Homogeneous Cr^{VI}-Catalyzed Benzylic, Allylic and Propargylic Oxidations by *tert*-Butyl Hydroperoxide

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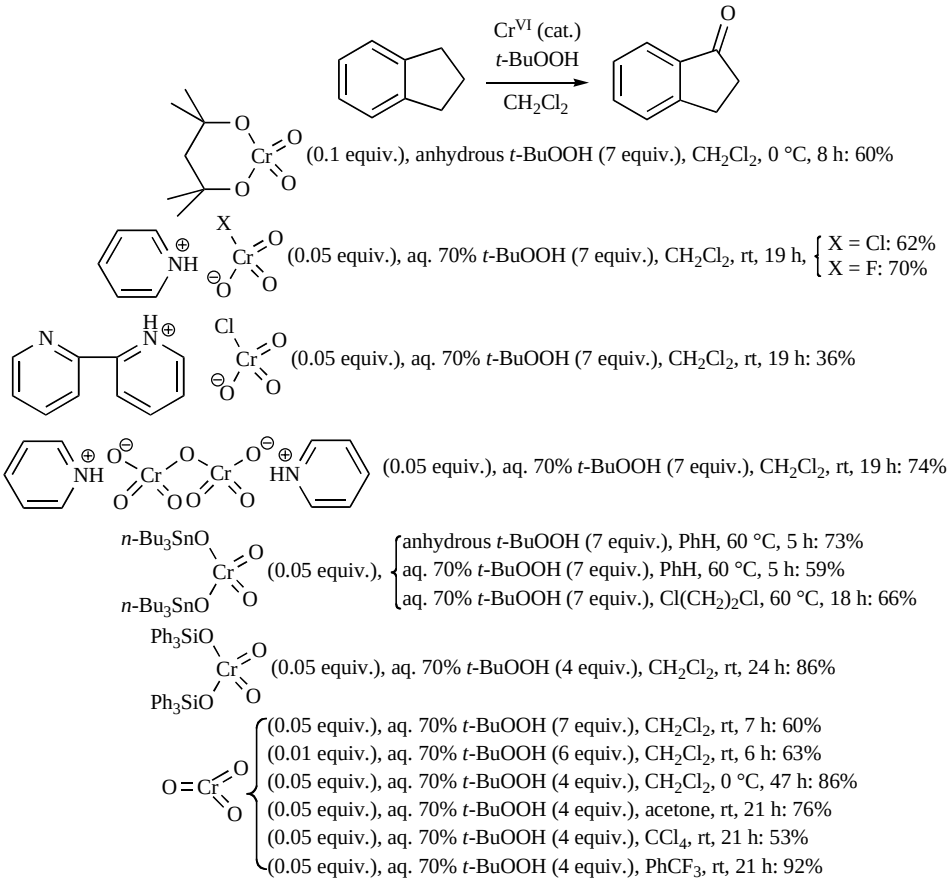
Abstract: Environmental factors urge to use catalytic rather than stoichiometric oxidation methods. Over the last thirty years, we have reported a large panel of Cr-catalyzed oxidations. This mini-review concerns the benzylic, allylic and propargylic oxidations using Cr^{VI} catalysts and *t*-BuOOH under homogeneous conditions, and summarizes our results and those of the literature.

This review is dedicated to E.J. Corey on the occasion of his 80th birthday.

Keywords: Chromium oxides, *tert*-butyl hydroperoxide, catalysis, benzylic oxidation, allylic oxidation, propargylic oxidation, mechanism.

1. INTRODUCTION

Our involvement in metal-catalyzed oxidations has been initiated by the discovery, in 1980, of the photochemical aerobic oxidation of η^3-allylpalladium complexes into α,β-unsaturated carbonyl compounds [1]. Studies on the mechanism of this reaction [2] and the research for catalytic procedures [3] led us to observe Pd-catalyzed allylic oxidations by *tert*-butyl hydroperoxide [4]. The almost simultaneous Corey report [5] of the oxidation of alcohols by peroxyacetic acid in the presence of catalytic amounts of $(OCMe_2CH_2CMe_2O)Cr^{VI}O_2$ urged us to use this homemade-prepared complex. This has led us to a fruitful journey with Cr-catalyzed oxidations. Indeed, we have disclosed conditions for Cr-catalyzed oxidations of alcohols [6-13], phenols [14], silyl ethers [15], C=C bonds [10,16,17], activated methylenes [8,11-13,17-28], anthracene [13], 1,3-diphenylisobenzofuran [29] and alkanes [13,30,31]. Three reviews, published in 1992, 1993 and 1995 respectively, contain some of these results [32-34].



Scheme 1.

The present mini-review is devoted to the Cr^{VI}-catalyzed benzylic, allylic and propargylic oxidations by *t*-BuOOH that are carried out under homogeneous conditions [35,36]. In the last section, we will discuss the interactions between CrO_3 and *t*-BuOOH, and the possible mechanisms.

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2. BENZYLIC OXIDATIONS

The oxidation of benzylic methylenes has been our first Cr-catalyzed reaction. Initially, we used Corey's catalyst, i.e. $(OCMe_2$

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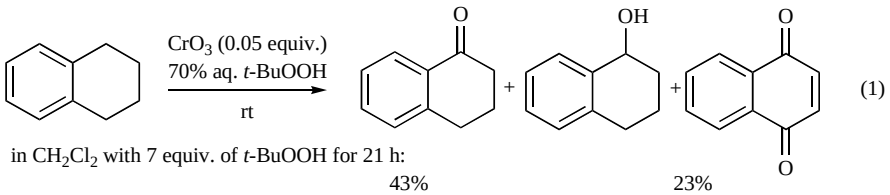
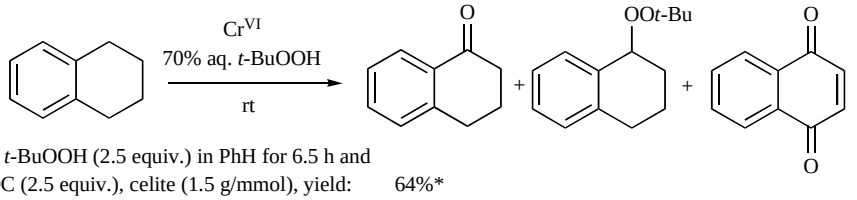


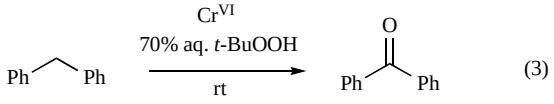
(1)

in CH_2Cl_2 with 7 equiv. of *t*-BuOOH for 21 h:
43% 23%
in $PhCF_3$ with 4 equiv. of *t*-BuOOH for 16 h:
77% 18% 0%



(2)

using *t*-BuOOH (2.5 equiv.) in PhH for 6.5 h and
PDC (2.5 equiv.), celite (1.5 g/mmol), yield: 64%*
using *t*-BuOOH (7 equiv.) in PhH for 22 h and
PDC (0.1 equiv.), conversion: nd, yields: 54%
using *t*-BuOOH (4 equiv.) in CH_2Cl_2 for 4 h and
PDC (0.01 equiv.), conversion: 76%, yields: 48% 5% 0%
or PDC (0.1 equiv.): conversion: 85%, yields: 74% 1% 8%
using *t*-BuOOH (4 equiv.) in CH_2Cl_2 for 24 h and
$(Ph_3SiO)_2CrO_2$ (0.05 equiv.), conversion: 100%,
yields: 88% 9%
*Chandrasekaran's result [37]



(3)

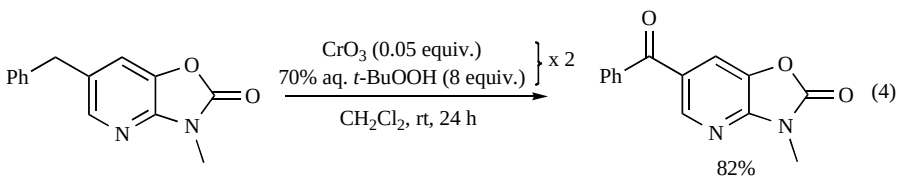
in PhH, PDC (4 equiv.), *t*-BuOOH (4 equiv.), celite (1.2 g/mmol), 14 h
conversion: 77%, yield: 56%*
in CH_2Cl_2:
- CrO_3 (0.05 equiv.), *t*-BuOOH (7 equiv.), 20 h
  conversion: 67%, yield: 53%
- [CrO_3 (0.05 equiv.), *t*-BuOOH (7 equiv.), 21-22 h] x 2
  conversion: 100%, yield: 90%
- $(Ph_3SiO)_2CrO_2$ (0.05 equiv.), *t*-BuOOH (4 equiv.), 24 h
  conversion: 83%, yield: 79%

*Chandrasekaran's result [37]

$CH_2CMe_2O)CrO_2$, and anhydrous *t*-BuOOH [18]. Subsequently, we disclosed that easier experimental conditions, i.e. CrO_3 and aqueous *t*-BuOOH, both commercial and cheap, were also effective [19]. The reactions were usually carried out at room temperature in CH_2Cl_2 under air atmosphere; CrO_3 is almost insoluble in this solvent but the addition of *t*-BuOOH mediates its immediate dissolution leading to a deep purple color of the mixture. With indan as the substrate, we tested a panel of Cr^{VI} catalysts and solvents at various temperatures using various quantities of reagents; some results are depicted in Scheme **1** [13,18,20,21]. With CrO_3, methylene chloride is usually the most convenient solvent, but some substrates provide increased yields and selectivities in benzotrifluoride (trifluoromethylbenzene) (Scheme **1** and Eq. 1) [11].

Subsequently to our first report, Chidambaram and Chandrasekaran described benzylic oxidations using over-stoichiometric amounts of pyridinium dichromate and *t*-BuOOH in benzene [37,38]. We have observed that the use of an excess of *t*-BuOOH in CH_2Cl_2 together with sub-stoichiometric amounts of various Cr^{VI} species, including PDC, can afford higher yields (Eqs. 2 and 3) [20, 21].

Our CrO_3/*t*-BuOOH procedure has been used by Viaud *et al.* for the efficient oxidation of the benzylic methylene of 6-benzyl-3-methyloxazolo[4,5-*b*]pyridine-2-(3*H*)-one, 6-benzyl-2-phenyloxazolo [4,5-*b*]pyridine and 6-benzyl-2-(benzyloxy)oxazolo [4,5-*b*]pyridine (Eqs 4 and 5) [39]. The complete consumption of these substrates required a second batch of the oxidation system when the color of the reaction mixture became yellow. The catalytic CrO_3/*t*-BuOOH system affords selectively 1-*t*-butylperoxy-5,8-dimethoxy-3-methylisochromane from 5,8-dimethoxy-3-methylisochromane (Eq. 6) [40], while methyl 5-benzyl-1-methyl-4-nitro-1*H*-pyrrole-2-carboxylate is reluctant to react (Eq. 7) [41]. A low efficiency of catalytic Cr^{VI}/*t*-



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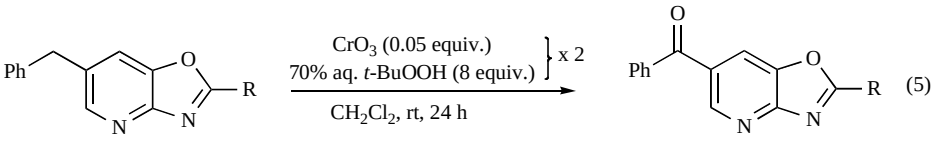
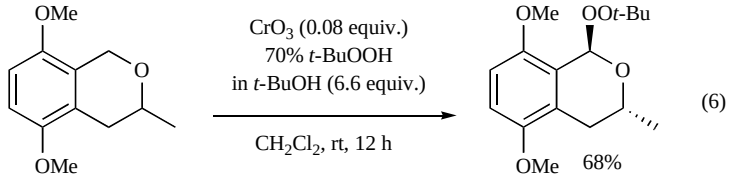


(5)

R = Ph (72%), OCH_2Ph (> 66%)



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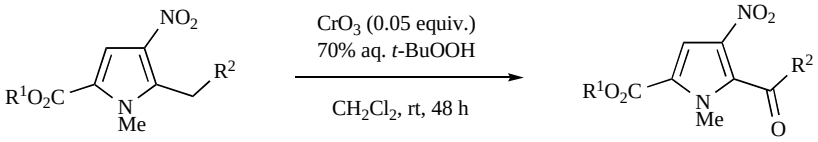
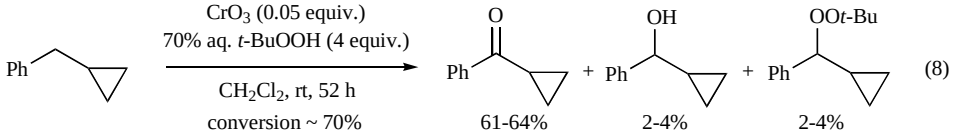


(7)

R^1 = Et, R^2 = H: complex mixture

R^1 = Me, R^2 = Ph: 15% + large amounts of the starting substrate



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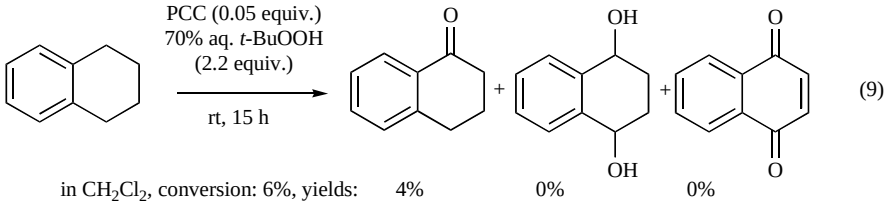
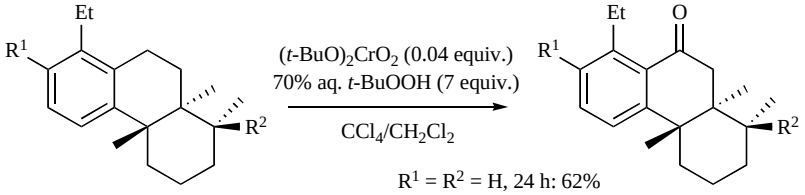


(9)

in CH_2Cl_2, conversion: 6%, yields:	4%	0%	0%
in DMF, conversion: 5%, yields:	3%	0%	0%
in *t*-BuOH, conversion: 70%, yields:	53%	4%	1%
in MeCN, conversion: 62%, yields:	53%	3%	0%
in PhH, conversion: 71%, yields:	61%	4%	2%



(10)

$R^1 = R^2$ = H, 24 h: 62%

R^1 = Me, $R^2 = CO_2Me$, 24 h: 70%

$R^1 = CO_2Me$, R^2 = Me, 48 h: 49%

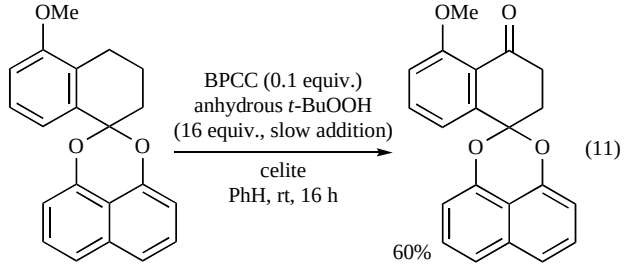
BuOOH systems (Cr^{VI} = CrO_3, PDC) has also been observed for the oxidation of the benzylic methylene of 17β-estradiol diacetate [42].

The reactivity of benzylcyclopropane under oxidative conditions has been a matter of studies [43]. When we subjected this substrate to our CrO_3/*t*-BuOOH procedure, cyclopropylphenylketone was the main isolated compound and we did not observe the cleavage of the cyclopropyl ring (Eq. 8) [24]. Under similar conditions, allylbenzene afforded a mixture of 1-phenylprop-2-en-1-one and cinnamaldehyde in low yields [25].

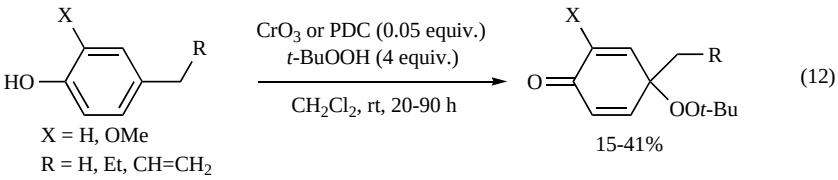
Antunes *et al.* have examined the pyridinium chlorochromate-catalyzed oxidation of tetralin by *t*-BuOOH in different solvents [44]. Surprisingly, CH_2Cl_2 was one of the worst solvent under their conditions (Eq. 9). With *t*-butyl chromate as the catalyst, these authors have selectively and effectively oxidized the intracyclic benzylic methylene of the substrates shown in Eq. 10 [45].

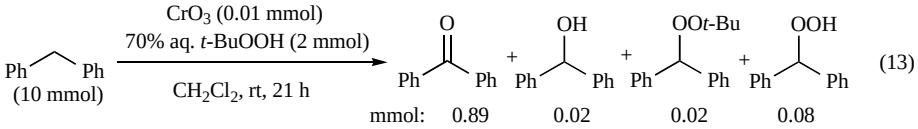
While the catalytic oxidation of indan with bipyridinium chlorochromate and aq. *t*-BuOOH in CH_2Cl_2 provided 1-indanone in a low yield (Scheme **1**), the benzylic oxidation of the substrate shown in Eq. 11 occurred efficiently, using the same catalyst, with anhydrous *t*-BuOOH and celite in benzene [46,47].

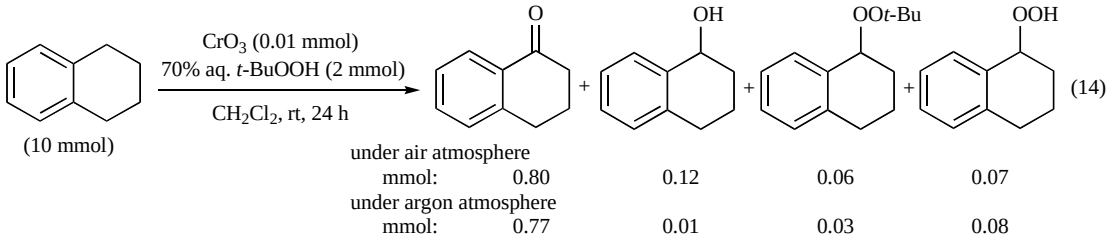
We have examined the oxidation of *para*-substituted phenols (eugenol, 2-methoxy-4-propylphenol, *p*-cresol) using *t*-BuOOH and catalytic amounts of CrO_3 or PDC: the main products were the corresponding 4-(*t*-butylperoxy)-cyclohexa-2,5-dienones (Eq. 12) [14,48].

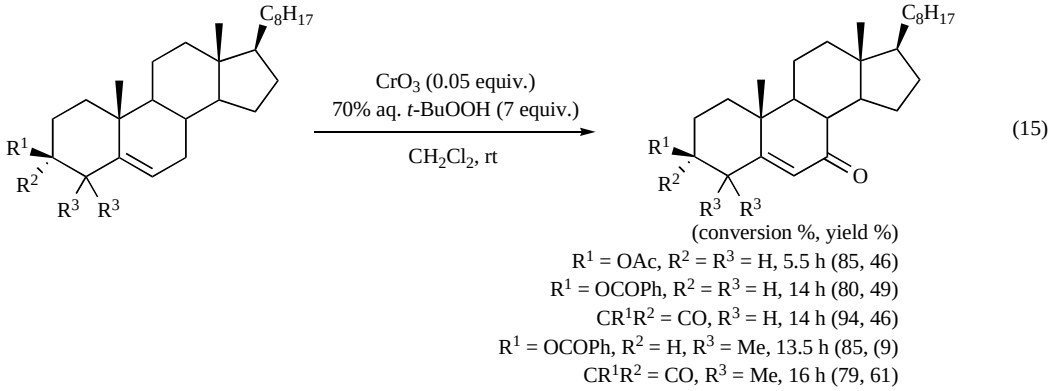


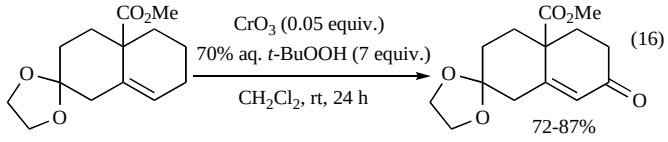
(11)

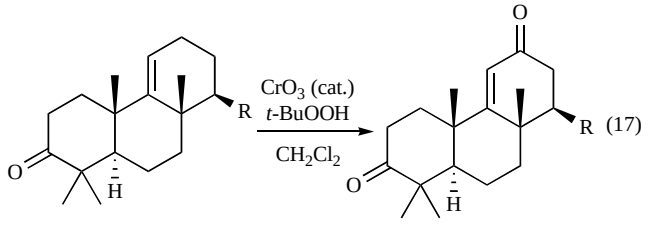


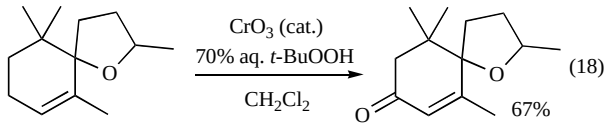










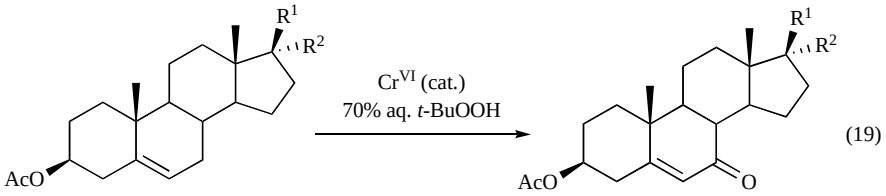


Owing to the simultaneous non-productive decomposition of *t*-BuOOH induced by chromium [49,50], an excess of this oxygen source was used, in all above summarized studies, to ensure high or full conversion of the substrate. To determine if an efficient transfer of oxygen from *t*-BuOOH to the substrate could occur, reactions have also been carried out using excesses of the benzylic compounds [22,23]. Since two equivalents of *t*-BuOOH are required to ketonize a methylene group, the results shown in Eqs 13 and 14 indicate a quasi-quantitative transfer of one oxygen atom from *t*-BuOOH to the benzylic methylene groups. The yields were slightly decreased for a reaction carried out under an argon atmosphere instead of air (Eq. 14). Using a 3:0.9 ratio of substrate/*t*-BuOOH and cetyltrimethylamonium chlorochromate in PhH at 80 °C instead of 5:1 ratio and CrO_3 in CH_2Cl_2 at room temperature (as reported in Eq. 13 [23]) for the oxidation of diphenylmethane, Agarwal *et al.* have only depicted the formation of benzophenone [51].

3. ALLYLIC OXIDATIONS

3.1. MONOALKENES

In 1987, we reported that the CrO_3/*t*-BuOOH/CH_2Cl_2 system induces the allylic oxidation of Δ^5-steroids with fair selectivities (Eq. 15) [25]. This procedure has been used by the teams of d'Angelo (Eq. 16) [52], Gribble (Eq. 17) [53,54] and Young (Eq. 18) [55] for the efficient and regioselective oxidation of polycyclic substrates. Recently, we have disclosed improved conditions for the allylic oxidation of Δ^5-steroids: PDC or the association of CrO_3 with an amine as the catalyst in CH_2Cl_2 or $PhCF_3$ leads, in most cases, to better yields (Eq. 19) [26]. Nevertheless, optimum yields in the 7-keto-Δ^5-steroids required fitting experimental conditions for each substrate. As previously [25], a minor reaction pathway was the epoxidation of the C=C bond [56]. Another catalyst, disclosed by Antunes *et al.*, for the allylic oxidation of cholesteryl acetate (Eq. 19) and other polycyclic alkenes is *t*-butyl chromate [45].



(19)

(conversion %, yield %)

CrO_3 (0.05 equiv.), *N*-methylimidazole (0.1 equiv.), *t*-BuOOH (7 equiv.), $PhCF_3$, 40 °C, 23 h

$R^1 = C_8H_{17}$, R^2 = H (100, 74); R^1 = COMe, R^2 = H (100, 81);

R^1 = NHAc, R^2 = H (100, 84); CR^1R^2 = CO (100, 83)

PDC (0.1 equiv.), *t*-BuOOH (7 equiv.), CH_2Cl_2, rt, 24 h

$R^1 = C_8H_{17}$, R^2 = H (95, 74); R^1 = COMe, R^2 = H (89, 71);

R^1 = NHAc, R^2 = H (85, 70); CR^1R^2 = CO (80, 60)

PDC (0.1 equiv.), *t*-BuOOH (4 equiv.), $PhCF_3$, rt, 72 h

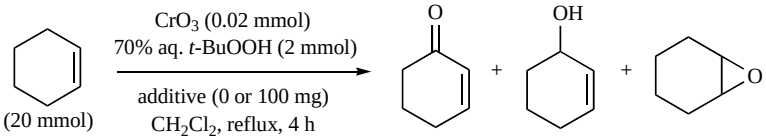
$R^1 = C_8H_{17}$, R^2 = H (91, 76); R^1 = COMe, R^2 = H (94, 80);

R^1 = NHAc, R^2 = H (91, 80); CR^1R^2 = CO (95, 82)

$(t\text{-BuO})_2CrO_2$ (0.04 equiv.), *t*-BuOOH (7 equiv.), CH_2Cl_2/CCl_4, rt, 24 h

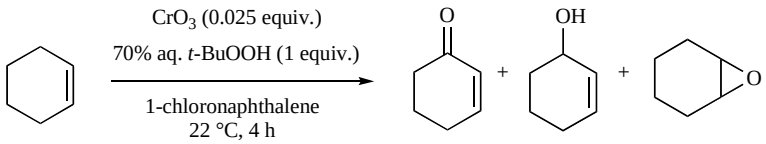
$R^1 = C_8H_{17}$, R^2 = H (nd, 50)*

*Antunes result [45]



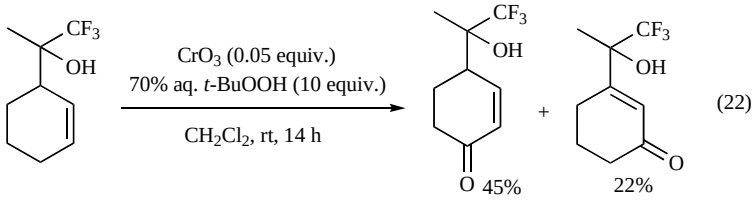
(20)

without additive, mmol:	0.281	0.007	0.021
with $NaHCO_3$, mmol:	0.131	0.0005	0.032
with pyridine, mmol:	0.05	0.008	0



(21)

conversion: 48%, yields: 35% traces 8%



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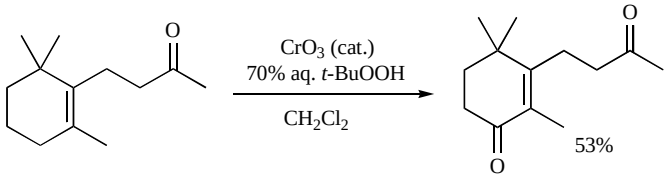

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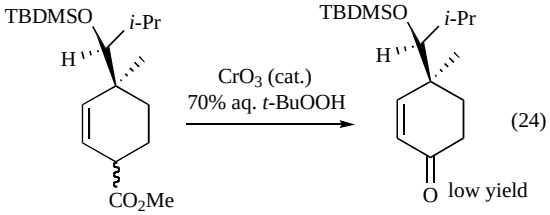
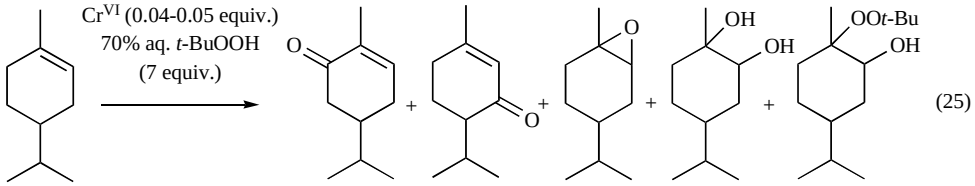


(24)

The reactivity of catalytic CrO_3/*t*-BuOOH mixtures towards monocyclic alkenes has also been studied. Agarwal *et al.* have oxidized cyclohexene in the presence of different additives [57] and using different solvents [58], CH_2Cl_2 and PhH were superior to MeCN and Me_2CO while additives decreased the activity (Eq. 20) [59]. Instead of an excess of cyclohexene (Eq. 20), Sasson *et al.* have used a 1:1 ratio of substrate/*t*-BuOOH; the main product was also 2-cyclohexenone (Eq. 21) [50]. Kumadaki *et al.* have obtained a mixture of two unsaturated ketones in 67% yield from 2-(cyclohex-2-enyl)-1,1,1-trifluoropropan-2-ol (Eq. 22) [60]. The oxidation of β-ionone occurred regioselectively at the level of the intracyclic methylene (Eq. 23) [55]. An oxidative decarboxylation has been reported by Renard and Lallemand (Eq. 24) [61].



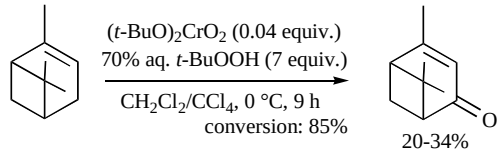
(25)

PCC, PhH, rt, 15 h, conversion: 71%

17% 12% 12% 1%

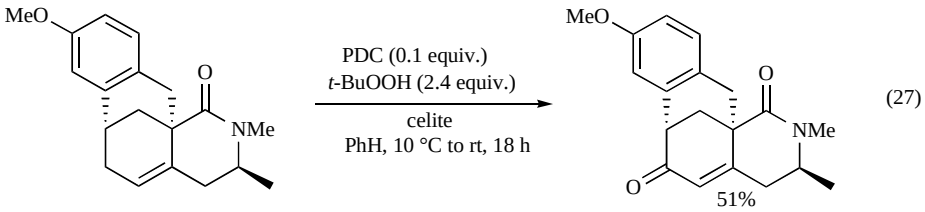
(t-BuO)$_2$CrO$_2$, CH_2Cl_2/CCl_4, 0 °C, 4 h, conversion: 100%

5-7% 8-32% 28-29% 0-3%



(26)

and 26). The catalytic oxidation of α-pinene has also been examined with PDC [63]. In the presence of celite, Schultz *et al.* carried out, in fair yield, the PDC-catalyzed allylic oxidation of the multifunctionalized substrate shown in Eq. 27 [64,65]. Another catalyst, (Me_3SiO)$_2$CrO$_3$, has been mentioned for the allylic oxidation of cy-



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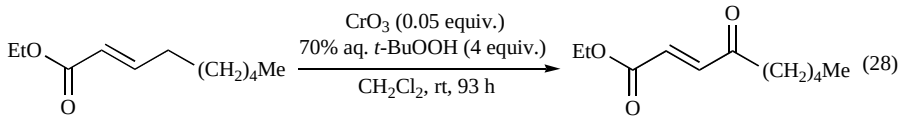
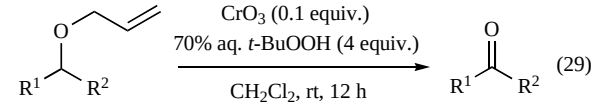


(28)

conversion: 65%
selectivity: 68%

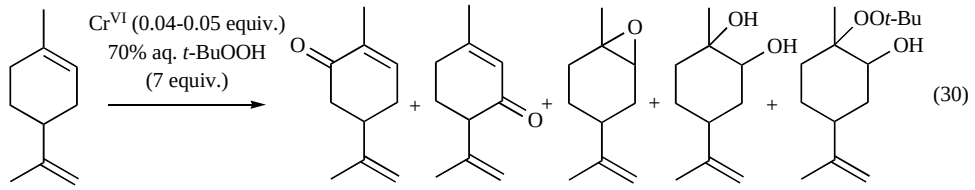


(29)

R^1 and R^2 = alkyl or aryl

55-77%

cloalkenes by *t*-BuOOH [66]. Agarwal *et al.* have used CTACC to catalyze the oxidation of cyclohexene, 1-phenylcyclohexene, cholesteryl acetate and monoterpenes: cyclohexene led to a mixture of cyclohexene oxide, 2-cyclohexen-1-ol and 2-cyclohexen-1-one while



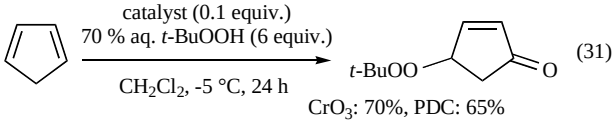
(30)

PCC, MeCN, rt, 15 h, conversion: 64%

25% 4% 5% 5%

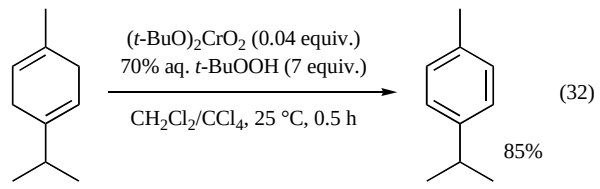
(t-BuO)$_2$CrO$_2$, CH_2Cl_2/CCl_4, 0 °C, 6 h, conversion: 100%

4-12% 18-43% 9-12% 0-4%



(31)

CrO_3: 70%, PDC: 65%



(32)

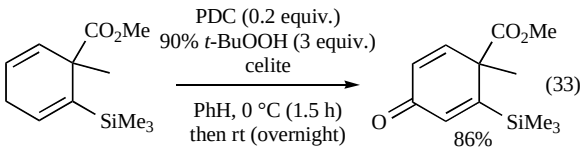
With PCC [44] or (t-BuO)$_2$CrO$_2$ [62] as the catalyst, the oxidation of cyclohexene and terpenes led to mixtures of compounds (Eqs 25

the allylic oxidation seems to proceed with a good selectivity from the other substrates; these experiments were however carried out with a 3:0.9 ratio of substrate/*t*-BuOOH [51,67].

While the use of the catalytic CrO_3/*t*-BuOOH/CH_2Cl_2 procedure yielded a number of compounds from acyclic compounds such as allylbenzene and 1-eicosene [25], this method leads to the fair allylic ketonization of the C=C bond of ethyl non-2-enoate (Eq. 28) [32]. Under similar conditions, allyl ethers are cleaved, affording the corresponding carbonyl compounds (Eq. 29) [68].

3.2. DIENES

With PCC [44] as with (t-BuO)$_2$CrO$_2$ [62] as the catalyst, the reactivity of limonene was similar to that of *p*-menthene (Eq. 25) since



(33)

a mixture of compounds was produced, without apparent involvement of the exocyclic C=C bond (Eq. 30).

Under Cr^{VI} catalysis, cyclopentadiene afforded 4-(*t*-butylperoxy) cyclopent-2-enone (Eq. 31) [69,70], while ethyl 1,5-dimethyl-4-nitro-1*H*-pyrrole-2-carboxylate yielded a complex mixture (Eq. 7) [41].

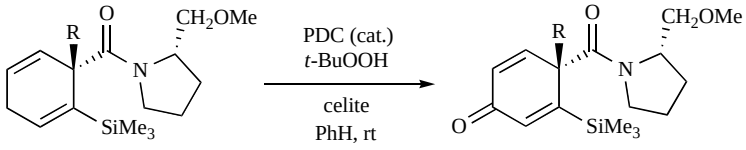
The $(t\text{-BuO})_2CrO_2$-catalyzed oxidation of γ-terpinene afforded *p*-cymene (Eq. 32) [62]. In contrast, bis-allylic oxidation of methyl 1-methyl-2-(trimethylsilyl)cyclohexa-2,5-dienecarboxylate occurred using *t*-BuOOH, celite and catalytic amounts of PDC, as disclosed in 1996 by Schultz and Antoulinakis (Eq. 33) [71]. Subsequently, Schultz team has carried out the bis-allylic oxidation of various 3-disubstituted-1,4-cyclohexadienes (Eqs 34 [72], 35 [73] and 36 [74]). As exemplified in Eq. 35, such a reaction pathway can be preferred to the benzylic oxidation [75]. Some oxidation at the level of a benzyl substituent can however occur since the procedure led to the aromatization of methyl 1-benzyl-3-phenylcyclohexa-2,5-dien-1-carboxylate (Eq. 37) [74,78].

4. PROPARGYLIC OXIDATIONS

The catalytic CrO_3/*t*-BuOOH system has been tested for the α-oxidation of alkynes. Better results were obtained with benzene as solvent and anhydrous *t*-BuOOH, than with CH_2Cl_2 and aq. *t*-BuOOH. Moreover, the yields were slightly increased with *p*-toluenesulfonic acid as additive. Under these conditions, the propargylic oxidation of an array of alkynes has been effectively carried out using a low amount of CrO_3 (Eq. 38) [27].

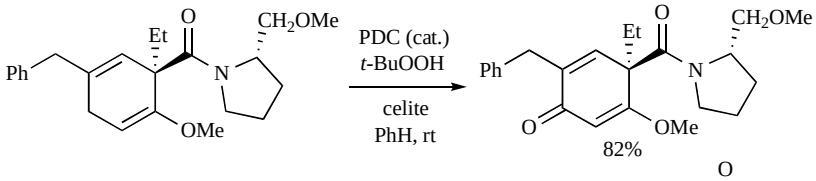
5. INTERACTIONS CRO_3/*T*-BUOOH, MECHANISMS

The addition of CH_2Cl_2 to CrO_3 led to its slight dissolution and to a light yellow color of the solution. As indicated at the beginning of this review, the addition of an excess of *t*-BuOOH to this heterogeneous mixture produced the instantaneous complete dissolution of CrO_3 leading to a deep purple color of the solution. In 1987, we postulated that the species thus formed was hydroxyl(*t*-butylperoxy)chromium complex $(t\text{-BuOO})(HO)CrO_2$ [6a] but, extensive UV and NMR studies using CH_2Cl_2 and CD_2Cl_2 respectively as the solvent, did not permit us its characterization, unreproducible results being obtained, even at low temperature [79]. Nevertheless, $(t\text{-BuOO})(HO)CrO_2$ has also been retained as the active oxidative species by Sasson *et al.* who have also carried out UV and NMR studies [50]. Subsequently, the comparison of the reactivity of the catalytic CrO_3/*t*-BuOOH and CrO_3/$PhCMe_2OOH$ systems towards the oxidation of allylic alcohols led us to demonstrate that the active chromium oxidative species of the former system contains the *t*-butyl moiety in its coordination sphere [6d]. This study, however, was not successful in determining whether the *t*-Bu is connected to chromium through an oxygen atom or a peroxo link, to give the *t*-BuOCr or *t*-BuOOCr unit respectively. Having observed that *t*-BuOOH is less prone to decomposition in

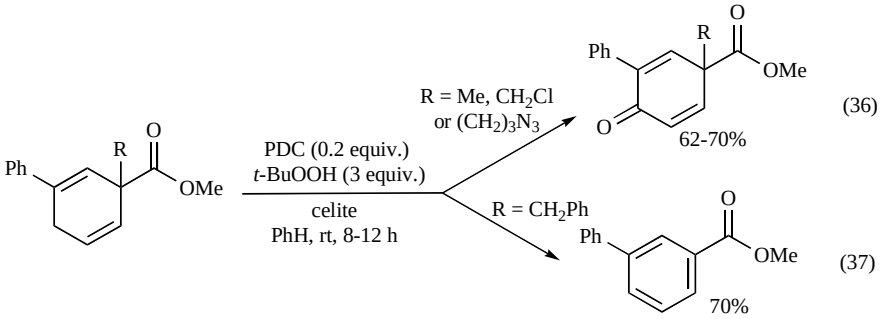


(34)

R = Me, Et, $CHMe_2$, CH_2Ph or $(CH_2)_2OAc$: 80-92%

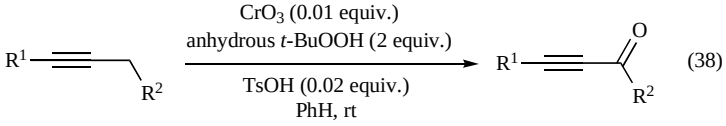


(35)



(36)

(37)



(38)

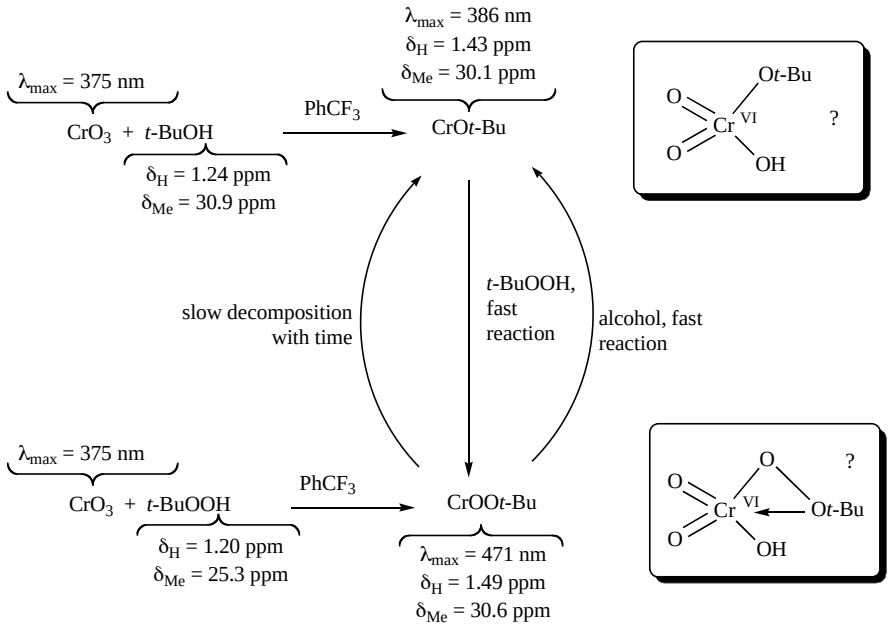
(conversion %, yield %)

R^1 = Ph, R^2 = $(CH_2)_2Me$, 66 h (78, 55)

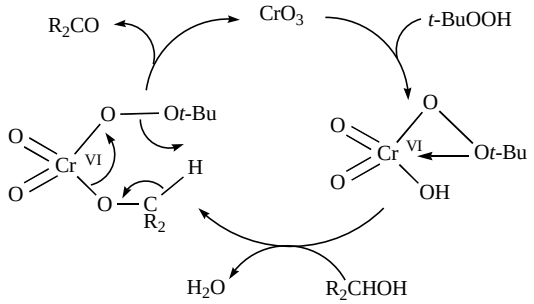
R^1 = Me, R^2 = $(CH_2)_5Me$, 46 h (67, 40)

R^1 = $(CH_2)_2Me$, R^2 = CH_2Me, 52 h (nd, 52)

R^1 = H, R^2 = $(CH_2)_8Me$, 72 h (38, 21)



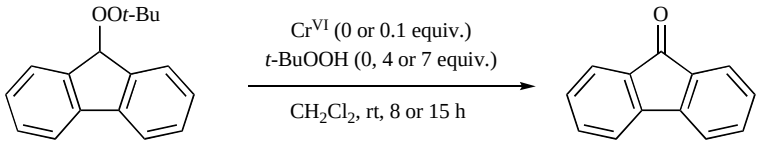
Scheme 2.



Scheme 3.

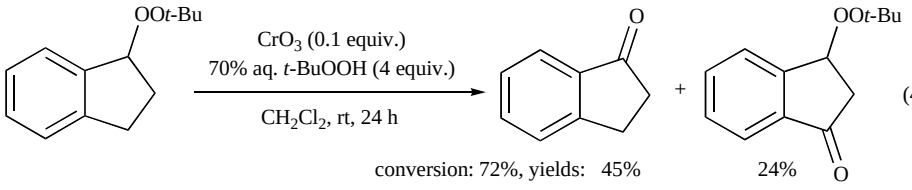
$PhCF_3$ than in CH_2Cl_2 [80], we carried out UV and NMR experiments in $PhCF_3$ using CrO_3 and various amounts of *t*-BuOH and *t*-BuOOH. Thus, reliable results have been obtained [81]. As depicted in Scheme **2**, the modifications of the UV, ^1H and ^{13}C NMR spectra induced by the addition of either *t*-BuOH or *t*-BuOOH to CrO_3 are strongly different. Given these spectra, we assumed the formation of *t*-BuOCr and *t*-BuOOCr units respectively. The most plausible corresponding complexes are (*t*-BuO)(HO)CrO_2 and (*t*-BuOO)(HO)CrO_2, but other *t*-butyloxy- and *t*-butylperoxy chromium species cannot been excluded, especially in the presence of increasing amounts of *t*-BuOH and *t*-BuOOH. The strong differences in the red shifts of λ_{max} induced by the addition of *t*-BuOH and *t*-BuOOH to CrO_3 suggest that both oxygen atoms of the *t*-BuOO ligand are simultaneously coordinated to chromium. Interestingly, we have observed that the addition of *t*-BuOOH to the *t*-BuOCr complex led to the formation of the *t*-BuOOCr complex. Moreover, the *t*-BuOOCr complex evolved with time towards the *t*-BuOCr complex, the rate of this reaction being greatly increased by addition of benzyl alcohol [81].

Let us come back to the different benzylic and allylic oxidation products obtained using the catalytic Cr^{VI}/*t*-BuOOH systems. Besides the ketones, benzylic or allylic alcohols (Eqs 1, 8, 9, 13, 14, 20 and 21), hydroperoxydes (Eqs 13 and 14) and *t*-butylperoxydes (Eqs 2, 6, 8, 13, 14 and 31) have been isolated. We have shown that the allylic alcohols [6] are effectively oxidized under the same oxidative experimental conditions via a mechanism preserving the Cr^{VI} oxidation state (Scheme **3**) [6d]. It is known that secondary hydroperoxides are decomposed into the corresponding ketones and alcohols in the presence of chromium [82]. As for the *t*-butylperoxy derivatives, we have demonstrated their transformation into the corresponding ketones under Cr^{VI}-catalysis, especially when *t*-BuOOH was used as additive (Eqs 39 and 40) [83]. Besides the ketone, 1-(*t*-butylperoxy)-indan led

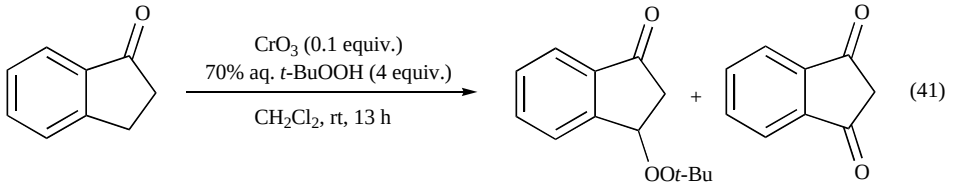


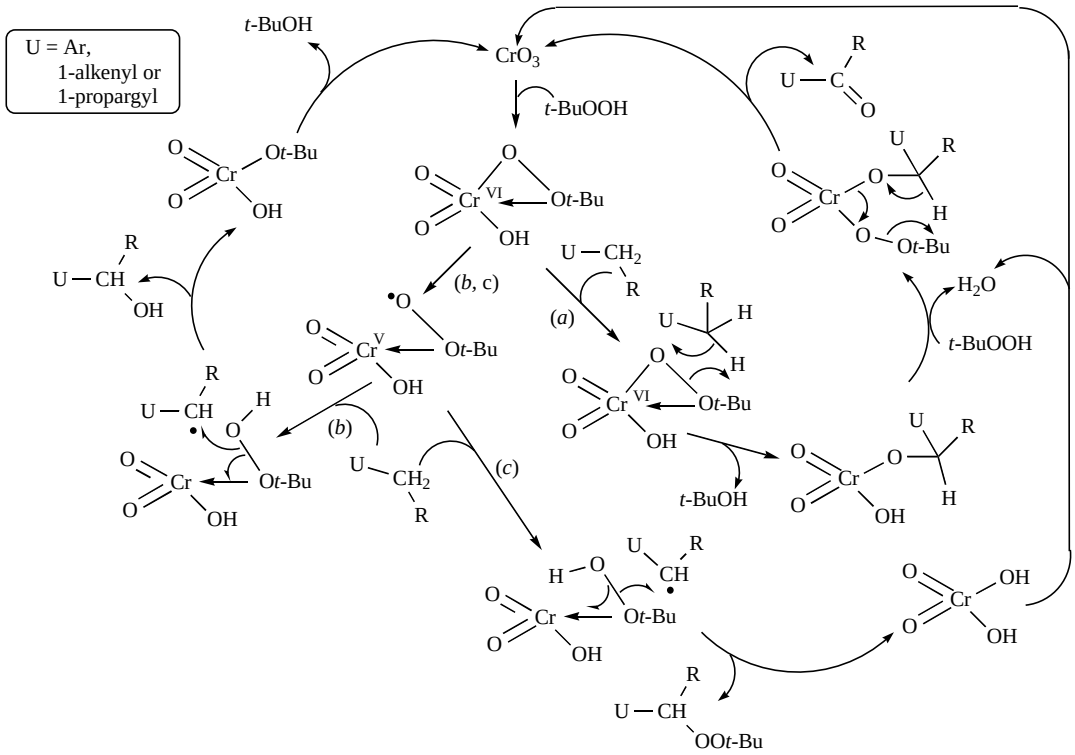
(39)

t-BuOOH (7 equiv.), 8 h, conversion: <4%
CrO_3 (0.1 equiv.), 15 h, conversion: 15%, yield: 14%
CrO_3 (0.1 equiv.) + *t*-BuOOH (4 equiv.), 15 h, conversion: 82%, yield: 81%
$(OCMe_2CH_2CMe_2O)CrO_2$ (0.1 equiv.), 8 h, conversion: <4%
$(OCMe_2CH_2CMe_2O)CrO_2$ (0.1 equiv.)
+ *t*-BuOOH (7 equiv.), 8 h, conversion: 81%, yield: 66%



(40)





Scheme 4.

to 1-(*t*-butylperoxy)-indan-3-one (Eq. 40); traces of this compound were also observed from the catalytic oxidation of 1-indanone (Eq. 41) [83]. The low conversion of 1-indanone leading to 1,3-indandione as main compound (Eq. 41) indicates that the generation of 1-(*t*-butylperoxy)-indan-3-one under the conditions of Eq. 40 is chiefly due to the oxidation of 1-(*t*-butylperoxy)-indan. Furthermore, the ketone/peroxyketone ratio obtained from 1-(*t*-butylperoxy)-indan (Eq. 40) seems to indicate that the CrO_3/*t*-BuOOH association prefers to react with the CHOO*t*-Bu unit of the substrate rather than with its benzylic methylene group although the relative ratio of hydrogen is 1:2, and the steric crowding of the methylene group is lower. This could explain why large amounts of ArCH(OO*t*-Bu)R are usually not isolated from the Cr-catalyzed oxidations of $ArCH_2R$ by *t*-BuOOH.

Let us now comment on the possible pathways leading to peroxy compounds, ketones and alcohols.

The synthesis of allylic hydroperoxides from alkenes using singlet oxygen is well known [84]. The formation of $^1O_2$ by metal-induced decomposition of *t*-BuOOH has been reported [85], and it has been assumed that some peroxochromium complexes produce $^1O_2$ [86,87]. Nevertheless, we suspect that under the catalytic Cr^{VI}/*t*-BuOOH conditions, these compounds are rather produced via the reaction of radical intermediates with *in-situ* produced $^3O_2$ [88]. Besides, the formation of a mixture of two isomeric α,β-unsaturated ketones from 2-(cyclohex-2-enyl)-1,1,1-trifluoropropan-2-ol, one of them implying the migration of the original C=C bond (Eq. 22) [60], is in agreement with the formation of allylic intermediates.

The ketone could be obtained from the reaction of the substrate (UCH_2R, U = Ar, 1-alkenyl, 1-propargyl) with the O-O bond of (*t*-BuOO)(HO)CrO_2. This reaction would occur via a heterolytic or homolytic cleavage to afford (URCHO)(HO)CrO_2 and *t*-BuOH (Scheme **4**, path *a*). The recombination of this complex with *t*-BuOOH, followed by the abstraction of the hydrogen of the OCHRU ligand, would release URC=O and CrO_3. According to the literature on the reactivity of *t*-butyperoxy complexes [89], the homolytic cleavage of the *t*-BuOO-Cr bond is also a possible reaction pathway (Scheme **4**, paths *b* and *c*). The Cr^V species [90] thus formed would abstract a hydrogen radical of UCH_2R to yield $UC^{\cdot}HR$ that evolves toward either UCH(OH)R (path *b*) or UCH(OO*t*-Bu)R (path *c*), both compounds being liable to afford the ketone [91].

A more traditional mechanism is described in Scheme 5. The species formed in the initiation step could be obtained from the reaction of CrO_3 with *t*-BuOOH, or from (*t*-BuOO)(HO)CrO_2 as proposed by Sasson *et al.* (Eq. 42) [50]. The hydrogen atom abstraction leading to $UC^{\cdot}HR$ could be mediated by either *t*-$BuO^{\cdot}$ (Scheme **5**) or *t*-$BuOO^{\cdot}$ (Eq. 43) [92,93]. ESR experiments have indicated the formation of Cr^{IV} and Cr^V species in the course of Cr^{VI}-catalyzed benzylic oxidations by *t*-BuOOH [94], but the identification of active species *via* this technique remains hazardous [95].

Given the results summarized in Sections 2 and 3 and the different intermediates possibilities, we suspect that more than a single reaction pathway leads to ketones. The enhanced reactivity of cyclic alkenes compared to acyclic alkenes towards the allylic hydrogen abstraction leading to allylic radicals is well known, and has led to theoretical studies by Rothenberg and Sasson [96]. The strong higher reactivity of Δ^5-steroids compared to 1-eicosene in the presence of the catalytic Cr^{VI}/*t*-BuOOH system [25], the regioselectivity of the oxida-

Initiation

$$Cr^{VI} + t\text{-BuOOH} \longrightarrow Cr^{V} + t\text{-BuOO}^{\bullet} + H^{+}$$

Propagation

$$Cr^{V} + t\text{-BuOOH} \longrightarrow Cr^{VI} + t\text{-BuO}^{\bullet} + HO^{-}$$

$$UCH_2R + t\text{-BuO}^{\bullet} \longrightarrow UC^{\bullet}HR + t\text{-BuOH}$$

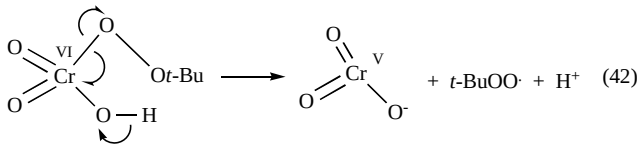
$$UC^{\bullet}HR + t\text{-BuOOH} + Cr^{VI} \longrightarrow UCH(OOt\text{-Bu})R + Cr^{V} + H^{+}$$

$$UCH(OOt\text{-Bu})R + Cr^{V} \longrightarrow URCHO^{\bullet} + Cr^{VI} + t\text{-BuO}^{-}$$

$$URCHO^{\bullet} + Cr^{VI} \longrightarrow URC{=}O + Cr^{V} + H^{+}$$

$$UCH_2R + 2\ t\text{-BuOOH} \xrightarrow{Cr^{VI}} URC{=}O + 2\ t\text{-BuOH} + H_2O$$

Scheme 5.



(42)

$$UCH_2R + t\text{-BuOO}^{\bullet} \longrightarrow UC^{\bullet}HR + t\text{-BuOOH} \qquad (43)$$

tion of β-ionone (Eq. 23) as the results of the oxidation of 2-(cyclohex-2-enyl)-1,1,1-trifluoropropan-2-ol (Eq. 22) indicate the formation of allylic radicals [97]. Allylic and benzylic radicals, $UC^{\bullet}HR$, under transition metal-catalyzed oxidations by *t*-BuOOH give usually rise to the appearance of UCH(OO*t*-Bu)R [93,98]. The marked difference of reactivity, in the presence of the catalytic CrO_3/*t*-BuOOH/CH_2Cl_2 system, between indan (Scheme **1**: formation of ≥60% of 1-indanone in 6-7 h at rt) and 1-(*t*-butylperoxy)-indan (Eq. 40: 72% conversion in 24 h at rt yielding 45% of 1-indanone) implies that the benzylic oxidations of $ArCH_2R$ cannot exclusively occur *via* ArCH(OO*t*-Bu)R. The obtaining of ArCH(OOH)R when the oxidation was carried out under air atmosphere (Eq. 14) agrees with the in-situ formation of $ArC^{\bullet}HR$, but the low difference of the results with a reaction carried out under argon atmosphere (Eq. 14) indicates that the whole transformation of $ArCH_2R$ cannot exclusively occur *via* free benzylic radicals. Moreover, the remarkable chemical yields dependence on the catalyst nature (Scheme **1**, Eqs 2, 19, 25 and 30) imply a determinant role of the catalyst.

The differences between Cr^{VI}-induced oxidations by O_2 and *t*-BuOOH is exemplified with α-pinene as substrate. Indeed, autoxidation mediated by CrO_3(bipyridine) led to 2,3-epoxypinane as the main product even in the presence of catalytic amounts of *t*-BuOOH as additive [99], while the catalytic $(t\text{-BuO})_2CrO_2$/t-BuOOH system yielded verbenone without appearance of the epoxide (Eq. 26) [62,100]. The use of PDC instead of $(t\text{-BuO})_2CrO_2$ seems also to selectively provide verbenone [63,101].

6. CONCLUSIONS

The mechanism of the Cr^{VI}-catalyzed ketonisation of activated methylenes by *t*-BuOOH remains a possible matter of debate. Nevertheless, this method constitutes, in a variety of cases, an efficient procedure. Moreover, no sophisticated or expensive catalyst is required, and the reaction occurs under simple experimental conditions. Hydrogen peroxide [17,58,102] and anhydrous forms of this peroxide, i.e. urea-H_2O_2 complex and sodium percarbonate [12,28], have also been used with Cr^{VI} catalysts for benzylic [12,17,28,102] and allylic [58] oxidations but these oxygen sources are much less effective than *t*-BuOOH.

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ABBREVIATIONS

aq.	=	aqueous
BPCC	=	bipyridinium chlorochromate
cat.	=	catalytic
CTACC	=	cetyltrimethylamonium chlorochromate
Eq.	=	Equation
equiv.	=	equivalent
nd	=	not determined
PCC	=	pyridinium chlorochromate
PDC	=	pyridinium dichromate
rt	=	room temperature

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