	84	*Y*	32	15	227
$(OCMe_2CH_2CMe_2O)CrO_2$ [1/7/0.1] CH_2Cl_2, 0 °C, 8 h	85	*Y*	32	17	287

[a] See section VIII for the definitions for the abbreviations and symbols.

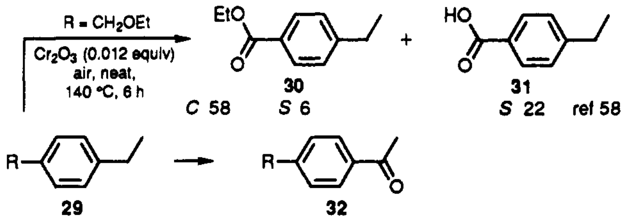
temperatures, under a stream of oxygen (eq 6 and Table 3).[54,55] In subsequent reports,[50,56–63] these chromium-promoted oxidations were generally carried out in the supplementary presence of other metal oxides[57,62] or "inert powders", principally calcium carbonate;[50,56–58,60] the degradation of the alkyl side chain being sometimes simultaneously observed (Table 5). Hydroperoxidation of alkenes[64,65] (Table 6) and alkanes[66–68] by O_2 has been carried out in the presence of small amounts of Cr_2O_3,[64–67] Cr_2O_3 + NiO,[64] or MCr_2O_4 (M = Co, Cu, Ni)[67]



27 28 (6)

C *S*
63 17 ref 54

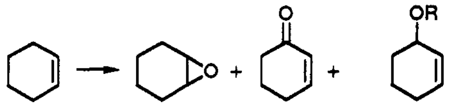
TABLE 5. Benzylic Oxidation of Para-Substituted Ethylbenzenes



reactants and conditions[a]	C	results		ref
			32	
R = Et				
chromia (0.01 equiv), $CaCO_3$ (0.04 equiv), air, neat, 130 °C, 40 h	30–35	S	45–50	50
R = CH_2COEt				
Cr_2O_3 (0.01 equiv), $CaCO_3$ (0.04 equiv), air, neat, 140–145 °C, 28 h	41	S	70	56
R = CH_2COMe				
Cr_2O_3 (0.01 equiv), $CaCO_3$ (0.04 equiv), air, neat, 140–145 °C	54	S	66	56
R = OAc				
Cr_2O_3 + Co-hydrate + $CaCO_3$ (1/1/8, 5%), O_2, neat, 140–15 °C, 15 h	24	S	79	57
R = CH_2OCOMe				
Cr_2O_3 (0.013 equiv), $CaCO_3$ (0.078 equiv), air, neat, 130–140 °C, 28 h	23	S	55	58
R = Cl				
Cr_2O_3 (0.01 equiv), air, neat, 140–155 °C, 6 h	26	S	76[b]	59
R = CO_2Me				
Cr_2O_3 (0.01 equiv), $CaCO_3$ (0.067 equiv), air, neat, 140–150 °C, 24 h	40–54	S	60–66	60

[a] See section VIII for the definitions for the abbreviations and symbols. [b] *m*-Chlorobenzoic acid was also isolated (*S* 1.4).

TABLE 6. Oxidation of Cyclohexene



33 34 35 **36a**: R = H
b: R = OH
c: R = O*t*-Bu

reactants and conditions[a]	C	results				ref
			34	35	36	
oxygen						
Cr_2O_3 or Cr_2O_3 + NiO, 60 °C		Y/O			80–95 (R = OH)	64
$Cr(acac)_3$ + $PtO_2(PPh_3)_2$ (0.1 equiv) [6000/∞/1] PhH, 65 °C, 12 h	53.4	R	6	68	26 (R = H)	98
Cr(TPP)Cl, $NaBH_4$ (0.3 equiv), Avicel [1000/∞/1] PhH, 20 °C, 5 h		T	780	3820[b]	5020 (R = H)	180
as above but for 24 h		T	820	540	16550 (R = H)	180
Cr(TPP)Cl, L-cysteine (0.09 equiv), $Mn(OAc)_3$ (0.0002 equiv) + $NaBH_4$ (0.13 equiv) [2800/∞/1] PhH, 20 °C, 1 h		T	170	2210	2360 (R = H)	179
as above but for 24 h		T	380	21180	1810 (R = H)	179
hydrogen peroxide						
CrO_3			c			222
$(Ph_3PO)OCr(O_2)_2$ [1/2/0.02] CH_2Cl_2–*t*-BuOH, 20 °C		T	0.023	1.66	0.35 (R = H)	221
tert-butyl hydroperoxide						
$Cr(acac)_3$ [1/1/0.01] PhH, 90 °C		Y/O	2	d	d (R = H) 30 (R = *t*-BuO)	82
sodium perborate						
CrO_3 + R_4NCl (0.2 equiv) [1/7/0.1] PhH–H_2O, 80 °C, 24 h		Y		(adipic acid 12)		254
iodosylbenzene						
Cr(TPP)Cl, RT		Y/O	3	14	50 (R = H)	167
Cr(m-salen)OTf + *N*-pyridine oxide (0.005 equiv) [100/5/1] MeCN, 25 °C		Y/O	2	2	1 (R = H)	204
pentafluoroiodosylbenzene						
Cr(2,6-Cl-P)Cl [1000/64/1] CH_2Cl_2, RT		Y/O	23	10	27 (R = H)	176
potassium hydrogen persulfate			39			
Cr(TPP)Cl [67/140/1], R_4NCl, CH_2Cl_2–H_2O, RT, 2 h	75	Y	10			301

[a] See section VIII for the definitions for the abbreviations and symbols. [b] Cyclohexanone was also obtained (*T* 300). [c] Small amounts of cyclohexane-1,2-diol + large quantities of adipic acid. [d] Significant amounts formed but exact yield not determined.

to decrease the induction period and to increase the conversion.

All of the preceeding reactions were heterogeneous and involved peroxide derivatives of the substrate as intermediates (Scheme 3). In studies with alkenes, it was claimed that Cr_2O_3 acted as the initiator of a radical chain reaction rather than as a catalyst.[64,65] The metal eliminated or decreased the induction period. It is very difficult to make correct mechanistic conclusions since alkyl hydroperoxides are ubiquitous in most starting hydrocarbon mixtures.[8,12] Hence, there are considerable differences in opinion concerning the reaction pathways

SCHEME 3

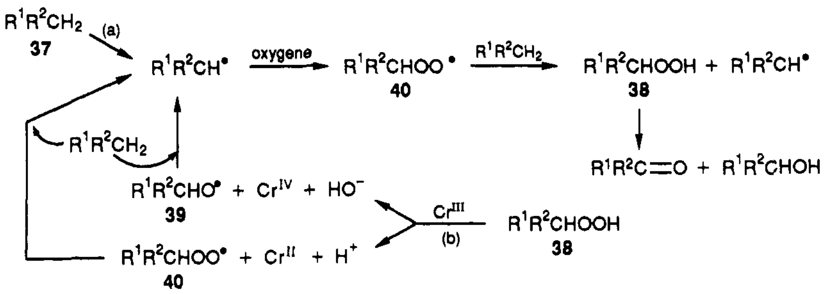
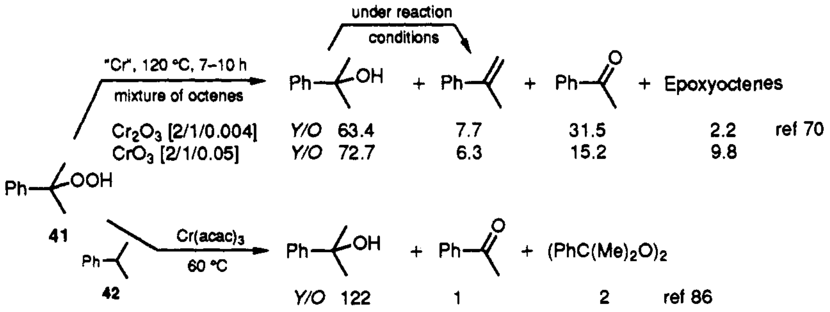
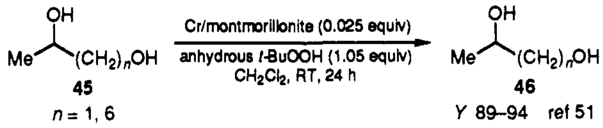


TABLE 7. Decomposition of Cumyl Hydroperoxide in the Presence of Either Octenes or Cumene



of these processes.[8] Although formation of $R^1R^2CH^•$ by Cr_2O_3 directly from the hydrocarbon $R^1R^2CH_2$ (37) has been postulated[64,65] (Scheme 3, path a), the first step has often been proposed to be an interaction between the metal and the hydroperoxide 38 already present in the starting hydrocarbon mixture.[8,12] This interaction will lead to homolysis[69] of 38 to produce the radicals 39 or 40 which can initiate a radical chain process (Scheme 3, path b). This Cr^{III}-catalyzed decomposition of hydroperoxides is a very efficient pathway since, in the presence of octenes and cumyl hydroperoxide (41), Cr_2O_3 induces decomposition of 41 rather than epoxidation of octenes[70] (Table 7). Furthermore, kinetic analysis has revealed that the limiting step in the Cr_2O_3-catalyzed decomposition of 2-nonyl hydroperoxide involves a complex between these two entities, while selective formation of 2-nonanone has been observed.[71] A chemisorption of oxygen at the metal centers of the heterogeneous catalyst can also be envisaged and this phenomenon would be amplified in the presence of additive powders.[8] Indeed, it was demonstrated that these "inert powders" generally contained very small or subanalytical amounts of transition-metal element impurities[72] which could participate in the oxidation process. Nevertheless, it seems that the catalytic efficiency is greatly dependent on the surface area of both the powder[72] and metal oxide.[55] Furthermore, it has been shown by photoacoustic spectroscopy that the incorporation of oxygen to zeolitic chromosilicates led to Cr^{VI} species from anchored Cr^{III}.[73] The free-radical nature of these oxidations precludes high selectivity as the percentage conversion increases. Thus, the reactions are generally carried out at low conversions to avoid excessive formation of byproducts.

Recently, a chromia-pillared montmorillonite catalyst prepared from chromium nitrate solutions[74] has been used in conjunction with t-BuOOH.[51] The intercalated Cr was described empirically[75] as $Cr(OH)_{3-q}{}^{q+}$ but the exact nature of the catalyst remains uncertain,[74] and the presence of a mixed-valence material, $Cr^{III}{}_2Cr^{VI}{}_3O_{12}$, has been recently suggested by Cr K-edge EXAFS data.[76] Nevertheless, this catalyst allows the oxidation of saturated, allylic or benzylic primary and secondary alcohols to aldehydes (not acids) and ketones in high yields. Since the oxidation of primary alcohols is relatively slow, the selective oxidation of secondary alcohols has been achieved in the presence of primary hydroxy groups[51] (Table 8 and eq 7). Furthermore, the



(7)

catalyst can be recycled but it seems necessary to carry out the oxidation under anhydrous conditions. The promoting effect of montmorillonite on the Cr^{III} catalyst is certain: in using small amounts of Cr_2O_3 instead of Cr^{III}/montmorillonite, no catalytic activity was observed for alcohol oxidation in the presence of t-BuOOH.[77]

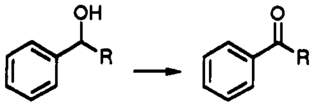
Chromium(III) oxide has also been used as an additive to improve a catalytic system containing copper and cobalt which performed the dehydrogenation of ethyl alcohol to acetaldehyde at 275–300 °C.[79] 2-Propanol was converted into acetone and propene with chromia or chromia–magnesia catalysts at 320–400 °C, the in situ formation of $MgCr_2O_4$ being postulated under the latter conditions.[52]

An original use of chromium(III) oxide as catalyst has been recently presented[80] in which the authors prepared Ti/Cr_2O_3 electrodes. The electrochemical oxidation of Cr^{III} to Cr^{VI} mediated the transformation of 2-propanol to acetone with 100% current efficiency. CrO_2 was formed in situ and was either directly reoxidized electrochemically or gave Cr_2O_3. Although the dissolution of Cr_2O_3 limited the lifetime of the electrode, turnover numbers of 100–10 000 were achieved.

2. Cr(acac)$_3$

The first use of tris(acetylacetonato)chromium as an oxidation catalyst was probably encountered in the

TABLE 8. Oxidation of Benzylic Alcohols

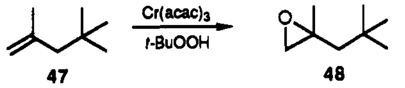


43 → 44

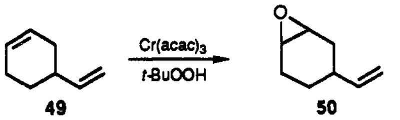
reactants and conditions[a]	C	results		ref
			44	
air				
R = H, $[NBu_4](Os(N)(CH_2SiMe_3)_2(CrO_4))$ [1/∞/0.05] MeCN, 70 °C, 72 h	57	*S*	100	276
R = H, $[NBu_4][Os(N)(CH_2SiMe_3)_2(CrO_4)]$ + $Cu(OAc)_2$ (0.1 equiv) [1/∞/0.05] MeCN, 70 °C, 72 h	100	*S*	100	276
anhydrous *tert*-butyl hydroperoxide				
R = Me, Cr(III)/montmorillonite [1/1.05/0.025] CH_2Cl_2, RT, 10 h		*Y*	96	51
R = CH_2OH, Cr(III)/montmorillonite [1/1.05/0.025] CH_2Cl_2, RT, 18 h		*Y*	92	51
R = $(CH_2)_2OH$, Cr(III)/montmorillonite [1/1.05/0.025] CH_2Cl_2, RT, 20 h		*Y*	88	51
R = Me, Cr/NAFK [1/4/0.034] PhCl–PhH, 85 °C, 6 h		*Y*	95	136
R = Ph, Cr/NAFK [1/4/0.034] PhCl–PhH, 85 °C, 6 h		*Y*	98	136
R = COPh, $(Bu_3SnO)_2CrO_2$ [1/4/0.05] CH_2Cl_2, 40 °C, 21 h	70	*Y*	34	227
70% aqueous *tert*-butyl hydroperoxide				
R = Et, CrO_3 [1/4/0.05] CH_2Cl_2, RT, 3 h	92	*S*	90	245
R = *n*-C_7H_{15}, CrO_3 [1/2/0.05] CH_2Cl_2, RT, 17 h	96	*Y*	94	214
R = CH_2OH, CrO_3 [1/4/0.05] CH_2Cl_2, RT, 24 h	59	*S*	49	245
R = COPh, CrO_3 [1/4/0.05] CH_2Cl_2, RT, 8 h	34	*S*	68	245
R = CO_2Me, CrO_3 [1/4/0.05] CH_2Cl_2, RT, 5 h	49	*S*	75	245
peroxyacetic acid				
R = Me, $(OCMe_2CH_2CMe_2O)CrO_2$ [1/2/0.02] CH_2Cl_2–CCl_4, 0 °C, 0.35 h		*Y*	96	286
bis(trimethylsilyl) peroxide				
R = H, PDC [1/3/0.1] CH_2Cl_2, 25 °C, 1.5 h		*Y*	91	228
R = Me, PDC [1/3/0.1] CH_2Cl_2, 25 °C, 1.5 h		*Y*	97	228
sodium perborate				
R = H, CrO_3 + R_4NCl (0.2 equiv) [1/7/0.1] PhH–H_2O, 80 °C, 24 h	25	*S*	80	254
R = COPh, CrO_3 + R_4NCl (0.2 equiv) [1/7/0.1] PhH–H_2O, 60 °C, 24 h	100	*Y*	51[b]	254
iodosylbenzene				
R = H, Cr(TPP)Cl RT		*Y/O*	56	167
R = *t*-Bu, Cr(TPP)Cl [1/1/0.18] CH_2Cl_2, 25 °C		*Y/O*	30[c]	273

[a] See section VIII for the definitions for the abbreviations and symbols. [b] Benzoic acid was also isolated (*Y* 38). [c] Benzaldehyde was also isolated (*Y/O* 14).

course of studies directed toward the epoxidation of olefins by *tert*-butyl hydroperoxide.[81] The epoxidation was regio- and stereospecific and provided fair yields at room temperature and low catalyst concentrations when oxygen was excluded from the medium (eqs 8–10).



47 48 *Y/O* 28–100 ref 81 (8)



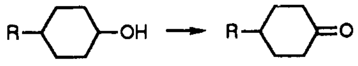
49 50 *Y/O* 13–60 ref 81 (9)

51 *E* or *Z* (10)

trans epoxide from *E*-51
cis epoxide from *Z*-51 ref 81

At higher temperatures, the epoxidation fell off dramatically and the major reactive pathway of cyclohexene became allylic oxidation[82] (Table 6). Early, it was recognized that $Cr(acac)_3$/ROOH mediates the oxygenation of alkanes (Table 1).[82–85] Such a system promotes the oxidation of alcohols[85] (Table 9) and the tertiary C–H bond of cumene[86] (Table 7) with low yields. Note however that the thermal decomposition of cumyl hydroperoxide led to the oxidation of the tertiary C–H bond of phenylcycloalkanes even in the absence of catalyst.[87] Recently, the efficient cleavage of the C═CH_2 group of methacrylic acid esters such as 54 was carried out with hydrogen peroxide and small amounts of $Cr(acac)_3$ (eq 11).[88,89]

TABLE 9: Oxidation of Cyclohexanols

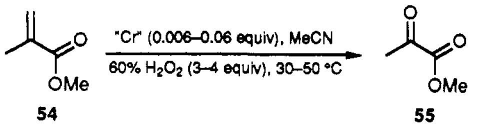


52 → 53

reactants and conditions[a]	results		ref
		53	
tert-butyl hydroperoxide			
R = H, $Cr(acac)_3$ [2/1/0.02] PhH, 80 °C, 6 h	*Y*	26	85
R = H, $Cr(st)_3$ [2/1/0.02] PhH, 80 °C, 6 h	*Y*	26	84, 85
R = *t*-Bu, Cr/NAFK [1/4/0.034] PhCl–PhH, 85 °C, 6 h	*Y*	81	136
bis(trimethylsilyl) peroxide			
R = *t*-Bu, CrO_3 [1/3/0.1] CH_2Cl_2, 25 °C, 1.5 h	*Y*	30	258
R = *t*-Bu, PCC [1/3/0.1] CH_2Cl_2, 25 °C, 1.5 h	*Y*	55	258
R = *t*-Bu, PDC [1/3/0.1] CH_2Cl_2, 25 °C, 1.5 h	*Y*	98	258
peroxyacetic acid			
R = *t*-Bu, $(OCMe_2CH_2CMe_2O)CrO_2$ [1/2/0.02] CH_2Cl_2–CCl_4, 0 °C, 0.35 h	*Y*	96	286

[a] See section VIII for the definitions for the abbreviations and symbols.

Stereospecific epoxidations achieved in high yields under appropriate conditions[81] suggest concerted mechanisms.[12] It has been envisaged that the epoxidation process involves a complex between the catalyst and *t*-BuOOH[81,90] which leads to the metal in its higher oxidation state.[82,90] Next, a transfer of oxygen from a *t*-BuOOH molecule coordinated at the metal was postulated through a cyclic transition state 56 where



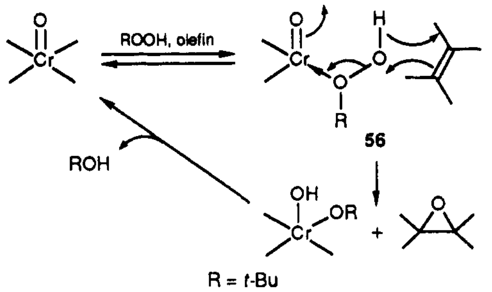
(11)

54 55

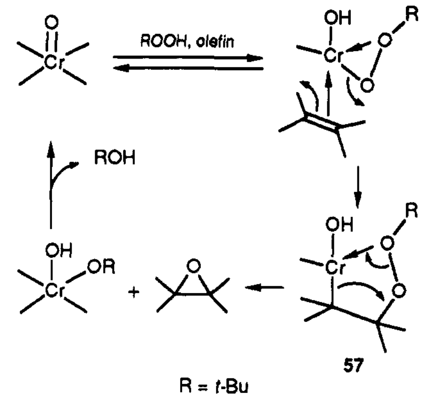
"Cr"	*C*	*S*	ref 88
Cr(acac)$_3$	96	74	
Cr(OAc)$_3$	96	74	
Cr(NO$_3$)$_3$	73	70	
CrO$_3$	53	30	
CrO$_3$ + Et$_3$N (1/1)	82	72	

a Cr=O group functions in a manner similar to the carbonyl group in organic peracids (Scheme 4).[82] This attractive interpretation of the oxygen transfer is however doubtful: the coordination of the olefin to the metal followed by an insertion reaction leading to a pseudo peroxymetallacycle 57 as an intermediate is more likely, as has been shown in more recent work (Scheme 5).[91–93] The decrease of the epoxide yield with the enhancement of either temperature or the amount of catalyst could be due to the decomposition of the epoxide and unproductive consumption of *t*-BuOOH.[90] Indeed, it is expected that an increase in temperature or of the amount of chromium which is a Lewis acid[82] would increase the proportions of both side reactions. If Cr^{VI} is formed in these mixtures,[90] the oxidations resumed precedently could also be explained by schemes considered for stoichiometric reactions,[1] followed by reoxidation of reduced chromium species with *t*-BuOOH. Another possibility would be the decomposition of the hydroperoxide initiated by Cr(acac)$_3$[82,84,85,90,94–96] or another chromium complex which could then promote a radical reaction leading to the oxidation of alkanes and alkenes (Scheme 6).[9,82] Such a reaction pathway could be responsible, at least in part, for the small amounts of epoxides produced under Sheldon's conditions[82] since epoxidations by *t*-BuOOH have been reported at 60–100 °C in the absence of catalyst.[81,97]

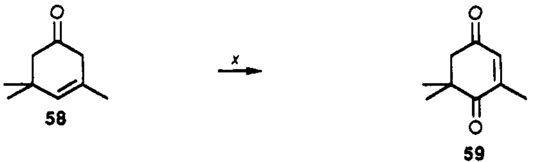
SCHEME 4



SCHEME 5



Cr(acac)$_3$-catalyzed oxidations with oxygen have also been investigated. Alkanes provided the corresponding ketones and alcohols with a ketone/alcohol ratio > 1.[84] Although both epoxidation and allylic oxidation have been observed with alkenes,[90,94,95,98–101] eventually in the presence of a second catalyst [Pt(PPh$_3$)$_2$O$_2$] (Table 6),[98] the selective oxidation of *β*-isophorone to 3,5,5-trimethylcyclohex-2-ene-1,4-dione was achieved with the Cr(acac)$_3$/O$_2$ system[102] in good yields, when pyridine was used as solvent (eq 12).[103] Note that this transformation, which furnishes a useful intermediate for the synthesis of vitamins and perfume components, was also catalyzed by Cr(OCOCH$_3$)$_3$ and chromium(III) naphthenate[103] and has been the subject of intensive investigations, notably by industrial companies.[104,105] The benzylic oxidation of tetralin 17 by the Cr(acac)$_3$/O$_2$ system has been particularly studied and led to tetralone 18, tetralol 19a, and hydroperoxide 19b (Table 3).[95,106–109] In contrast, the oxidation of cumene by this system was inefficient.[110] Under alkaline conditions, the Cr(acac)$_3$/O$_2$ system oxidized nitro- or chlorotoluenes and 4-nitro-*m*-xylene to the corresponding carboxylic acid salts.[111] Hydroperoxidation and cleavage of ethers occurred in the presence of the Cr(acac)$_3$/O$_2$ system.[112,113]



(12)

58 59

X	*Y*	
Cr(acac)$_3$ (0.005 equiv), neat, air, 50 °C	28.8	ref 102
Cr(acac)$_3$ (0.02 equiv), pyridine, O$_2$, 70 °C	75	ref 103

Since the rate and efficiency of oxidation by Cr(acac)$_3$/O$_2$ generally increased on either addition of a hydroperoxide[90,94,95,107,109] or by irradiation by UV light,[107] the usual autooxidation mechanism as outlined in Scheme 3 can once again be operative here. Indeed, the decomposition of R$_1$R$_2$CHOOH to R$_1$R$_2$CHOH and R$_1$R$_2$CO catalyzed by Cr(acac)$_3$ has been fully reported under thermal and photochemical conditions.[84,85,90,96,106,107,109,114–116] Nevertheless, some experiments did not fully agree with a general autooxidation mechanism.[110]

3. Cr(OCOR)$_3$

Chromium esters have often been examined with the objective of obtaining catalysts soluble in organic media. With this aim, a cheap fatty acid has been generally employed for the ester part, the catalyst most considered being chromium(III) stearate.[37,84,85,100,108,117–134] The efficiency of chromium(III) acetate has been less investigated[37,88,106,134–141] while chromium(III) trifluoroacetate,[134] chromium(III) naphthenate,[108,142–145] and chromium(III) octoate[146] have been rarely used. Chromium esters have been used mainly in conjunction with oxygen. When they were employed with ozone to oxidize cyclohexane to cyclohexanone, they were less efficient than Cr(CO)$_6$.[37]

a. Chromium(III) Stearate

Chromium(III) stearate has been used to promote the autooxidation of alkanes,[84,117–121,123–131,133,134] alkenes,[100] primary[122] or secondary[108] benzylic carbons, and ke-

SCHEME 6

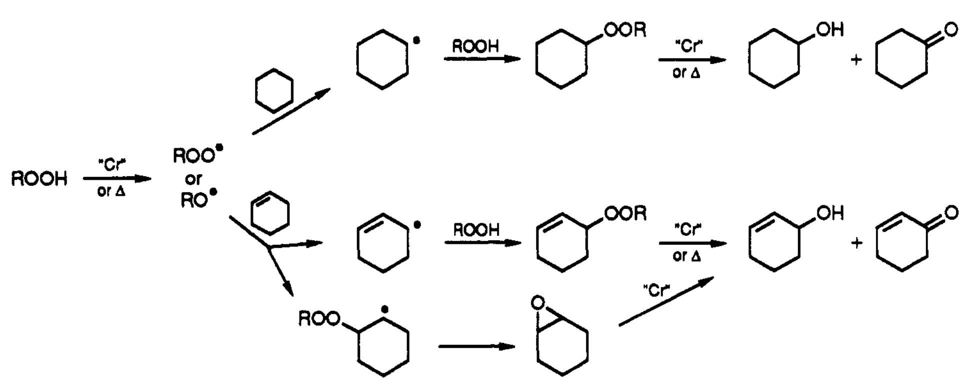
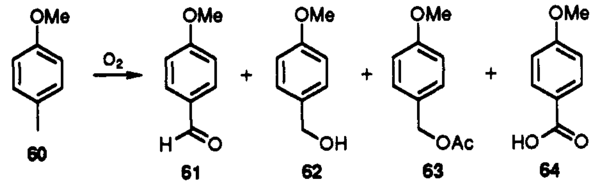


TABLE 10. Oxidation of *p*-Methoxytoluene



reactants and conditions[a]	*C*		results 61	 62	 63	 64	ref
O_2 (3 atm), AcOH, 110 °C, 3 h							138
$Co(OAc)_3$ (0.28 equiv) + $Cr(OAc)_3$ (0.095 equiv)	100	*Y*	1.6	3.6	0	trace	
$Co(OAc)_3$ (0.28 equiv) + $Ce(OAc)_3$ (0.095 equiv)	100	*Y*	67.9	0	21.7	0	
$Co(OAc)_3$ (0.28 equiv) + $Ce(OAc)_3$ (0.095 equiv) + $Cr(OAc)_3$ (0.095 equiv)	99.9	*Y*	72.7	0	14.1	0	
O_2 (1 atm), diglyme, 90 °C, 5 h							164
$CoCl_2$ (0.1 equiv)	69	*Y*	50	0		19	
$CrCl_3$	0						
$CoCl_2$ (0.1 equiv) + $CrCl_3$ (0.05 equiv)	55	*Y*	55	0		0	

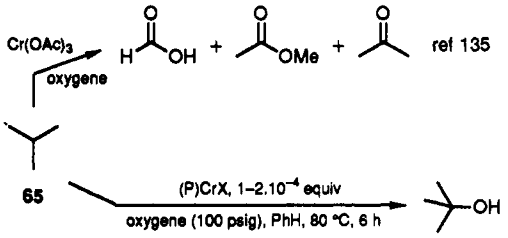
[a] See section VIII for the definitions for the abbreviations and symbols.

tones.[132] In fact, the catalyst has often consisted of a binary[118,119,122,124–126,128,129] or ternary[119,127] mixture of metal stearates. Ultrasonic irradiation[133] or addition of cobalt stearate or nickel stearate[122,124] increased the efficiency of these processes while aluminum stearate as additive gave a negative effect.[119] The reaction of the resulting hydroperoxides has been extensively studied under similar conditions.[96,100,114,115,123,147–153] In general, ketones were selectively obtained,[84,96,117,121,125,126,151,153] with lower amounts of alcohols, acids, and esters being formed. However, the presence of manganese stearate as cocatalyst has favored the formation of carboxylic acids.[117,127] The activity of $Cr(st)_3$ for cyclohexyl hydroperoxide decomposition was better than that of $Cr(acac)_3$.[115]

Following studies where the decomposition of cyclohexyl hydroperoxide by $Cr(st)_3$ has been considered to proceed through homolytic or heterolytic pathways,[84,85,115,148–151] a radical chain process has been finally accepted.[84] A ternary complex between alkane, chromium, and oxygen was envisaged as the initiator of the chain reaction leading to the oxidation of *n*-pentadecane.[120] Subsequently, an ESR study of valence transformations of $Cr(st)_3$ at the initial stage of the oxidation of *n*-pentadecane indicated the presence of alkylchromates(VI) which decomposed heterolytically to give ketones.[123]

Chromium(III) stearate used in conjunction with alkyl hydroperoxides has been examined as a reagent for the oxidation at 80–125 °C of alkanes (low yields) and secondary alcohols (Tables 1 and 9).[84,85]

TABLE 11. Autooxidation of Isobutane



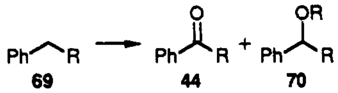
reactants and conditions[a]		results			ref
Cr(TPP)Cl	*T*	0			181
$Cr(TPP)N_3$	*T*	264	*S*	89	181
Cr(TPP)N	*T*	0			181
$Cr(TFPP)N_3$	*T*	450	*S*	97	182

[a] See section VIII for the definitions for the abbreviations and symbols.

b. Cr(OAc)₃

During the screening of catalysts which promote the autooxidation of tetralin **17** in acetic acid, it was observed that the order of the activities of metal acetates in producing oxidation correlated with that in producing decomposition of α-tetralin hydroperoxide **19b**, and that chromium acetate led to the highest tetralone/tetralol ratio (Table 3).[106] Later, chromium acetate was used in association with other metal acetates to carry out the autooxidation of benzylic methyl groups;[138–141] the mixture $Co(OAc)_2/Ce(OAc)_3/Cr(OAc)_3$ being particu-

TABLE 12. Benzylic Oxidations


69 44 70

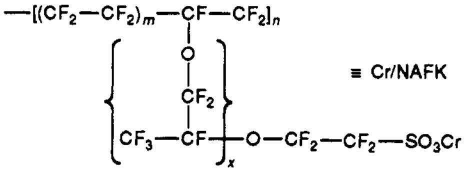
			results		
reactants and conditions[c]	C		44	70	ref
oxygen or air					
R = Ph					
$K_2Cr_2O_7$/neutral alumina [1/∞/0.02] neat, 150 °C, 116 h		*Y*	82		281
R = H					
$K_2Cr_2O_7$ + Bu_4NBr (0.0007 equiv) + *hν*[1/∞/0.0005] CH_2Cl_2–H_2O, 17 °C, 120 h		*T*	5		280
R = Me					
CrO_3 + RCO_2H (0–0.003 equiv) [1/∞/0.001] MeCN, 25 °C, 400 h		*T*	3		230
CrO_3 + *hν*[1/∞/0.001] MeCN, 25 °C, 15 h		*T*	3		230
hydrogen peroxide					
R = Me					
CrO_3 [1/0.2/0.001] MeCN, 20 °C, 168 h		*T*	9.4	5.6 (R = H)	224
$(Bu_4N)_2Cr_2O_7$ [1/0.2/0.001] MeCN, 20 °C, 24 h		*T*	9.6	5.0 (R = H)	224
$(Bu_4N)_2Cr_4O_{13}$ [1/0.2/0.001] MeCN, 20 °C, 24 h		*T*	6.4	3.8 (R = H)	224
tert-butyl hydroperoxide					
R = H					
Cr/NAFK [∞/4/0.034] 85 °C			no yield data		137
R = Ph					
$(OCMe_2CH_2CMe_2O)CrO_2$ [1/7/0.1] CH_2Cl_2–CCl_4, 0 °C, 8 h	46	*S*	87	8 (R = *t*-BuO)	287
CrO_3 [1/14/0.04] CH_2Cl_2, RT, 43 h		*Y*	90		240
$(Bu_3SnO)_2CrO_2$ [1/7/0.05] PhH, 60 °C, 10 h	90	*Y*	83	2 (R = *t*-BuO)	227
R = CH_2Ph					
$(OCMe_2CH_2CMe_2O)CrO_2$ [1/7/0.1] CH_2Cl_2–CCl_4, 0 °C, 8 h	28	*S*	29		287
CrO_3 [1/7/0.05] CH_2Cl_2, RT, 48 h	44	*Y*	21		240
$(Bu_3SnO)_2CrO_2$ [1/7/0.05] PhH, 60 °C, 25 h	58	*Y*	27	(+ benzil: 9)	227
benzyl hydroperoxide					
R = H					
$Cr(naph)_3$ + pyridine (0.1 equiv) [∞/1/0.005] PhMe, 100 °C, 1 h		*Y*/*O*	88	20 (R = H)	155
iodosylbenzene					
R = Me					
CrO_3 [1/0.02/0.001] MeCN, 25 °C, 300 h		*T*	2		230
as above + *α*-picolinic acid (0.002 equiv)		*T*	22	4 (R = H)	230, 261

[a] See section VIII for the definitions for the abbreviations and symbols.

larly efficient (Table 10). The autooxidation of alkanes has been induced by $Cr(OAc)_3$[134,135] or $Cr(OCOCF_3)_3$,[134] isobutane **65** furnishing a mixture of formic acid, methyl acetate, and acetone (Table 11).[135] The rate of Cr(III)-catalyzed autooxidation of cyclohexane to cyclohexanol and cyclohexanone slightly increased in the presence of acetic acid, which further promotes the decomposition of the hydroperoxide intermediate.[154]

The cleavage of methyl methacrylate (**54**) carried out with $Cr(OAc)_3/H_2O_2$ led to results identical to those achieved using $Cr(acac)_3$ as a catalyst and superior to those obtained with other Cr^{III} salts: $Cr(acac)_3$ = $Cr(OAc)_3$ > $Cr(NO_3)_3$ ≫ $CrPO_4$ ≫ $CrCl_3$ or $Cr_2(SO_4)_3$ (eq 11).[88]

The impregnation of $Cr(OAc)_3$ on a perfluorinated resin (NAFK) led to an interesting reusable catalyst, Cr/NAFK (**66**), useful for oxidation of secondary alcohols by anhydrous *t*-BuOOH at 85 °C (Tables 8 and 9).[136,137] Under these conditions, the oxidation of primary alcohols was sluggish and led to aldehydes and acids,[136] double bonds were not affected (eq 13), and toluene was oxidized into benzaldehyde (Table 12).[137]


$$-[(CF_2-CF_2)_m-CF(\{O-CF_2-CF(CF_3)\}_x-O-CF_2-CF_2-SO_3Cr)-CF_2]_n \equiv \text{Cr/NAFK}$$

66

The recovered catalyst retained more than 95% of Cr^{III} when the oxidation was carried out under anhydrous conditions while approximately 80% of the chromium dissolved from the resin when performing the reaction with 70% aqueous *t*-BuOOH.[136,137]


67 **68** (13)

x	*Y*	
Cr/NAFK (0.034 equiv), anhydrous *t*-BuOOH (4 equiv), PhCl, 85 °C, 6 h	82	refs 136, 137
PDC (0.1 equiv), $Me_3SiOOSiMe_3$ (3 equiv), CH_2Cl_2, 25 °C, 1.5 h	81	refs 228, 258

c. Chromium(III) Naphthenate

The autooxidation of cyclohexane under pressure at about 150 °C has been achieved in the presence of chromium naphthenate, the cyclohexyl hydroperoxide thus produced reacting with cyclohexane to give a mixture of cyclohexanol and cyclohexanone.[142,143] The chromium(III) naphthenate-catalyzed decomposition of isolated cycloalkyl hydroperoxides provided mixtures of the expected ketone (main product) and alcohol[114,142] which evolved to diacids under oxygen pressure.[142]

The autooxidation of cyclohexanone in the presence of chromium(III) naphthenate furnished the corresponding *α*-ketol which led successively to *α*-diketone, *ϵ*-caprolactone, adipic acid, and adipic anhydride.[145]

The oxidation by O_2 of tetralin to α-tetralone was achieved at 60–140 °C in the presence of chromium(III) naphthenate and an aliphatic or aromatic amine with about 95% selectivity for low conversions (Table 3).[108,144] The decomposition of benzyl hydroperoxide, in toluene at 100 °C, in the presence of chromium naphthenate and pyridine, afforded benzaldehyde and smaller amounts of benzyl alcohol, a very low percentage of the oxidized products coming from oxidation of the solvent by the initial hydroperoxide (Table 12).[155]

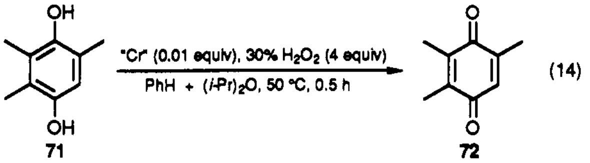
d. Others

Chromium trioctoate and chromium trioctanoate were principally used to decompose cyclohexyl hydroperoxide into cyclohexanol and cyclohexanone with a high ratio of one/ol.[114,146] Simultaneously, the chromium trioctoate catalyzed oxidation of cyclohexanol by cyclohexyl hydroperoxide was demonstrated by use of ^{14}C-labeled cyclohexanol.[146] The autooxidation of tetralin **17** and the decomposition of its hydroperoxide **19b** have been examined in the presence of a variety of catalysts including chromium tris(dibromostearate)[156] and chromium trioleate.[157] A mixture of chromium trioctanoate and cobalt trioctanoate catalyzed the autooxidation at 115 °C of *p*-xylene to *p*-toluic acid.[140]

The oxidation of ascorbic acid by H_2O_2 catalyzed by $[Fe_2CrO(OAc)_6(H_2O)_3]^+$ and $[FeCr_2O(OAc)_6]^+$ clusters, has been achieved. Spectroscopic studies suggested the conversion of the former cluster by H_2O_2 to provide a reaction initiator with subsequent reaction occurring as a chain process.[158] In contrast, the second cluster could directly initiate the oxidation.[159]

4. Chromium(III) Halides

Chromium(III) halides have been primarily used to promote the decomposition of primary and secondary alkyl hydroperoxides to the corresponding acids[160] and ketones.[161] Chromium(III) bromide seems to be one of the best additives for improving the autooxidation of alkenes under aqueous conditions in the presence of a phase-transfer catalyst.[162] The $CrCl_3$-catalyzed oxidation of trimethylhydroquinone (**71**) to the corresponding 1,4-quinone **72** by H_2O_2 has been achieved with low efficiency (eq 14).[163]



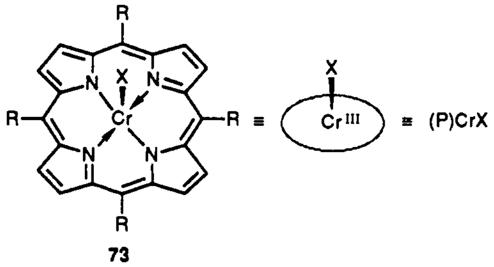
71 **72**

"Cr"	*C*	*Y*	ref 163
$Cr(acac)_3$	10	5	
$CrCl_3$	45	30	
$(Bu_3SnO)_2CrO_2$	98	98	

Recently, chromium(III) chloride has been employed as a cocatalyst.[164,165] It was initially observed that Cr(III) increased the rate of the stoichiometric oxidation of allyl alcohol by Ce^{IV}.[166] The presence of $CrCl_3$ improved the cobalt(II) chloride catalyzed oxidation of *p*-methylanisole (**60**) by oxygen to *p*-anisaldehyde (Table 10) but was not beneficial for the similar oxidation of ethylbenzene.[164] The autooxidation of alkanes catalyzed by a μ^3-oxo trinuclear ruthenium carboxylate, $[Ru_3O(OCOCF_2CF_2CF_3)_6(Et_2O)_3]^+$, was greatly improved by the addition of small amounts of $CrCl_3$ and furthermore the selectivity toward the alcohol was largely increased (Table 1).[165]

5. (Porphyrin)CrX

Chloro(tetraphenylporphyrinato)chromium(III) [(TPP)CrCl] has been the main chromium catalyst employed to mimic the biological activity of cytochrome P-450. Cytochrome P-450 is a hemeprotein, used by enzymes known as monooxygenases, and is able to catalyze selective monooxygenations by molecular oxygen under very mild conditions in living organisms.[12,19,21,24–26,49] Modifications of the porphyrin ligand (P) have been undertaken to increase the stability, selectivity, and efficiency of the catalyst. The use of phthalocyanine instead of porphyrin as ligand coordinated to chromium has been briefly mentioned for benzylic autooxidations.[111]



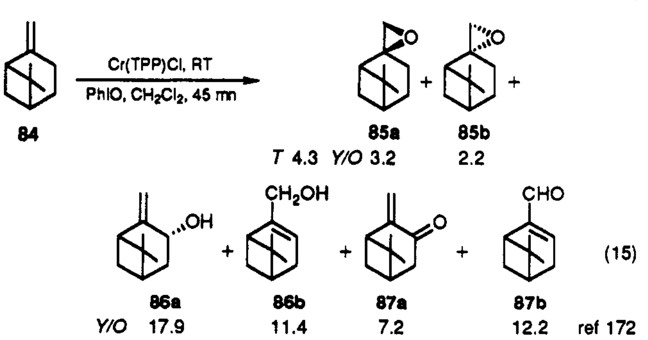
73

(TPP)CrX: R = Ph
(TFPP)CrX: R = C_6F_5
(TTP)CrX: R = *p*-methylphenyl
(2,6-Cl-P)CrX: R = 2,6-dichlorophenyl

a. (TPP)CrX

Chloro(tetraphenylporphyrinato)chromium(III) has been employed as catalyst in conjunction with iodosylbenzene,[167–175] substituted iodosylbenzenes,[171,172,176] cumyl hydroperoxide,[169] *p*-cyano-*N*,*N*-dimethylaniline *N*-oxide,[177,178] or oxygen[179,181] as the oxygen atom source.

The epoxidation of alkenes has been generally performed with (TPP)CrX/ArIO,[167,168,170,172,176] but simultaneous rearrangement, isomerization, or cleavage of the starting substrate was often observed (Tables 13–15 and eq 15).[172,176] Allylic oxidation generally became the major reactive pathway when an allylic hydrogen was available, as in the case of cyclohexene (**33**) (Table 6 and eqs 15 and 16).[167,168,170,174,176] However,



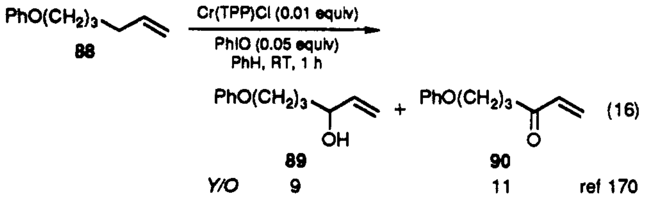
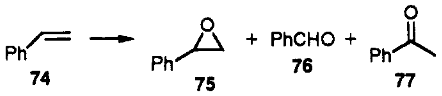


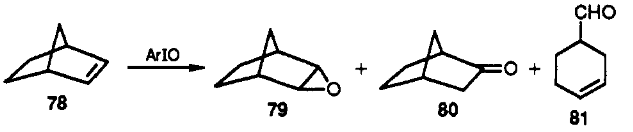
TABLE 13. Oxidation of Styrene



reactants and conditions[a]		results			ref
		75	76	77	
oxygen					
Cr(ONO)(salen)(H_2O) [8/∞/0.1] MeOH, 26 °C, 7 h	*T*	0.15	5	trace	208
hydrogen peroxide					
CrO_3 [1/0.2/0.001] MeCN, 20 °C, 168 h	*T*	0.2	32	2	224
$(Bu_4N)_2CrO_4$ [1/0.2/0.001] MeCN, 20 °C, 168 h	*T*	1.6	56	0.4	224
$(Bu_4N)_2Cr_2O_7$ [1/0.2/0.001] MeCN, 20 °C, 24 h	*T*	3.2	50	2.4	224
$(Bu_4N)_2Cr_4O_{13}$ [1/0.2/0.001] MeCN, 20 °C, 168 h	*T*	6	84	2.4	224
$(Bu_3SnO)_2CrO_2$ [1/0.2/0.001] CH_2Cl_2, RT, 16 h	*T*	0.1	3	0.1	226
iodosylbenzene					
Cr(TPP)Cl [1/0.05/0.01] PhH, RT, 1 h	*Y/O*	65			167, 170
Cr(salen)$(H_2O)_2PF_6$ + pyridine (0.015 equiv) [1/0.03/0.005] CH_2Cl_2, RT	*Y/O*	24			203
Cr(m-salen)OTf + *N*-pyridine oxide (0.005 equiv) [1/0.05/0.01] MeCN, 25 °C	*Y/O*	40			204
Cr(salen)$(H_2O)_2Cl$ [1/0.2/0.02] H_2O, RT, 5 h	*Y/O*	(75 + 76): 12			205
as above + β-cyclodextrin (0.03 equiv)	*Y/O*	(75 + 76): 22			205
CrO_3 [1/0.1/0.005] MeCN, 100 h	*T*	1	8	2	261
as above + α-picolinic acid (0.1 equiv) and 240 h	*T*	0.5	9	1	261
$NaNO_2$					
Cr(salen)$(H_2O)_2Cl$ [8/0.66/0.1] CH_2Cl_2–H_2O, 26 °C, 7 h	*T*	0.2	0.2	trace	208
$NaNO_2$ + oxygen					
Cr(salen)$(H_2O)_2Cl$ [8/0.66/0.1] CH_2Cl_2–H_2O, 26 °C, 7 h	*T*	0.15	0.65	trace	208
sodium hypochlorite + air					
Cr(TPP)Cl [1/7/0.025] R_4NCl, CH_2Cl_2–H_2O, RT, 3 h (*C* 24)	*Y*	8			300

[a] See section VIII for the definitions for the abbreviations and symbols.

TABLE 14. Oxidation of Norbornene



reactants and conditions[a]		results			ref
		79	80	81	
iodosylbenzene					
Cr(TPP)Cl	*Y/O*	99, (exo/endo: 32)			167
Cr(salen)$(H_2O)_2Cl$ [1/0.2/0.02] H_2O, RT, 5 h	*Y/O*	21			205
as above + β-cyclodextrin (0.03 equiv)	*Y/O*	40			205
as above + 4-methylpyridine (0.06 equiv)	*Y/O*	44			205
Cr(salen)$(H_2O)_2PF_6$ + pyridine (0.015 equiv) [1/0.03/0.005] CH_2Cl_2, RT	*Y/O*	82			203
Cr(m-salen)OTf + *N*-pyridine oxide (0.005 equiv) [1/0.05/0.01] MeCN, 25 °C	*Y/O*	85, exo			204
CrO(m-salen)(OTf) + *N*-pyridine oxide (0–0.4 equiv) [1/0.5/0.1] MeCN, 25 °C	*Y/O*	70–85			204
pentafluoroiodosylbenzene					
Cr(TPP)Cl [1000/64/1] CH_2Cl_2, RT	*Y/O*	32, (exo/endo: 1000)	0.2	0.6	176
Cr(TFPP)Cl [1000/64/1] CH_2Cl_2, RT	*Y/O*	75, (exo/endo: 422)	0.4	2.4	176
Cr(2,6-Cl-P)Cl [1000/64/1] CH_2Cl_2, RT	*Y/O*	74, (exo/endo: 362)	0.3	1.1	176
$NaNO_2$					
Cr(salen)$(H_2O)_2Cl$		trace			208

[a] See section VIII for the definitions for the abbreviations and symbols.

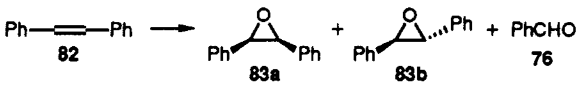
it has been pointed out that some allylic oxidations of **33** by PhIO occurred even in the absence of the catalyst.[174] The oxidation of alkanes with (TPP)CrCl/ArIO led to the corresponding alcohols and ketones in low yields (Tables 1 and 16).[169,171] At low conversions, substituted toluenes have been oxidized to the corresponding aryl alcohols by this system.[175] Nevertheless, (TPP)CrCl/ArIO can oxidize benzylic alcohols[167,168,173] and 2-cyclohexenol to the corresponding carbonyl compounds (Tables 8 and 17).[172] However, cleavage accompanied the oxidation of *tert*-butylphenylcarbinol since benzaldehyde was produced simultaneously (Table 8).[173]

In the presence of (TPP)CrCl, cumyl hydroperoxide was much more efficient as an oxygen source than iodosylbenzene for the oxidation of alkanes, hydroxylation being the main process (Table 1).[169] Such a system however did not epoxidize olefins.[169]

The cleavage of vicinal diols was carried out with the (TPP)CrCl/*p*-cyano-*N*,*N*-dimethylaniline *N*-oxide system under photocatalysis conditions: 1-phenylethane-1,2-diol led to quantitative yields of benzaldehyde and formaldehyde.[177,178]

The use of molecular oxygen associated with (TPP)CrCl requires the presence of a reducing agent.[179,180] Two systems were tested with cyclohexene as substrate, (TPP)CrCl/Mn$(OAc)_3$/L-cysteine/$NaBH_4$/O_2 and (TPP)CrCl/Avicel/$NaBH_4$/O_2, producing mainly allylic oxidation (Table 6). The (TPP)CrCl/O_2 system did not allow oxidation of isobutane in the absence of other

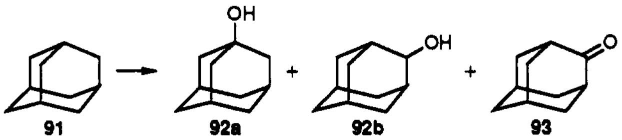
TABLE 15. Oxidation of (*E*)- and (*Z*)-Stilbenes



reactants and conditions[a]		results			ref
		83a	83b	76	
(*E*)-stilbene					
iodosylbenzene					
Cr(TPP)Cl	*Y*/*O*		17		167
Cr(m-salen)OTf + *N*-pyridine oxide (0.005 equiv) [1/0.05/0.01] MeCN, 25 °C	*Y*/*O*	<0.5	58	1	204
tert-butyl hydroperoxide					
CrO_3 [1/4/0.05] CH_2Cl_2, RT, 47 h	*Y*		33		214
$NaNO_2$ with or without oxygen		low yields			
Cr(salen)$(H_2O)_2$Cl					208
(*Z*)-stilbene					
iodosylbenzene					
Cr(TPP)Cl	*Y*/*O*	23			167
Cr(m-salen)OTf + *N*-pyridine oxide (0.005 equiv) [1/0.05/0.01] MeCN, 25 °C	*Y*/*O*	44	3	5	204
tert-butyl hydroperoxide					
CrO_3 [1/4/0.05] CH_2Cl_2, RT, 115 h	*Y*		15		214

[a] See section VIII for the definitions for the abbreviations and symbols.

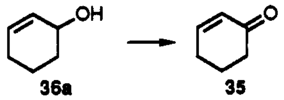
TABLE 16. Oxidation of Adamantane



reactants and conditions[a]	*C*		results			ref
			92a	92b	93	
tert-butyl hydroperoxide						
$(Bu_3SnO)_2CrO_2$ [1/7/0.05] PhH, 60 °C, 68 h	69	*Y*	19		6	227
CrO_3 [1/7/0.04] CH_2Cl_2, RT, 16 h	50	*Y*	10			239
iodosylbenzene						
Cr(TPP)Cl [1/0.25/0.025] PhH + NaCl-saturated H_2O		*Y*/*O*	2.2	0.5	3.1	171
pentafluoroiodosylbenzene						
Cr(TPP)Cl [1/0.25/0.025] PhH + NaCl-saturated H_2O		*Y*/*O*	1.5	0.4	1.3	171

[a] See section VIII for the definitions for the abbreviations and symbols.

TABLE 17. Oxidation of Cyclohexen-2-ol



reactants and conditions[a]	*C*		results	ref
			35	
air				
$[NBu_4][Os(N)(CH_2SiMe_3)_2(CrO_4)]$ [1/∞/0.05] MeCN, 70 °C, 72 h	28	*S*	100	276
$[NBu_4][Os(N)(CH_2SiMe_3)_2(CrO_4)]$ + $Cu(OAc)_2$ (0.1 equiv) [1/∞/0.05] MeCN, 70 °C, 72 h	99	*S*	100	276
bis(trimethylsilyl) peroxide				
PDC [1/3/0.1] CH_2Cl_2, 25 °C, 1.5 h		*Y*	90	228
iodosylbenzene				
Cr(TPP)Cl, RT			no yield data	172
peroxyacetic acid				
$(OCMe_2CH_2CMe_2O)CrO_2$ [1/2/0.1] CH_2Cl_2–CCl_4, 0 °C, 0.3 h		*Y*	80	286

[a] See section VIII for the definitions for the abbreviations and symbols.

coreagents but it is interesting to note that the exchange of the chloride anion for an azido group led to an efficient catalyst for this type of oxidation.[181] (TPP)-CrN_3/O_2 thus furnished *t*-BuOH (main product), acetone, and carbon dioxide (Table 9).[181,182] In contrast, the *μ*-nitride complex, (TPP)CrN, was not capable of producing this transformation.[181]

b. Others

The nature of the substituents on the porphyrin ligand can greatly modify the ratios of epoxidation/allylic oxidation and epoxidation/rearrangement obtained from alkenes with ArIO as oxygen source[176] (Tables 6 and 14).

Chloro(tetratolylporphyrinato)chromium(III) [(TTP)CrCl] in association with hydrogen peroxide was used to oxidize cyclohexane **1** to cyclohexanone **2** and cyclohexanol **3a**.[184] The efficiency of (TTP)CrCl/H_2O_2 was improved by the addition of a nitrogen base, and the best results were obtained with 4-aminopyridine (Table 1). The **2**/**3a** ratio was superior to 1 although **3a** was not oxidized to **2** under the reaction conditions.

(TTP)CrX/O_2 has been used with propionaldehyde as a reducing agent. Such a system achieved the epoxidation of propene (X = Cl)[185] and the oxygenation of **1** (Table 1) to **2** and **3a** (X = I),[186] both in very low yields and after long induction periods.

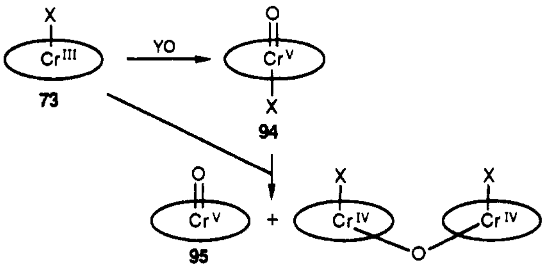
The replacement of the phenyl groups in the porphyrin ligand (TPP) by pentafluorophenyl substituents (TFPP) greatly increased the catalytic activity of (P)-CrN_3 in the reaction of isobutane **65** with molecular oxygen[182] (Table 11). Studies of this autooxidation showed that modification of the ligand P can greatly change the order of the efficiency of transition metals toward the oxygen transfer: (TPP)CrN_3/O_2 was more efficient than (TPP)FeN_3/O_2 and (TPP)MnN_3/O_2 for oxygenation of **65**,[181] while with a TFPP ligand, the order of the catalyst turnovers became Fe ≫ Mn > Cr.[182] (TFPP)CrX (X = Cl, OH, N_3) has been used also for the oxidation of *n*-butane to methyl ethyl ketone.[183]

The α-hydroperoxidation of ethylbenzene has been reported in the presence of oxygen and a heterogeneous catalyst in which the chromium atom is linked through a nitrogen atom to the conjugate system of the coal structure;[187] to the authors, this catalyst looks like a chromium porphyrin.

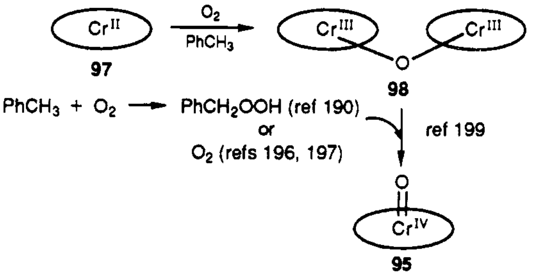
c. Mechanisms

The mechanisms of the oxidations induced by (P)-CrX depend on the nature of the oxygen source, porphyrin P, anion X, and the experimental conditions. The characteristic ESR spectrum of (TTP)$ClCr^V$=O has been observed from studies of solutions of (TTP)-$Cr^{III}Cl$ containing H_2O_2 or PhIO,[184,188] and the experimental magnetic susceptibility of these solutions was also in good agreement with the presence of this Cr^V species.[167,168] The study of visible spectra can be another powerful method for following the formation of the (P)Cr complexes. Although the first published visible spectra of (TPP)ClCrO[167,168] were false, and were in fact the spectra of (TPP)CrO,[189] it now appears that the characteristic λ_{max} values of (P)$Cr^{III}X$ **73**, (P)-Cr^{IV}=O **95**, (P)Cr^{II} **97**, and (P)XCr^V=O **94**, occur respectively at approximatively 450, 430, 420, and 410 nm.[173,177,189-198] In order to understand the mechanism of these catalytic reactions, a variety of oxygen atom donors have been employed to oxidize (P)CrX: ArIO, hydroperoxides, percarboxylic acids, 2-(phenylsulfonyl)-3-(*p*-nitrophenyl)oxaziridine, alkaline hypochlorite, or *p*-cyano-*N*,*N*-dimethylaniline *N*-oxide and light.[167,168,178,188-194] Visible spectra studies have indicated that the formation of **95** occurs more often than that of **94**;[177,189-191] this has to be interpreted with caution since **94** competes with the oxygen donor for the oxidation of **73** and a comproportionation reaction generally ensues to yield **95**[189-191] or [(P)XCr^{IV}]$_2$O **96**[192,193] (Scheme 7). From these results and depending on the nature of the oxygen source, either **94**[167-169,184] or **95**[177] has been proposed to be the true active oxygen species. The addition of ArIO to a methylene chloride solution of (TPP)Cr^{IV}=O led to (TPP)ClCr^V=O[190] but such a complex was not produced from PhIO and a Cr^{IV}–O–Cr^{IV} complex.[192] The electrochemical abstraction of an electron from (TPP)Cr^{IV}O has been another way to achieve access to the chromium(V) species [(TPP)Cr^VO]$^+$.[193,195] The complex (TPP)Cr^{IV}O was obtained from (TPP)Cr^{II} and dioxygen through a reaction which involves the formation of the μ-oxochromium(III) intermediate **98** (Scheme 8).[196,197,199]

SCHEME 7



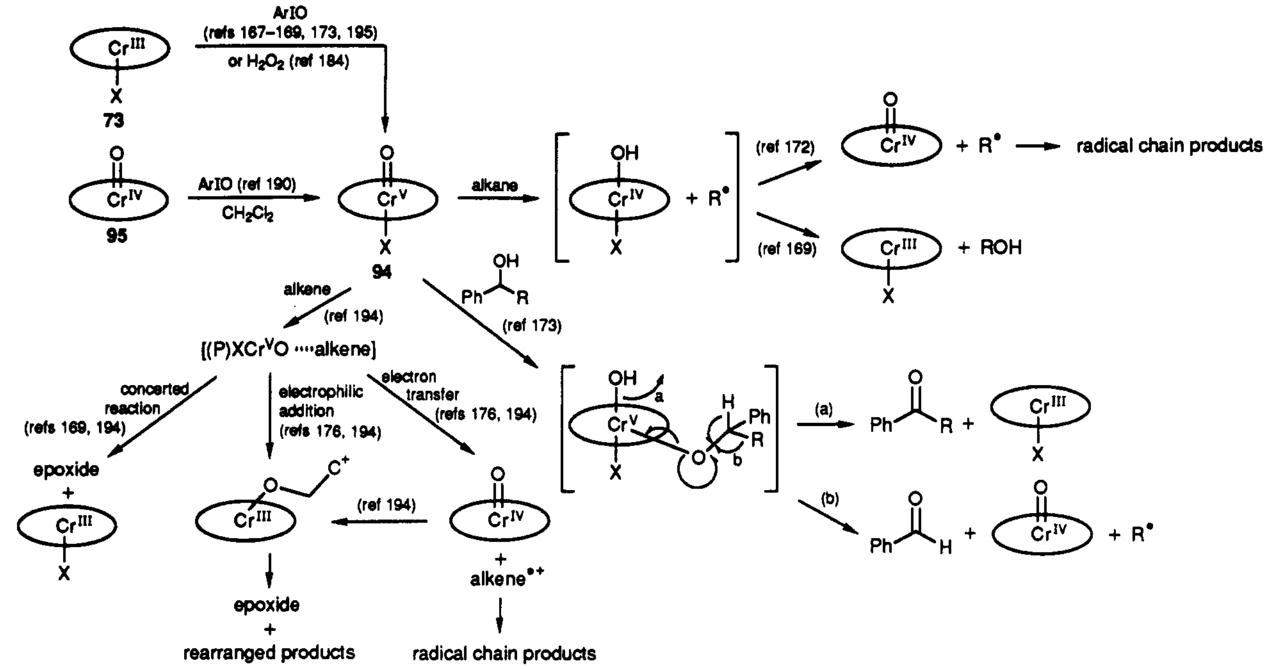
SCHEME 8



This summary of the literature illustrates the difficulties in understanding the interactions between (P)-CrX and the oxygen donors even for stoichiometric reactions (see also the reviews of Holm[23] and Jørgensen[29]). Furthermore, it has been shown that the proportions of Cr^{III}, Cr^{IV}, and Cr^V obtained in a mixture of (TTP)$Cr^{III}Cl$ and PhIO depend on the ratio of the reagents: for example, (TTP)ClCr^VO was the only chromium species obtained for a ratio of (TTP)-$Cr^{III}Cl$/PhIO > 11.9.[191,192]

Since oxidations catalyzed by (P)$Cr^{III}X$/YO often seem to involve higher valence states of chromium, it is interesting to summarize the following stoichiometric reactions. Alkenes and alcohols have been oxidized by stoichiometric amounts of a few (P)XCr^V=O complexes.[193,194,198] Norbornene, (*Z*)-cyclooctene, and cyclohexene afforded exclusively the corresponding epoxides while (*Z*)-stilbene furnished a mixture of diphenylacetaldehyde and benzaldehyde, due at least in part to the instability of *cis*-stilbene oxide in the presence of (P)XCr^V=O (**94**). The reduction of **94** to a mixture of (P)$Cr^{III}Cl$ (**73**) and (P)Cr^{IV}=O (**95**) was achieved simultaneously except in the case of the less reactive (*Z*)-cyclooctene where only **95** was formed.[193] It has been shown that (TPP)Cr^{IV}O is very unreactive toward saturated and unsaturated hydrocarbons.[189,195] The epoxidation of norbornene could however be observed by using **95** produced by comproportionation of (P)ClCr^V=O and (P)$Cr^{III}Cl$.[193] (TPP)Cr^{IV}=O was unreactive toward alcohols at room temperature but achieved the oxidation of benzylic alcohols at 70 °C with some cleavage: *tert*-butylphenylcarbinol led to benzaldehyde and *tert*-butyl phenyl ketone (ratio: 10/1).[173]

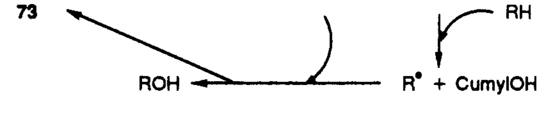
SCHEME 9



Some (P)Cr^{III}-catalyzed oxidations with ArIO (epoxidation and alkane oxidation)[167-169,173,175,195] and H_2O_2 (alkane oxidation)[184] have been considered to involve a $Cr^V{=}O$ complex as the true active oxygen species but some uncertainty remains concerning the exact mechanism. Indeed, stoichiometric and catalytic procedures sometimes lead to different results. These differences can be attributed in part to the fact that both procedures were sometimes carried out under different conditions and did not generally use the same porphyrin P. The role of P in the oxygen transfer to olefinic substrates has been exemplified by studies using a variety of substituted oxochromium(V) porphyrins.[176,193,194] Recently, a correlation between Hammett values and the reactivity of substituted toluenes has indicated that these atom abstraction reactions proceed through polar transition states with substantial charge transfer from the substrate to the electrophilic oxo complex.[175] Nevertheless, the mechanisms of the oxidations with (P)Cr^{III} and ArIO or H_2O_2 can be broadly illustrated by Scheme 9.

The oxygenation by cumyl hydroperoxide of alkanes catalyzed by various metalloporphyrins including (TPP)CrCl has shown that the reactive pathways are different from those involved with PhIO as oxidant since the results were almost independent of the nature of the metal and of its environment.[169] Thus, the oxidations with cumyl hydroperoxide have been rationalized[169] by suggesting a "Fenton-type" mechanism called also the "Haber–Weiss" mechanism[12,200] (Scheme 10).

SCHEME 10



From the work of Bruice concerning the mechanism of oxygen atom transfer to (TPP)CrCl,[191] it seems surprising that different pathways for the oxidation of cyclohexane have been proposed for (TPP)CrCl/cumyl hydroperoxide[169] and (TTP)CrCl/H_2O_2.[184] However, these methods employed different porphyrin ligands and the former procedure was principally used in the presence of an extra ligand.

It was initially concluded from visible spectral studies that the mechanism of the oxidation of 1-phenyl-1,2-ethanediol by the (TPP)CrCl/*p*-cyano-*N*,*N*-dimethylaniline *N*-oxide system involved (TPP)$Cr^{IV}O$.[177] Later, it was shown that the transfer of the oxygen atom from the *N*-oxide to the Cr^{III} complex required photoexcitation of the reaction mixture[191] and finally, it was concluded that (TPP)Cl$Cr^V{=}O$ was the true active oxygen species.[178]

The mechanisms of (P)Cr^{III}-catalyzed oxidations with oxygen probably depend on the reactions conditions. In the absence of added coreductants, an intermediate metalloporphyrin–O_2 complex containing singlet oxygen has been postulated,[201] but the reaction could correspond to a free-radical autooxidation with the complex, acting as an initiator, generating free radicals.[202] When a coreductant is added to the oxidative mixture, it can act as an electron source playing the role of NADPH required with cytochrome P-450 for oxidative conversions in living systems.[49,202] However, a similar mechanism has not seemed to have been retained for the chromium model, and the contribution of HO• as one of the possible active oxygen species has been suggested.[180] When propionaldehyde was added,[185,186] it played the role of reductant: there is in situ production of (P)Cr^{II} and an acyl radical leading to a peroxy acid[186] (Scheme 11) which is a more efficient oxidant than molecular oxygen and could induce the formation of Cr^V from Cr^{III}. The low efficiency of (TTP)Cr^{III}Cl as catalyst was attributed to the high value of its reduction potential (−1.06 V), which renders difficult the first step

SCHEME 11

$$[(P)Cr^{III}]^+ + EtCHO \longrightarrow (P)Cr^{II} + EtCO^\bullet + H^+$$

$$EtCO^\bullet + O_2 \xrightarrow{EtCHO} EtCOOOH + EtCO^\bullet$$

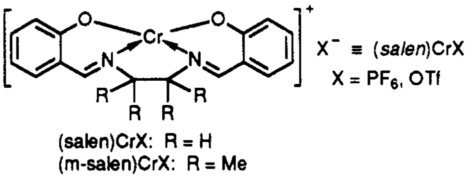
$$[(P)Cr^{III}]^+ + EtCOOOH \longrightarrow [(P)Cr^VO]^+ + EtCOOH$$

of the Scheme 11.[185] Nevertheless, the oxidations catalyzed by (TTP)$Cr^{III}I$ were also inefficient although larger amounts of the peroxy acid were produced.[186]

It will probably require a great deal of time and effort to explain all of the procedures catalyzed by (P)$Cr^{III}X$ since even the mechanisms of stoichiometric oxidations with (P)$XCr^{V}{=}O$ are not firmly established and that they seem to depend on the nature of the substrate.[193,194]

6. (*Salen*)CrX

Like the preceeding (P)$Cr^{III}X$ complexes, the (*salen*)$Cr^{III}X$ ones (**99**) are principally employed to mimic the monooxygenase model systems and they have been mainly used to catalyze the oxidation of alkenes by PhIO.[203,204] The rate of oxidation was accelerated by the addition of a promoter which played the role of a donor ligand such as pyridine[203] or pyridine *N*-oxide[204] in CH_2Cl_2 or CH_3CN respectively. Stereoselective epoxidation, giving fair yields, was obtained from norbornene, cyclooctene, (*E*)- and (*Z*)-β-methylstyrenes, and (*E*)- and (*Z*)-stilbenes (Tables 14 and 15), while this reaction was very inefficient with cyclohexene (Table 6) and linear alkenes. Some cleavage of the double bond was observed for both styrene and stilbenes but remained a minor reaction (Tables 13 and 15). Recently, these epoxidations have been performed in the biphasic system, CH_2Cl_2/H_2O, with the water-soluble (salen)$Cr(H_2O)_2Cl$.[205] Both the rates and the yields were often increased in the presence of β-cyclodextrin as a phase-transfer agent and the addition of 4-methylpyridine also led to further increases in the rates (Tables 13 and 14). At the end of the consumption of PhIO, the catalyst was still active: the addition of a supplementary amount of PhIO afforded more epoxide.[205] The mechanism of the oxygen transfer from PhIO to the substrate has been carefully studied but a general mechanism has not been established.[204] PhIO led to the stable and fully characterized oxochromium(V) adduct (**100**) with the promotor as an axial ligand.[204,206] This electrophilic complex attacks the olefin to form a transient intermediate **101a** or **101b** which could be close to a chromium–oxygen–carbon–carbon ring[207] and provides the starting (*salen*)Cr^{III} cation and the epoxide or the cleavage products (Scheme 12).[204]



99

SCHEME 12

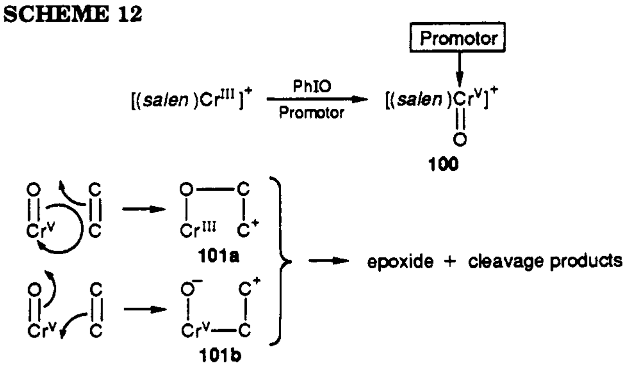
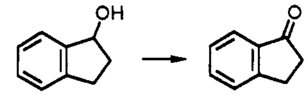


TABLE 18. Oxidation of Indan-1-ol



102 **103**

reactants and conditions[a]	*C*	results		ref
			103	
tert-butyl hydroperoxide				
CrO_3 [1/4/0.05] CH_2Cl_2, RT, 3 h	100	*Y*	77	245
CrO_3 + TsOH (0.1 equiv) [1/7/0.05] PhH, RT, 4 h		*Y*	90	242
$(Bu_3SnO)_2CrO_2$ [1/4/0.05] CH_2Cl_2, 40 °C, 5.2 h		*Y*	80	227
$C_5H_5NHCrO_2Cl$ [1/7/0.05] CH_2Cl_2, RT, 7 h	98	*Y*	78	78
$C_5H_5NHCrO_2F$ [1/7/0.05] CH_2Cl_2, RT, 3.2 h	98	*Y*	68	78
sodium perborate				
CrO_3 + R_4NCl [1/7/0.1] 60 °C, 24 h		*Y*	13	259

[a] See section VIII for the definitions for the abbreviations and symbols.

Recently, the catalytic properties of (salen)$Cr(H_2O)_2Cl$ and (salen)$Cr(ONO)(H_2O)$ for oxidations with $NaNO_2$ under both aerobic and anaerobic conditions have been examined.[208] Cyclohexene was unreactive while the epoxidation of styrene **74** (Table 13), stilbene **82** (Table 15), allyl alcohol, and norbornene **78** (Table 14) was achieved in poor yields, with low conversions, and with some cleavage of the double bond in the case of **74** and **82**. The product distribution depends on the presence of oxygen and these processes were inhibited by addition of a radical trap. The reaction of (salen)$Cr(H_2O)_2Cl$ with $NaNO_2$ did not lead to $Cr^{V}{=}O$ species but to (salen)$Cr(ONO)(H_2O)$. This latter complex was able to promote the oxidation of styrene by O_2 (Table 13) but not by $NaNO_2$. Finally, it has been concluded that different mechanisms occur under aerobic and anaerobic conditions.[208]

IV. Chromium(IV) as Catalyst

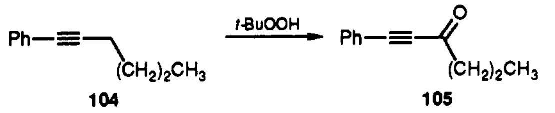
Chromium complexes in the formal oxidation state (IV) have been rarely used as oxidation catalysts. It has been briefly mentioned that (a) stoichiometric amounts of (TPP)$Cr^{IV}O$ oxidize benzyl alcohol to benzaldehyde and that the reduced species, probably (TPP)$Cr^{III}OH$, induces the formation of more PhCHO in the presence of PhIO, (b) (TPP)$Cr^{IV}O$ did not catalyze the hydroxylation of alkanes and the epoxidation of alkenes by PhIO.[189]

The Cr(IV) complexes $C_5H_5NHCrO_2X$, easily obtained[209] from pyridinium chlorochromate (X = Cl)[210] or pyridinium fluorochromate (X = F),[211] have been employed in conjunction with *tert*-butyl hydroperoxide[78] and presented similar activities. With these systems, benzylic secondary alcohols, propargylic and benzylic carbons were oxidized to ketones in fair yields (Tables 18–20). Small amounts of alcohols or *tert*-butylperoxy derivatives were obtained from benzylic hydrocarbons. Minute amounts of epoxides were isolated from cyclic ethylenic substrates, the main product being the α,β-unsaturated ketones (Table 2).

V. Chromium(V) as Catalyst

It seems that the use of a Cr^{V} catalyst has been only mentioned twice in the literature. PhIO was used as an oxygen source in both papers to achieve the epoxidation of norbornene catalyzed by (m-salen)$Cr^{V}O$-

TABLE 19. Oxidation of 1-Phenylhex-1-yne



104 105

reactants and conditions[a]	C	results		ref
			105	
$C_5H_5NHCrO_2Cl$ [1/7/0.05] PhH, RT, 20 h	71	*Y*	51	78
$C_5H_5NHCrO_2F$ [1/7/0.05] PhH, RT, 20 h	60	*Y*	37	78
CrO_3 [1/7/0.05] CH_2Cl_2, RT, 21 h	65	*Y*	41	242
CrO_3 [1/7/0.05] PhH, RT, 44 h	85	*Y*	57	242
CrO_3 + TsOH [1/7/0.05] PhH, RT, 44 h	88	*Y*	62	242
$(Bu_3SnO)_2CrO_2$ [1/7/0.05] PhH, 60 °C, 8 h	57	*Y*	29	227

[a] See section VIII for the definitions for the abbreviations and symbols.

(OTf)[204] (Table 14), and the cleavage of ylides 108 by (salen)$Cr^VO(OTf)$ (eq 17).[212] The catalytic cycle of these reactions probably proceeds via the reduced form $Cr^{III}(OTf)$ as described previously (section III.6).

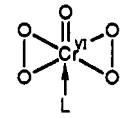
$$\underset{\mathbf{108}}{Ph_3P{=}CR^1R^2} \xrightarrow[PhIO]{(salen)CrO(OTf)} \underset{\mathbf{109}}{R^1R^2C{=}CR^1R^2} + \underset{\mathbf{110}}{O{=}CR^1R^2} \qquad (17)$$

T 5 ref 212

Attempts to employ 1,10-phenanthroline complexes of oxochromium(V), (phen)H_2CrOCl_5, and (phen)$CrOCl_3$,[213] with *t*-BuOOH were thwarted by the rapid decomposition of this hydroperoxide by these catalysts.[214]

VI. Chromium(VI) as Catalyst

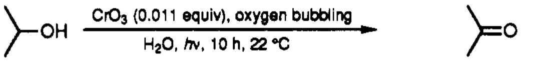
The association of a Cr^{VI} salt with an oxygen donor began a long time ago. In 1843, Barreswil communicated to the French Academy of Sciences that the addition of hydrogen peroxide to an acidic solution of potassium dichromate developed a blue color.[215] Investigations concerning the nature of this blue species called "blue perchromic acid" led to considerable controversy for more than a century.[216,217] Finally, the structure $(O_2)_2Cr{=}O$ with two peroxidic groups has been retained and corresponding complexes 111 have been isolated in the presence of Lewis bases.[217,218] During and after this time, the mixture Cr^{VI}/H_2O_2 has been used for oxidations under stoichiometric[219,221] and catalytic[166,220–228] conditions.



111

1. CrO_3

The autooxidation of benzylic carbons[229,230] has been carried out in the presence of small amounts of chromium(VI) oxide. Tetraline led to α-tetralone with high selectivity when dimethylformamide or better *N*,*N*-dimethylacetamide was used as solvent, minute amounts of α-tetralol and α-tetralin hydroperoxide being formed (Table 3).[229] Ethylbenzene furnished acetophenone with a rate and yield only slightly modified in the presence of an organic acid (picolinic or trifluoroacetic acid) but both greatly increased under irradiation (Table 12).[230] The radical character of these reactions precludes high conversion of starting substrates if good selectivities are desired. Under UV irradiation, catalytic amounts of CrO_3 and 1 atm of oxygen oxidize 2-propanol 112 to acetone 113 (eq 18).[231,232]



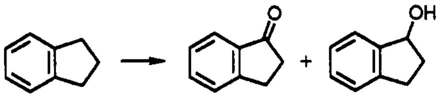
(18)

112 113

Y 54.3 refs 231, 234

The role of the light remains poorly understood,[234] but

TABLE 20. Benzylic Oxidation of Indan



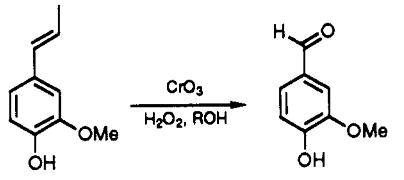
106 103 107

reactants and conditions[a]	C	results			ref
			103	107	
hydrogen peroxide					
CrO_3 [1/7/0.1] acetone, RT, 79 h		*Y*	27		225
CrO_3 + R_4NCl (0–0.2 equiv) [1/7/0.1] H_2O or CH_2Cl_2, RT, 18 h		*T*	<1		214, 225, 226
CrO_3 [1/0.2/0.01] CH_2Cl_2, RT, 26 h		*T*	5		226
$(Bu_3SnO)_2CrO_2$ [1/0.2/0.001] CH_2Cl_2, RT, 16 h		*T*	6		226
hydrogen peroxide urea adduct ($CH_4N_2O{\cdot}H_2O_2$)					
CrO_3 + TsOH (0.05 equiv) [1/10/0.05] *t*-BuOH, RT, 23 h		*Y*	8		226
CrO_3 [1/10/0.05] acetone, RT, 70 h		*Y*	44		226
tert-butyl hydroperoxide					
$(OCMe_2CH_2CMe_2O)CrO_2$ [1/7/0.1] CH_2Cl_2, 0 °C, 8 h	86	*Y*	60		287
CrO_3 [1/6/0.1] CH_2Cl_2, RT, 6 h		*Y*	63		240
CrO_3 [1/7/0.1] water-saturated CH_2Cl_2, RT, 24 h		*Y*	56		214
CrO_3 [1/4/0.05] CH_2Cl_2, 0 °C, 47 h		*Y*	86		225
$(Bu_3SnO)_2CrO_2$ [1/7/0.05] PhH, 60 °C, 3 h		*Y*	73		227
$C_5H_5NHCrO_2Cl$ [1/7/0.05] CH_2Cl_2, RT, 3.2 h	90	*Y*	46	1	78
$C_5H_5NHCrO_2F$ [1/7/0.05] CH_2Cl_2, RT, 4.2 h	89	*Y*	63	3	78
PDC [1/7/0.05] CH_2Cl_2, RT, 19 h		*Y*	74		225
PFC [1/7/0.05] CH_2Cl_2, RT, 19 h		*Y*	70		225
PCC [1/7/0.05] CH_2Cl_2, RT, 19 h		*Y*	64		225
BPCC [1/7/0.05] CH_2Cl_2, RT, 19 h		*Y*	36		225

[a] See section VIII for the definitions for the abbreviations and symbols.

the photoassisted formation of peroxy derivatives of **113** could be involved as suggested for oxidations by a Pd/$h\nu$/O_2 system.[235]

As mentioned previously, the interaction of hydrogen peroxide with Cr^{VI} was recognized very early.[215] However, a catalytic procedure based on blue perchromic acid was "only" reported in 1937, about a century later.[222] Catalytic amounts of chromium(VI) oxide induced the oxidation of saturated and unsaturated compounds by H_2O_2.[222-226] Oxygenation of cyclohexane[224,226] (Table 1), monohydroxylation of the aromatic ring,[222] dihydroxylation,[222,223] epoxidation,[224,226] and cleavage[88,222-224,226] of double bonds (Tables 6 and 13 and eqs 11 and 19), benzylic oxidation[224-226] (Tables 12 and 20), and oxidation of primary alcohols to aldehydes and carboxylic acids[228] have been achieved, generally with low yields even in the presence of a phase-transfer catalyst.[225,226] The oxidative cleavage seemed sometimes to be more efficient in the presence of triethylamine (eq 11),[88] or when the double bond was substituted by an aromatic group[222] but in the case of **114**, the reproducibility of yields is questionable (eq 19).[236] The use of acetone (caution[237]) as solvent and/or a hydrogen peroxide/urea adduct instead of H_2O_2 can improve the efficiency of benzylic oxidations[225,226] (Table 20). It was noticed early that the reaction stops at the formation of a bluish-green precipitate having the properties of chromium(III) oxide and which cannot be reactivated by H_2O_2.[222] Hydroxyl radicals[222] and peroxochromium(VI) complexes[224] have been successively proposed as the active species. In the case of the first proposal, a mechanism as indicated in Scheme 6 would operate. The intermediates of the second proposal would be similar to "blue perchromic acid" and could enter into the catalytic cycle suggested in working from isolated peroxo species (see section VI.4, Scheme 18). Some participation of singlet oxygen in the oxidative process is possible.[238] The low efficiency of the CrO_3/H_2O_2 procedure can be explained by the decomposition of H_2O_2 by CrO_3[163,222] and/or by an irreversible reduction of the chromium under the reaction conditions.[223]



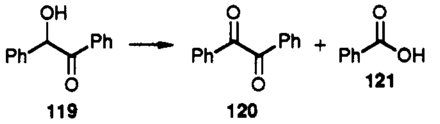
114 **115**

Y 58 ref 222
Y 6 ref 236

(19)

Chromium(III) oxide has been tested as catalyst for the epoxidation of octenes at 120 °C by cumyl hydroperoxide[70] but only low amounts of epoxides have been produced (Table 7). Under milder conditions (room temperature), the oxidation of the secondary allylic alcohol **116** to the **117** and **118** was achieved in moderate yields (eq 20).[239] Nevertheless, this process presented an efficiency inferior to the CrO_3/t-BuOOH association discussed in the following paragraph.

TABLE 21. Oxidation of Benzoin

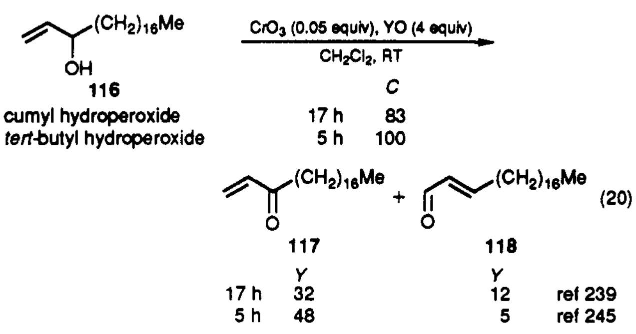


119 **120** **121**

reactants and conditions[a]	*C*	results			ref
			120	121	
CrO_3 (0.05–0.1 equiv)					
70% *t*-BuOOH (4 equiv), CH_2Cl_2, RT, 8 h	34	*Y*	23		245
methyltridecylammonium chloride (0.2 equiv) $NaBO_3$ (7 equiv), PhH/H_2O (1/1), 60 °C, 24 h	100	*Y*	51	38	259
(n-$Bu_3SnO)_2CrO_2$ (0.05 equiv)					
t-BuOOH (4 equiv), CH_2Cl_2, 40 °C, 21 h	70	*Y*	34		227

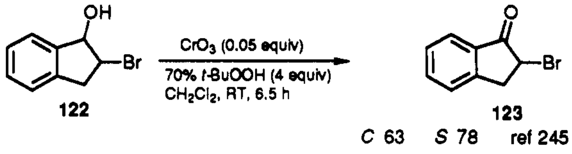
[a] See section VIII for the definitions for the abbreviations and symbols.

Catalytic amounts of CrO_3 with an excess of commercial aqueous 70% *t*-BuOOH were used to oxidize benzylic[226,240] (Tables 3, 4, 12, and 20), allylic[241] (Table 2) and propargylic[242] (Table 19) carbons with fair yields at room temperature. Methylene chloride was a good solvent used to achieve benzylic and allylic oxidations while propargylic oxidations were best carried out in benzene. The selectivity of the benzylic oxidations can be increased by decreasing the reaction temperature to 0 °C,[225,240] while, as noted for stoichiometric chromium procedures,[18] the allylic oxidation was efficient only for cyclic substrates.[241] The increase in the efficiency of the propargylic oxidation in the presence of small amounts of *p*-toluenesulfonic acid,[242] (Table 19) seems to indicate the in situ formation of protonated Cr(VI) species.[243] It is interesting to point out that propargylic ketones have been obtained with yields far superior to those reached with stoichiometric chromium procedures.[244] In the presence of allylic hydrogens, the epoxidation of double bonds remained a minor reaction pathway[241],[245] which furthermore can be decreased by using benzene rather than methylene chloride as solvent.[239] In contrast, the oxygenation of double bonds has been observed in the absence of available allylic hydrogen:[214] both (*E*)- and (*Z*)-stilbenes afforded *trans*-stilbene oxide (**83b**) (Table 15) as the major compound with benzophenone, benzil, and benzoin benzoate as side products. The CrO_3/t-BuOOH system also accomplished the oxidation of primary and secondary alcohols to carbonyl compounds (Tables 8, 18, and 21 and eq 20). Particularly efficient for secondary benzylic alcohols and compatible with inactivated halogen groups, it brought about the selective oxidation of 1-phenyl-1,2-ethanediol to α-hydroxyacetophenone (Table 8) and 2-bromoindan-1-ol to 2-bromoindan-1-one, respectively[245] (eq 21). The CrO_3/t-BuOOH me-



116 **117** **118**

(20)

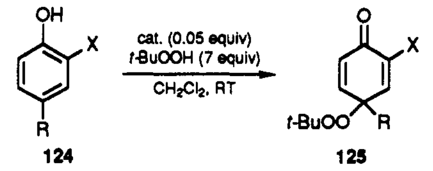


122 **123**

C 63 *S* 78 ref 245

(21)

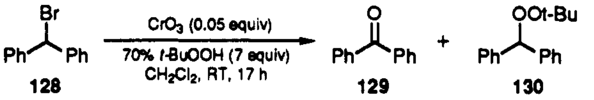
TABLE 22. Oxidation of Para-Substituted Phenols



reactants and conditions[a]	results		ref
		125	
X = H			
R = Me			
CrO_3, 86 h	Y	15	246
PDC, 4 h	Y	41	246
X = OMe			
R = $CH_2CH_2CH_3$			
CrO_3, 86 h	Y	26	246
PDC, 16 h	Y	24	246
R = $CH_2CH{=}CH_2$			
CrO_3, 90 h	Y	26–30	246
PDC, 20 h	Y	26	246

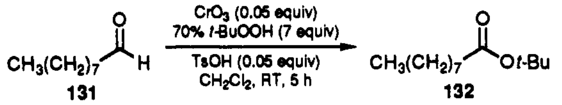
[a] See section VIII for the definitions for the abbreviations and symbols.

thod led to the peroxidation of the para position of para-substituted phenols but with yields no better than 30% (Table 22).[246] This catalytic system has also produced the oxidation of benzylic trimethylsilyl ethers to ketones (Table 23),[247] benzyltrimethylsilane to benzaldehyde and benzoic acid,[248] bromodiphenylmethane to benzophenone and *tert*-butylperoxydiphenylmethane (eq 22),[239] aldehydes to *tert*-butyl esters (eq 23),[239] α,β-unsaturated esters to α,β-unsaturated γ-keto esters (eq 24),[214] and the cleavage of hydrazones and oximes to ketones (eq 25).[249] As with CrO_3/H_2O_2, the oxidative properties of the CrO_3/*t*-BuOOH system disappears with the change of the mixture coloration from initially red-purple to green-yellow. At this stage, the catalytic species cannot be reformed by the addition of *t*-BuOOH since this hydroperoxide is usually immediately destroyed by the green-yellow mixture.[214,240]



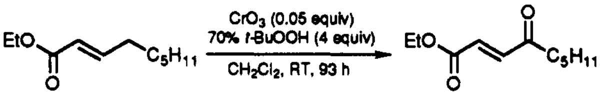
128 129 130 (22)

Y 62 31 ref 239



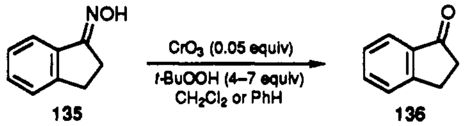
131 132 (23)

Y 30 ref 239



133 134 (24)

C 65 S 68 ref 214

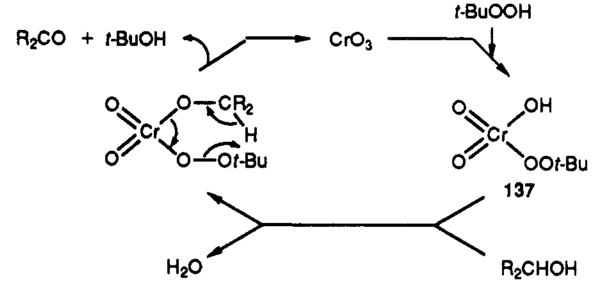


135 136 (25)

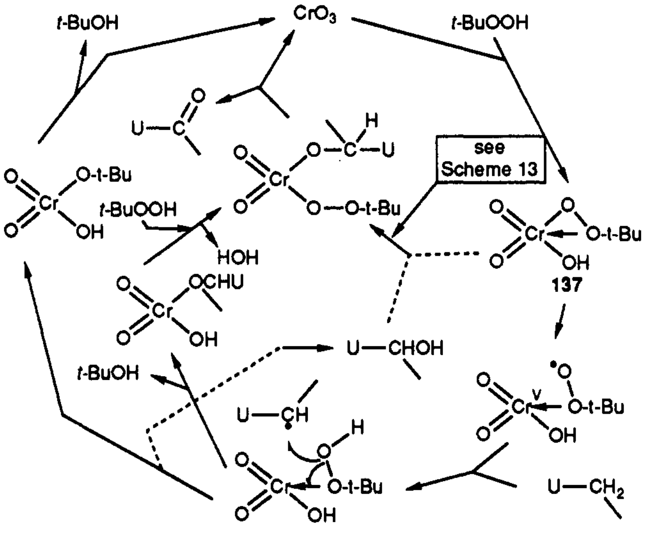
Y 60–80 ref 249

The addition of ROOH (R = *t*-Bu, $PhCMe_2$) to a yellow methylene chloride suspension of CrO_3 immediately produced solubilization of the metal oxide followed by formation of a red-purple color in the mixture. These observations suggest that the active oxidative species is not CrO_3. The results of the oxidation of 6-methoxy-1,2,3,4-tetrahydronaphthalene (**20**) are in agreement with this interpretation. Indeed, the stoichiometric oxidation of this compound by CrO_3 furnished almost exclusively 6-methoxy-1-tetralone (**21**)[250] while a 2/1 mixture of **21** and **22** was obtained with the CrO_3/*t*-BuOOH system (Table 4). The formation of a peroxochromium(VI) complex seemed to be excluded[228] but comparisons with selected oxygenated complexes of vanadium[98,251,252] and molybdenum[253] have led to considering a *tert*-butylperoxychromium(VI) complex as a possible intermediate.[242,245] Indeed, the difference in rates and ratios observed in using either *t*-BuOOH or $PhCMe_2OOH$ (eq 20) suggests that the R group of ROOH may be present in the active oxidative species.[254] The catalytic cycle could conserve the formal (VI) oxidation state in the case of alcohols as starting substrates (Scheme 13)[245] while the oxidation of activated methylene groups could involve Cr^V species with formation of hydroxy or *tert*-butylperoxy derivatives of the substrate as intermediates (Scheme 14 or 15).[242] ESR experiments have indicated the formation of Cr^{IV} and Cr^V species in the course of chromium(VI)-catalyzed benzylic oxidations by *t*-BuOOH[255] but the identification of active species while using this technique remains hazardous. Obviously, the intervention of radicals, at least in some cases, has to be accepted in order to rationalize reactions given by the CrO_3/*t*-BuOOH system

SCHEME 13

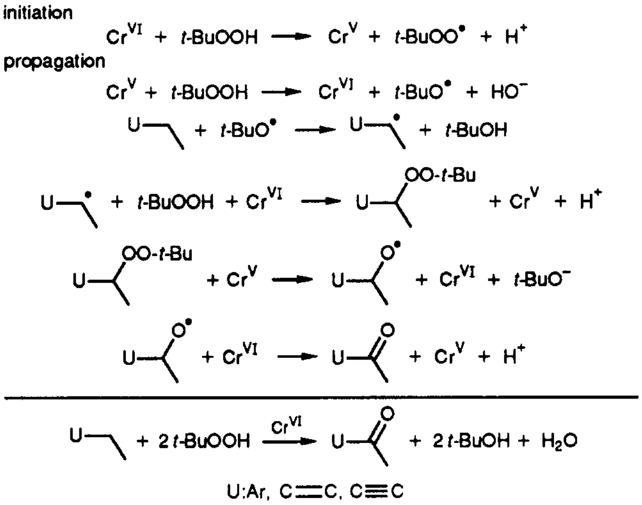


SCHEME 14

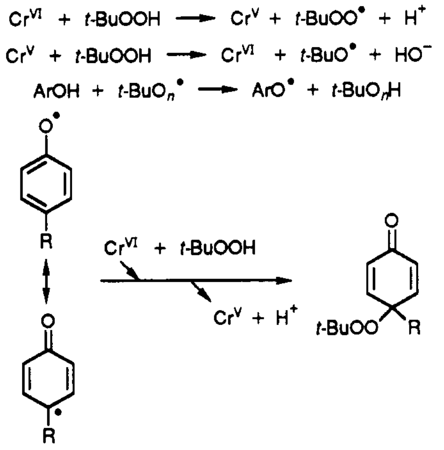


U:Ar, C═C, C≡C

SCHEME 15



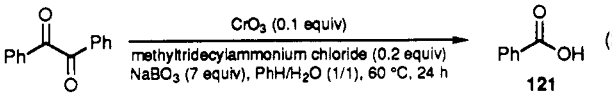
SCHEME 16



(Scheme 16).[246] The difference in the amount of water present in the procedures which used either 30% H_2O_2 or 70% *t*-BuOOH, cannot explain the difference in reactivities; indeed, the CrO_3-catalyzed oxidation of indan in CH_2Cl_2 by either aqueous 70% *t*-BuOOH or aqueous 30% *t*-BuOOH afforded similar results[214] (Table 20). The better results obtained in using *t*-BuOOH rather than H_2O_2 as the oxygen atom source can be explained by its higher stability, and better solubility in nonpolar solvents.[13,256] The difference in basicity between these hydroperoxides, pK_a (*t*-BuOOH) = 12.8, pK_a (H_2O_2) = 11.6[257] could also be involved.[70,220]

The association of CrO_3 with bis(trimethylsilyl) peroxide instead of *t*-butyl hydroperoxide has only been reported for the oxidation of 4-*tert*-butylcyclohexanol to the corresponding ketone with a 30% yield[228,258] (Table 9).

The use of a fifth peroxide, sodium perborate, has been recently investigated.[259] The CrO_3/$NaBO_3$ mixture required a temperature of 60–80 °C in a biphasic system with a phase-transfer catalyst to bring about the oxidation of alcohols but also to the cleavage of some C—C and C=C bonds (Tables 6, 8, 18, and 21 and eq 26). The presence of small amounts of CrO_3 allows oxidations by $NaBO_3$ which in the absence of catalyst necessitate higher temperatures and acetic acid as solvent.[260]



(26)

120

121

Y 60 ref 259

Following studies with the (porphyrin)CrX/PhIO, this oxygen source was tested with CrO_3 in reactions with cyclohexane 1,[261] ethylbenzene,[230,261] and styrene 74[261] (Tables 1, 12, and 13). As with some stoichiometric oxidations by Cr^{VI},[262] the addition of α-picolinic acid accelerated the accumulation of the oxidation products, giving cyclohexanone from 1, acetophenone (main product) and 1-phenylethan-1-ol from ethylbenzene (Tables 1 and 12). The opposite occurred with 74 but larger amounts of α-picolinic acid were added: the rate of the formation of the oxidation products, benzaldehyde (main product), acetophenone, and styrene oxide, decreased and furthermore, the ratio of acetophenone/styrene oxide was reversed (Table 13). It is interesting to note that with ethylbenzene as a substrate the regeneration of the active Cr species could be achieved at the end of the reaction by the addition of PhIO.[230]

Recently, a Polish patent has described the use of catalytic amounts of both CrO_3 and pyridine in an aqueous medium to carry out the oxidation of 2-methylnaphthalene to the corresponding quinone (vitamin K_3), the regeneration of the catalytic species being continually assured through an electrochemical step.[263]

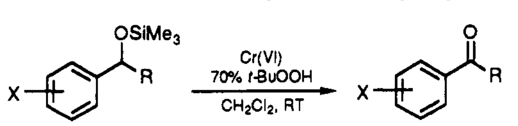
2. $(XO)_nCr_m(=O)_p$

As for stoichiometric oxidations, CrO_3 has often been associated with basic ligands for catalytic studies. Pyridinium chlorochromate (PCC)[210] and pyridinium dichromate (PDC)[264] have been most commonly used but similar species have often been formed in situ. However, the present chapter includes only those papers which describe the use of preformed catalysts which contain *n* ammonium (X), *p* oxo group (=O), and *m* Cr atoms ($n,m,p \geq 1$). The representation of their structure by $(XO)_nCr_m(=O)_p$ is not strictly exact since they can contain one or more Cr–O–Cr binding units.

A variety of ammonium–chromium(VI) oxides have been employed to promote the autooxidation of tetralin but conversions and selectivities were inferior to those obtained by simply using CrO_3 as catalyst.[229] Irradiation at $\lambda > 520$ nm of aerated acetonitrile or methylene chloride solutions of cyclohexane (1) in the presence of catalytic amounts of either $(Bu_4N)_2Cr_4O_{13}$ or $(Bu_4N)_2CrO_4$ afforded cyclohexanol and larger quantities of cyclohexanone[265,266] (Table 1). Although the $(Bu_4N)_2CrO_4$/PhIO/$h\nu$ association did not oxidize an oxygen-free methylene chloride solution of 1, the addition of catalytic amounts of PhIO to the $(Bu_4N)_2CrO_4/O_2/h\nu$ system increased the rate and the yields of the oxidation of this alkane[266] (Table 1). Coordination of PhIO to the complex was postulated to explain its promoting effect. The radical character of these oxidations of 1 was exemplified by the concomitant formation of cyclohexyl chloride when using methylene chloride as solvent.[265,266]

Switching from CrO_3 to $(Bu_4N)_2CrO_4$, $(Bu_4N)_2Cr_2O_7$, or $(Bu_4N)_2Cr_4O_{13}$ as catalyst for the oxidation of ethylbenzene, cyclohexane, and styrene by H_2O_2 did not greatly modify the results except that $(Bu_4N)_2CrO_4$ was less efficient (Tables 1, 12, and 13).[224]

TABLE 23. Oxidation of Benzylic Trimethylsilyl Ethers



126 127

	results	
reactants and conditions[a]	127	ref
X = H		
R = H, $(Ph_3SiO)_2CrO_2$ [1/3/0.05], 14 h	*Y* 42[b]	247
R = Me, $(Ph_3SiO)_2CrO_2$ [1/3/0.05], 14 h	*Y* 97	247
R = Et, $(Ph_3SiO)_2CrO_2$ [1/3/0.05], 14 h	*Y* 97	247
R = Ph, $(Ph_3SiO)_2CrO_2$ [1/3/0.05], 14 h	*Y* 98	247
X = *m*-MeO		
R = C_7H_{15}, $(Ph_3SiO)_2CrO_2$ [1/3/0.05], 24 h	*Y* 96	247
R = C_7H_{15}, CrO_3 [1/7/0.05], 45 h	*Y* 84[c]	247

[a] See section VIII for the definitions for the abbreviations and symbols. [b] Benzoic acid was also isolated (*Y* 47). [c] Corresponding alcohol was also isolated (*Y* 14).

For the Cr-catalyzed oxidation of indan by *t*-BuOOH at room temperature, the yields of indanone (**103**) followed the decreasing order: PDC > PFC = CrO_3 > PCC ≫ BPCC (Table 20).[225] The oxidation of tetralin with the PDC/*t*-BuOOH system[267] was more efficient in CH_2Cl_2 than in benzene; tetralone (**18**) was the main product, with small amounts of naphthoquinone and α-*tert*-butylperoxy tetralin being formed (Table 3).[225] Note that a better yield of **18** was obtained using catalytic amounts of PDC and an excess of *t*-BuOOH, than when using an excess of both *t*-BuOOH and PDC.[225,267,268] The rate of peroxidation of the para position of *para*-substituted phenols by *t*-BuOOH was higher with PDC as catalyst rather than CrO_3 (Table 22), and the yields were sometimes increased.[246]

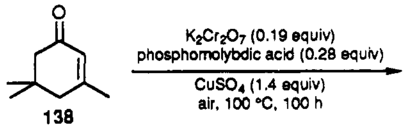
The coordination of amines to Cr^{VI} was even more interesting in the case of chromium-catalyzed oxidations of alcohols in the presence of $Me_3SiOOSiMe_3$.[228,258] The order of efficiency was PDC ≫ PCC > CrO_3 (Table 9). Good to high yields of aldehydes or ketones were obtained from alcohols with the PDC/$Me_3SiOOSiMe_3$ system[228,258] (Tables 8, 9, and 17). The oxidation of 1-(trimethylsilyl)pent-2-yn-4-ol by PCC associated to $Me_3SiOOSiMe_3$ has led to the corresponding ketone with less than 40% yield.[270] The overoxidation of aldehydes and the epoxidation of unsaturated alcohols were not observed. From UV analysis, it was concluded that similar peroxo complexes **111** resulted from Cr^{VI} and either H_2O_2 or $Me_3SiOOSiMe_3$ and that they were stabilized by the pyridine ligand[228] (see the introduction of section VI). However, the oxidation was much more efficient when using the latter peroxide.

A number of metal-chromium catalysts, especially copper-chromium catalysts, have been prepared from ammonium dichromate. They have been used for the dehydrogenation of alcohols to aldehydes and ketones by heating at 250–350 °C,[271-273] but subsequent reactions were also observed.[274]

3. $K_2Cr_2O_7$

Potassium dichromate has been mainly used as catalyst in association with oxygen. Its effect on the autooxidation of paraffins has been studied.[275]

$K_2Cr_2O_7$ associated with $Cu(OAc)_2$ did not catalyze the oxidation of benzyl alcohol by oxygen,[276] but a mixture containing an excess of $CuSO_4$, and catalytic amounts of both phosphomolybdic acid and $K_2Cr_2O_7$ successfully achieved the allylic oxidation of cyclohexenones at 100 °C under an air atmosphere (eq 27).[277]



(27)

138

59

Y 60 ref 277

The production of 3,5,5-trimethylcyclohex-2-ene-1,4-dione (**59**) directly from α-isophorone (**138**) was interesting[276] since only a few less efficient catalytic methods had been previously available for the synthesis of this useful dione from **138** in one step.[18,278] Generally, the oxidation was carried out on β-isophorone (**58**)[102-105] (eq 12) obtained from **138** through a deconjugation step which has been extensively studied.[102,104,279]

Light and catalytic amounts of $K_2Cr_2O_7$ and Bu_4NBr in a water/methylene chloride mixture induced the oxidation of toluene by air to benzaldehyde with selectivity approaching 100%[280] (Table 12).

$K_2Cr_2O_7$ supported on alumina catalyzed the oxidation of diphenylmethane to benzophenone by air at 150 °C[281,282] (Table 12). Use of neutral alumina resulted in a more efficient catalyst than basic or acidic alumina, silica, charcoal, or montmorillonite. The rate of the reaction was enhanced by cosupporting very small amounts of $CoCl_2$. Several thousand turnovers with respect to chromium have been reached and the catalyst can be reused. The $K_2Cr_2O_7$/alumina/O_2 system has also been shown to catalytically oxidize benzyl alcohol to benzaldehyde and chlorodiphenylmethane to benzophenone.[281]

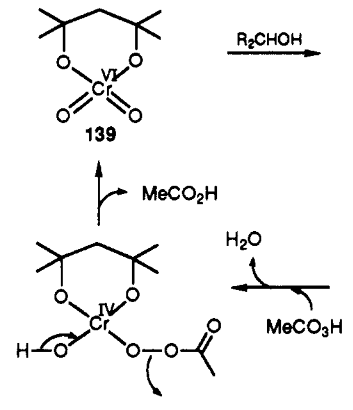
A mixture of $K_2Cr_2O_7$ and SiO_2 catalyzed the formation of small amounts of phenol from benzene under an air atmosphere. In using H_2O_2 instead of O_2, the yield was increased 100 times.[283]

4. Others

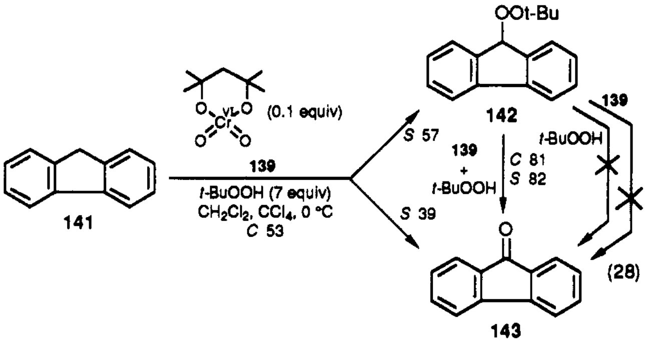
tert-Butyl chromate, (*t*-BuO)CrO_2(OH),[284] catalyzed the oxidation of cyclohexanol to cyclohexanone by an excess of cyclohexyl hydroperoxide with simultaneous complete decomposition of the hydroperoxide to cyclohexanol and cyclohexanone.[285]

A catalytic amount of the cyclic chromate ester $(OCMe_2CH_2CMe_2O)Cr^{VI}O_2$ (**139**) in conjunction with peroxyacetic acid oxidized saturated and unsaturated alcohols to ketones with good yields[286] (Tables 8, 9, and 17), and it was claimed that primary alcohols were oxidized to aldehydes (yields ≈ 80%) with this reagent mixture.[286] The catalytic cycle proposed involved the starting complex **139** as the real oxidative species (Scheme 17). The role of the ditertiary diol ligand could be in maintaining the reduced Cr^{IV}, arising from the alcohol oxidation process, in a soluble form, which allows its reoxidation to Cr^{VI}. *tert*-Butyl hydroperoxide[286,287] and hydrogen peroxide[286] were found to be ineffective in the regeneration of the catalyst from the reduced Cr intermediate. In contrast, efficient benzylic oxidations were achieved using **139** and an excess of anhydrous *t*-BuOOH[287] (Tables 3, 4, 12, and 22). The simultaneous formation of small amounts of *tert*-butylperoxy compounds, beside the aromatic ketones, was

SCHEME 17

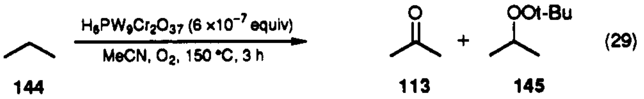


noted in a few cases and particularly from fluorene (eq 28). The 9-*tert*-butylperoxyfluorene was unchanged



in a solution of either **139** or *t*-BuOOH but was transformed to fluorenone in the presence of both **139** and *t*-BuOOH. Thus, *tert*-butylperoxy derivatives of the aromatic hydrocarbon could be the intermediates leading to ketones. From these results, it appears that the $(OCMe_2CH_2CMe_2O)Cr^{VI}O_2$-catalyzed oxidations of alcohols with $MeCO_3H$ and benzylic carbons with *t*-BuOOH respectively involve different chromium intermediates. The intervention of a *tert*-butylperoxychromium(VI) complex and a mechanism similar to that of Scheme 14 is conceivable for the latter oxidations. Such interpretations of these benzylic oxidations have not postulated **140** as intermediate since it would be resistant to reoxidation by *t*-BuOOH.[286]

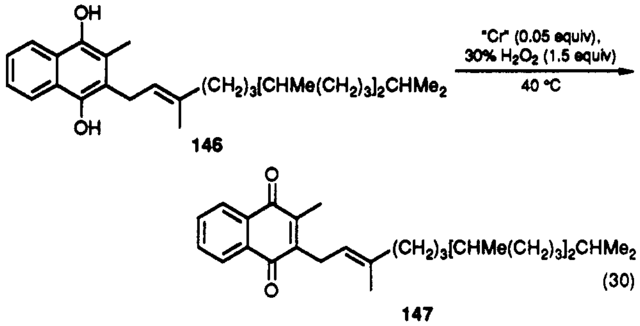
Polyoxometal salts and heteropoly acids containing chromium have been used to catalytically oxidize alkanes to ketones, acids, and esters (eq 29),[275,288] and methacrolein to methacrylic acid by oxygen.[289] The



T 4473 *S* 68 32 ref 288

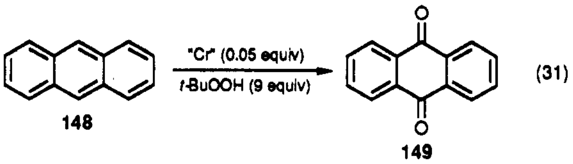
oxidative amination of *o*-chlorotoluene to *o*-chlorobenzonitrile has been carried out under an NH_3/O_2 atmosphere using a mixture of catalysts partly containing Cr^{VI}.[290]

Bis(tributyltin oxide) dioxochromium(VI), easily prepared from CrO_3 and $(Bu_3SnO)_2$,[163] was inefficient in inducing the autooxidation of cyclohexane[266] but catalyzed the oxidation of 1,4-hydroquinones and 1,4-naphthalenediols to the corresponding quinones[291] with 30% aqueous H_2O_2 in yields much higher than with other Cr compounds: $(Bu_3SnO)_2CrO_2 \gg CrCl_3 \gg Cr(acac)_3 > CrO_3$[163] (eq 14). The value of this process has been illustrated by the oxidation of dihydrovitamin K_1 (**146**) to vitamin K_1 (**147**) without affecting the exocyclic double bond (eq 30). The adsorbtion of $(Bu_3SnO)_2CrO_2$



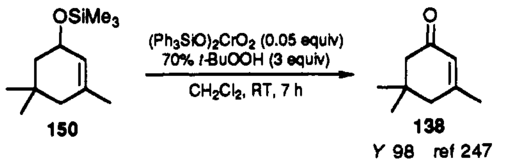
	C	*Y*	ref 163
$(Bu_3SnO)_2CrO_2$, 15 min	100	81	
$(Bu_3SnO)_2CrO_2$/charcoal, 90 min	100	97	
recovered $(Bu_3SnO)_2CrO_2$/charcoal, 90 min	100	95	

on charcoal increased the yield of **147** and furthermore allowed the recovery of the catalyst which could be used repeatedly. It was considered that the process kept the catalyst in the chromium(VI) state and involved peroxochromium compounds. The $(Bu_3SnO)_2CrO_2/H_2O_2$ system gave very low yields when used for the oxygenation of alkanes, arylalkanes, and olefins[226,227] (Tables 1, 13, and 20). A change from 30% H_2O_2 to 70% *t*-BuOOH or better to anhydrous *t*-BuOOH provided a dramatic improvement in these oxidations.[227] The comparison of the CrO_3/*t*-BuOOH and $(Bu_3SnO)_2CrO_2$/*t*-BuOOH systems has been made for oxidations of benzylic alcohols, benzylic, allylic, propargylic, aromatic, or saturated carbons. Except for propargylic oxidations, yields were generally superior when using the latter procedure (Tables 2, 4, 8, and 19–21 and eq 31)[227,292] but in contrast to the CrO_3/*t*-BuOOH method where room temperature is employed, the reaction must be carried out at 40–60 °C. The fact that similar ratios of **21**/**22** are obtained from the oxidation of 6-methoxy-1,2,3,4-tetrahydronaphthalene by *t*-BuOOH using catalytic amounts of CrO_3, $(OCMe_2CH_2CMe_2O)Cr^{VI}O_2$, or $(Bu_3SnO)_2CrO_2$ (Table 4) suggests that analogous mechanisms occur for these three procedures. In contrast, the mechanisms must be very different from that for the $Cr(CO)_6$/*t*-BuOOH system which furnished only **21** (Table 4).



	C	*Y*	
CrO_3, $ClCH_2CH_2Cl$–PhH, RT, 48 h	98	59	ref 239
$(Bu_3SnO)_2CrO_2$, $ClCH_2CH_2Cl$, 80 °C, 19 h	100	95	ref 227

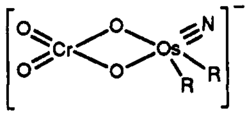
Bis(triphenylsilyl) chromate, easily prepared from CrO_3 and Ph_3SiOH,[293,294] efficiently catalyzed the one-pot oxidation of benzylic and allylic trimethylsilyl ethers with aqueous 70% *t*-BuOOH: secondary ethers led selectively to ketones while a primary benzylic ether led to a mixture of the corresponding aldehyde and carboxylic acid (Table 23 and eq 32).[247] $(Ph_3SiO)_2CrO_2$ as catalyst produced higher selectivities and reaction rates than CrO_3. The oxidation of **126** to **127** involves



(32)

at least in part the formation of the corresponding alcohol as an intermediate.[214] Under similar conditions, benzylic *t*-butyldimethyl-, triphenyl-, and thexyldimethylsilyl ethers were much less reactive, and the main reaction of saturated trimethylsilyl ethers was simply their deprotection.[247]

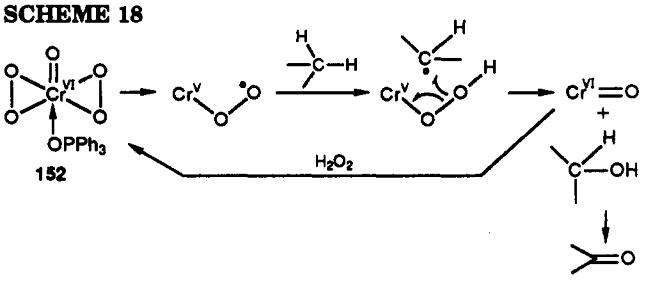
Two other heterobimetallic catalysts, *cis*-$[NBu_4][Os(N)(CH_2SiMe_3)_2(CrO_4)]$ (**151a**) and *cis*-$[PPh_4][Os(N)Me_2(CrO_4)]$ (**151b**) have been introduced to promote the oxidation of both saturated and unsaturated primary and secondary alcohols to the corresponding carbonyl compounds in air at 70 °C.[276] The reaction is highly chemoselective: olefins, amines, and ethers were not affected and overoxidation of aldehydes was not observed (Tables 8 and 17). The turnover number can be increased by the addition of catalytic amounts of $Cu(OAc)_2$ and the rate is dependent on the nature of both catalyst and alcohol. **151b** is more reactive than **151a** and the reactivity of alcohols follows the order: benzylic and allylic > primary > secondary. Molecular oxygen, which is required as secondary oxidant in order for the process to be catalytic is converted to water, which then decomposes the osmium chromate complexes under the reaction conditions, and therefore limit the efficiency of the process.[276]



151a: R = CH_2SiMe_3
b: R = Me

All the previously described catalysts are oxochromium(VI) complexes with no peroxo group in their initial form. However, an oxodiperoxochromium(VI) compound, $(Ph_3PO)O{=}Cr(O_2)_2$ (**152**), seemed to present some possibilities for catalytic oxidation.[221] Initially, **152** was added to an excess of cyclohexene **33** diluted in a mixture of methylene chloride and *tert*-butyl alcohol. When **152** was completely transformed by reduction with **33**, addition of 70% H_2O_2 regenerated an active Cr species, possibly the starting peroxo complex, and which was thus activated for further oxidation of **33**. Under these conditions, preferential allylic oxidation to **36a** and mostly **35** was observed rather than epoxidation (Table 6). The oxygen transfer to the allylic carbon would imply principally the involvement of a peroxo group of **152** and the radical abstraction of a hydrogen (Scheme 18). However, the promoting role of *t*-BuOH remains obscure, possibly coordinating to the metal. Although the turnover number reported was inferior to four, preliminary experiments have shown that the regeneration of the catalyst by H_2O_2 could be repeated several times.[221]

SCHEME 18



VII. Conclusion

The studies devoted to oxidations catalyzed by chromium have proved to be more numerous than we initially suspected when we embarked upon this review. Our original project is only partially complete because of the following problems. Firstly, a great deal of the work is published in patents or in the Russian literature which are not always clear and/or easily available. Secondly, some catalytic chromium oxidations are hidden in papers describing other catalytic methods. Consequently, part of the literature described in the present review has come directly from the corresponding *Chemical Abstracts* and valuable studies have possibly been missed or are badly reported. I apologize to the authors concerned and also to my readers for these omissions. Thirdly, the overall oxygenation for a definite process cannot be discussed as a simple sequence of successive reactions with some branching. On the contrary, the overall oxygenation generally involves many reaction pathways which are very sensitive to small modifications of reaction conditions. Therefore, the mechanisms indicated in this review are often highly speculative. Fourthly, the catalytic oxidations have been carried out using a plethora of experimental conditions and furthermore, different purposes have often been sought in these studies; the comparison of results is therefore not always straightforward.

The oxygen sources most employed are generally the least expensive: air, oxygen, hydrogen peroxide, or *tert*-butyl hydroperoxide.

In many examples, the reaction with oxygen, does not really involve catalysis, the metal is rather an initiator of a radical chain reaction leading primarily to peroxy derivatives of the substrate. However, the evolution of these peroxides can be catalyzed by chromium through a pathway referred to as the Haber–Weiss mechanism.

The oxidations by hydroperoxides depend on their nature, the ligands around the metal, and the oxidation state of the chromium. Hydrogen peroxide can give peroxochromium $Cr(O_2)_2$ while *tert*-butyl hydroperoxide could lead to *tert*-butylperoxychromium CrOOt-Bu. The ligands can modify the acidity of the chromium and stabilize complexes with the oxygen source. Chromium(III) gives preferentially oxochromium Cr=O while chromium(VI) produces $Cr(O_2)$ or eventually CrOO*t*-Bu. As with oxygen, radical reaction pathways can be involved, in some cases, for oxidations in the presence of hydroperoxides. Besides, all oxidation states of chromium[295] are able to react with peroxides whose unproductive decomposition can compete with the oxidation of the substrate.

Due principally to cost considerations and in spite of the lack of selectivity associated with radical reactions, oxygen is most often used in industry, fair selectivity being obtained by limiting the conversion of the substrate to a low level. Hydroperoxides and particularly *tert*-butyl hydroperoxide are preferred mainly for smaller scale reactions and when high or full conversion of the starting material is desired.

VIII. Abbreviations and Glossary

In the tables, the ratios of starting material/oxidant/catalyst have been indicated in brackets in this order [SM/O/M]. When SM is used as the solvent, the SM part has been represented by ∞. When the oxidant is oxygen or air, the ratio has been indicated by [SM/∞/M].

auto-oxidation	oxidation with molecular oxygen
Avicel	microcrystalline form of cellulose
acac	acetylacetonate(−1)
BPCC	bipyridinium chlorochromate
C	conversion %
2,6-Cl-P	*meso*-tetrakis(2,6-dichlorophenyl)-porphyrinate(−2)
DMA	dimethylacetamide
DMF	dimethylformamide
equiv	equivalent, calculated on the amount of SM
ESR	electron spin resonance
EXAFS	extended X-ray absorption fine structure
M	catalyst
m-salen	8,8,8′,8′-tetramethylsalen
NAFK	Nafion 511, registered trademark of E.I. du Pont de Nemours & Co, is the potassium salt of a perfluorinated resin sulfonic acid
naph	naphthenate
naphthenate	chromium(III) naphthenate does not have a definitive formula. It is the chromic salt of naphthenic acid which itself is a mixture of saturated organic acids ($C_nH_{2n-2}O_2$)[296]
O	oxidant
octoate	2-ethylhexanoate[146]
P	any porphyrinate(−2)
PCC	pyridinium chlorochromate
PDC	pyridinium dichromate
PFC	pyridinium fluorochromate
PrCC	pyrazinium chlorochromate
PrDC	pyrazinium dichromate
PtCC	phthalazinium chlorochromate
PtDC	phthalazinium dichromate
R	ratio of the formed products
RT	room temperature
S	selectivity % = yield % calculated on the amount of SM consumed
salen	1,2-bis(salicylideneamino)ethane(−2)
salen	any substituted or unsubstituted 1,2-bis(salicylideneamino)ethane(−2)
SM	starting material
st	stearate
T	turnover number = number of moles of product per mole of catalyst
TPP	*meso*-tetraphenylporphyrinate(−2)
Tf	triflate, O_2SCF_3
TTP	*meso*-tetrakis(*p*-tolyl)porphyrinate(−2)
TFPP	*meso*-tetrakis(pentafluorophenyl)-porphyrinate(−2)
TsOH	*p*-toluenesulfonic acid
Y	yield % calculated on the amount of starting material introduced, Y = C × S
Y/O	yield % calculated on the amount of oxidant
YO	oxygen source

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Addendum

Methane oxidation at 500–700 °C has been carried out in the presence of Cr_2O_3 impregnated on mordenites.[297] Cyclohexanol dehydrogenation has been induced by copper–chromium catalysts.[298] A new process for the preparation of chromium(III) naphthenate used to autooxidize cyclohexane has been proposed.[299] It has been briefly reported that Cr(TPP)Cl catalyzes the epoxidation of respectively styrene by NaOCl,[300] and cyclohexene by $KHSO_5$,[301] both with low efficiency.

Registry No. Cr, 7440-47-3.

X. References and Notes

*The references followed by a superscript asterisk correspond to publications where the exact nature or the oxidation state of the chromium catalyst used was not clearly established from reading either the original paper or the summary of *Chemical Abstracts* (in the case of unavailable literature).

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