Pergamon

Tetrahedron Letters 40 (1999) 2303–2306

TETRAHEDRON
LETTERS

Homogeneous Chromium(VI)-Catalyzed Oxidations of Allylic Alcohols by Alkyl Hydroperoxides: Influence of the Nature of the Alkyl Group on the Product Distribution

Abdelkhalek Riahi, Françoise Hénin, Jacques Muzart*

Unité Mixte de Recherche "Réactions Sélectives et Applications",
CNRS - Université de Reims Champagne-Ardenne, B.P. 1039, 51687 Reims Cédex 2, France

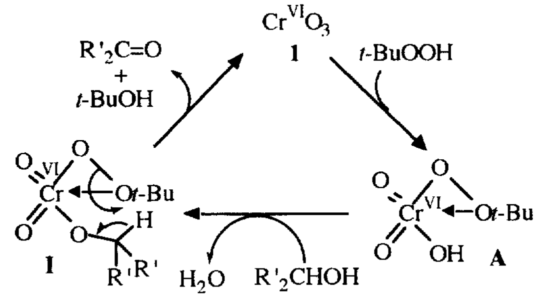
Received 1 December 1998; accepted 17 January 1999

Abstract: The chromium oxide-catalyzed oxidation of allylic alcohols - $R^1CH(OH)CR^2{=}CHR^3$ - by ROOH (R= *t*-Bu, $PhCMe_2$) affords generally a mixture of $R^1COCR^2{=}CHR^3$ and $R^1CH{=}CR^2COR^3$. The rate of the reaction and the ratio between the two oxidized compounds both depend on the nature of R. It has been concluded that the oxidative species and the reactive intermediates contain this R group.

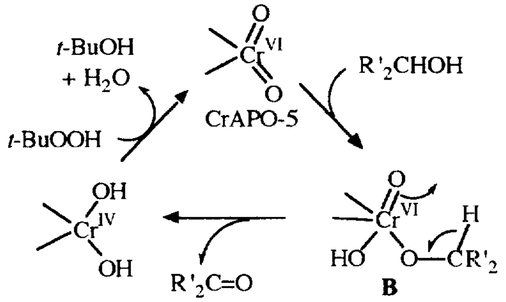
Keywords: Alcohols, Chromium, Peroxides, Oxidation.

Over recent years, our group has been fervently involved in studying chromium-catalyzed oxidations with *tert*-butyl hydroperoxide (TBHP).[1] On the basis of the literature regarding the interactions of transition metals with TBHP,[2] we have suggested that the oxidation of alcohols catalyzed by CrO_3 (**1**) involves a peroxometal pathway which would preserve the Cr(VI) oxidation state (Scheme 1). This comprises i) formation of the *tert*-butylperoxychromium complex **A** as the active oxidative species, ii) reaction of the alcohol with **A** to afford the alkoxy-*tert*-butylperoxychromium complex **I** and iii) intramolecular hydrogen abstraction by the *tert*-butyloxy group to release the ketone and **1**.[1a,3]

Scheme 1



Scheme 2



Using a chromium(VI)-substituted aluminophosphate - CrAPO-5 - as catalyst for the oxidation of alcohols by TBHP,[4] Sheldon's group has subsequently proposed an oxometal pathway (Scheme 2): i) addition of the alcohol to the oxochromium(VI) catalyst to provide the alkoxy-oxochromium complex **B**, ii) hydrogen elimination from **B** giving the ketone with concomitant reduction of Cr(VI) into Cr(IV) and iii) regeneration of Cr(VI) by TBHP.[5,6]

Previously, we have observed that the oxidation of 1-eicosen-3-ol (**2a**) by TBHP in the presence of catalytic amounts of **1** led to a mixture of 1-eicosen-3-one (**3a**) and 2-eicosenal (**4a**).[3] A comparative experiment using

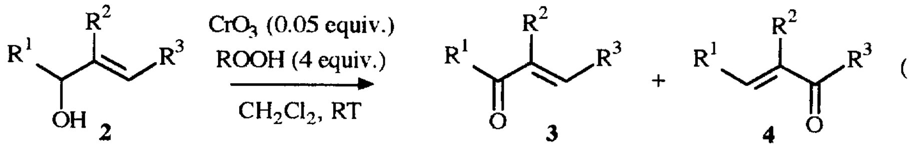
---

* Fax: 03 26 05 31 66. e-mail: jacques.muzart@univ-reims.fr

PII: S0040-4039(99)00168-9

cumyl hydroperoxide (CHP) instead of TBHP has revealed the influence of the nature of the peroxide on both the rate of the oxidation of **2a** and the product distribution. These observations led us to suspect that steric interactions between the alkyl chain of the alcohol and the *t*-butyl or cumyl substituent of the hydroperoxide intervene in the course of the process. Therefore, we carried out the chromium oxide-catalyzed oxidation of a number of variously substituted allylic alcohols by commercial TBHP and CHP with the aims i) to explore the generality and scope of this reaction (Eq. 1, Table 1) and ii) to give insight into its mechanism.

Firstly, our preliminary work was repeated using 0.05 equiv. of **1** and 4 equiv. of ROOH in methylene chloride at room temperature: complete consumption of **2a** was obtained in 5 h when R= *t*-Bu while the oxidation of 80% of **2a** required 24 h when R= cumyl. Accurate values of the ratios between **3a** and **4a** were determined by ^1H NMR analysis on the partially purified crude mixtures. Thus, we observed that the proportion of the rearranged product was higher with CHP than with TBHP (Table 1, runs 1 and 2).



(1)

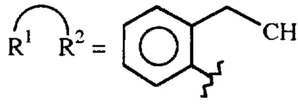
a : $R^1 = (CH_2)_{16}Me$, $R^2 = R^3 = H$

b : $R^1 = Ph$, $R^2 = R^3 = H$

c : $R^1 = R^2 = H$, $R^3 = Ph$

d : R^1 = cyclohexyl, $R^2 = R^3 = H$

e : R^1 = cyclohexyl, $R^2 = H$, $R^3 = Me$

f :


, R^3 = 2-naphthyl

When the primary alkyl side-chain of **2a** was exchanged for a phenyl group, the large difference in the oxidation rates between TBHP and CHP was maintained (runs 3 and 4). The primary alcohol **2c** which is isomeric to the secondary alcohol **2b** was then subjected to the same oxidation conditions (runs 5 and 6): no rearranged product was formed and the reaction with CHP was sluggish.

Two secondary alcohols with a cyclohexyl group in the geminal position to the hydroxy, and which differ by the substitution of the β-position, were then oxidized (runs 7-10). Both **2d** and **2e** led to a mixture of unrearranged and rearranged products. The proportion of **3** - *ie* **3d** and **3e** respectively - was higher when using TBHP and the reaction with this hydroperoxide was much faster than with CHP.

The behaviour of the alcohol **2f**, which has each of the two extremities of its allyl group substituted by an aryl, was examined. A mixture of **3f** and **4f** was obtained with both hydroperoxides and the rate was again slower with CHP (runs 11 and 12).

From the results assembled in Table 1, it appears that under our conditions, i) the reaction rates were always higher with TBHP than with CHP and ii) the **3**/**4** ratios depended highly on the nature of ROOH, the percentage of the rearranged compound (**4**) being higher with CHP. Therefore, it is clear that the process i) involves oxidative species formed from interactions between **1** and ROOH and ii) these species and the reactive intermediates contain at least one R group. In the course of the oxidation, ROOH is reduced into ROH; it is accepted that the reaction of *t*-BuOH with **1** affords $(t\text{-}BuO)(HO)CrO_2$[7] and $(t\text{-}BuO)_2CrO_2$.[8] Similar adducts such as **A** (Scheme 1) are conceivable using *t*-BuOOH instead of *t*-BuOH.

Chromium oxide is not soluble in methylene chloride. The addition of TBHP (1 mmol) to such a heterogeneous mixture (**1**: 0.05 mmol, CH_2Cl_2: 10 ml) caused the instantaneous dissolution of **1** with the appearance of a clear burgundy color for the organic phase. When *t*-BuOH was used instead of TBHP, a yellow-orange solution was obtained; this is certainly due to the formation of *t*-butyl chromate. When TBHP (4 mmol) was added into this latter mixture, the yellow-orange color turned to cloudy orange-red over 30 min. This seems to correspond to a *t*-BuO/*t*-BuOO exchange of ligands.[9] As noted by Talsi and Zamarev, it is natural to expect that with the excess of TBHP, *t*-BuOO will replace *t*-BuO as a ligand.[10]

We have tried to demonstrate the coordination of ROO to Cr by UV-visible, ^1H and ^{13}C NMR spectroscopies. Extensive studies[11] allowed us to observe new signals when adding TBHP to **1**. Obviously, more than one species was produced. Since an excess of TBHP versus **1** was used, the peroxidation of more than one Cr=O could be supposed. Furthermore, the Cr-catalyzed formation of *t*-BuOH from TBHP allows the appearance of *t*-BuOCr species. Thus, we have not been able to ascribe particular signals to the formation of *t*-BuOOCr with certainty. However, we are aware that a TBHP-**1** adduct has been exemplified by Sasson's team in recent studies on the reaction between **1** and TBHP under particular conditions.[12] Therefore, the coordination of ROO to Cr is certainly a reaction which took place under our oxidation conditions.[13] Nevertheless, this does not mean that the oxidation of the alcohol involves the participation of the ROO group rather than Cr=O in the abstraction of the hydrogen *gem* to the hydroxy group.

Table 1. Chromium(VI) oxide-catalyzed oxidation of allylic alcohols by either TBHP or CHP.[a]

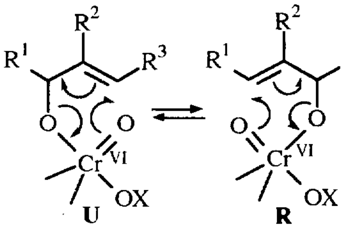
Run	Allylic alcohol	ROOH	Time h	Conv. %	Products	
					3/4 ratio	**3 + 4** yield %
1	**2a**	TBHP	5	100	8.1/1	85
2	**2a**	CHP	24	80	4.0/1	70
3	**2b**	TBHP	3	100	Unrear.	83
4	**2b**	CHP	48	27	Unrear.	23
5	**2c**	TBHP	24	100	Unrear.	82[b]
6	**2c**	CHP	64	10	Unrear.	7
7	**2d**	TBHP	3	100	11.5/1	78
8	**2d**	CHP	41	43	1.4/1	29
9	**2e**	TBHP	3	100	2.1/1	84
10	**2e**	CHP	92	80	1.3/1	79
11	**2f**	TBHP	3	100	7.7/1	84
12	**2f**	CHP	12.5	80	1.3/1	68

[a]*General procedure:* In a round-bottom flask containing a stirred mixture of CrO_3 (0.05 mmol) in methylene chloride (10 ml) was added sequentially either aqueous 70% *t*-BuOOH or $PhCMe_2OOH$ (4 mmol), and alcohol (1 mmol). The stirring was maintained at room temperature under an air atmosphere for the time indicated. Then, the mixture was filtrated over a short pad of alumina. After evaporation of solvents, the residue was analyzed by ^1H NMR to determine the **3/4** ratio (Unrear. means that the rearranged product was not detected; this implies that the **3/4** ratio was superior to 95/5) and then purified by chromatography on silica gel. The **3** + **4** yields are for isolated compounds and are calculated on the amount of **2** introduced. [b]Contains cinnamic acid (10%).

The transposition of α,β-unsaturated secondary alcohols in the course of their stoichiometric oxidation by oxochromium(VI) complexes is usually a very limited pathway[16,17] which however can depend on the nature of the ligands surrounding the metal.[17,18] This kind of transposition probably involves chromate esters.[19] Interestingly, no rearrangement has been reported when 1-octen-3-ol - whose structure is similar to that of **2a** - and **2d** were oxidized by pyridinium dichromate in methylene chloride.[20] Similarly, the ammonium dichromate-catalyzed oxidation of **2a** by sodium percarbonate, which probably involves (η^2-peroxo)chromium complexes,[21] afforded selectively **3a**.[22]

In the present study, the **3/4** ratios depend strongly on the ROOH we used. This leads us to propose an equilibrium between **U** and **R** for the present transposition (Scheme 3, X= R or OR).

Scheme 3



In conclusion, we have shown that the CrO_3-catalyzed oxidation of allylic alcohols by ROOH implied a hydrogen elimination from an allyoxychromium intermediate whose the coordination sphere contains the R group.

Acknowledgments: We thank O. Letsch and M. Eschard (Undergraduate students, 1993 and 1994 respectively) for their contribution to these studies. The work was partly carried out within an INTAS project (94-1515). We are grateful to G. Rothenberg and U. Schuchardt for personal communications and preprints, and to Dr G. Bird (Zeneca Pharma, Reims) for help with the text.

References and notes:

1 a) Muzart, J. *Chem. Rev.* **1992**, *92*, 113-140. b) Muzart, J. *Synthesis* **1993**, 11-27. c) N'Aït Ajjou, A.; Aït-Mohand, S.; Muzart, J.; Richard, C, Sabo-Etienne, S. *New. J. Chem.* **1996**, *20*, 571-577.

2 a) Di Furia, F.; Modena, G.; Curci, R.; Bachofer, S.J.; Edwards, J.O.; Pomerantz, M. *J. Mol. Catal.* **1982**, *14*, 219-229. b) Mimoun, H.; Chaumette, P.; Mignard, M.; Saussine, L.; Fischer, J.; Weiss, R. *New. J. Chem.* **1983**, *7*, 467-475. c) Ledon, H.J.; Varescon, F. *Inorg. Chem.* **1984**, *23*, 2735-2737. d) Mimoun, H.; Mignard, M.; Brechot, P.; Saussine, L. *J. Amer. Chem. Soc.* **1986**, *108*, 3711-3718.

3 Muzart, J. *Tetrahedron Lett.* **1987**, *28*, 2133-2134.

4 Chen, J.D.; Dakka, J.; Neeleman, E.; Sheldon, R.A. *J. Chem. Soc., Chem. Commun.* **1993**, 1379-1380.

5 a) Sheldon, R.A.; Chen, J.D.; Dakka, J.; Neeleman, E. *Stud. Surf. Sci. Catal.* **1993**, *83*, 407-416. b) Chen, J.D.; Haanepen, M.J.; van Hooff, J.H.C.; Sheldon, R.A. *Stud. Surf. Sci. Catal.* **1994**, *84*, 973-980. c) Chen, J.D.; Lempers, H.E.B.; Sheldon, R.A. *J. Chem. Soc., Faraday Trans* **1996**, *92*, 1807-1813. d) Sheldon, R.A. *J. Mol. Catal. A: Chem.* **1996**, *107*, 75-83.

6 Recent studies have shown that the use of chromium substituted silicate or aluminophosphates with TBHP affords small amounts of leached chromium which are indeed the real catalyst; thus, the corresponding catalyzed oxidations proceed at the level of a homogeneous medium: a) Lempers, H.E.B.; Sheldon, R.A. *Stud. Surf. Sci. Catal.* **1997**, *105*, 1061-1068; b) Sheldon, R.A. *Stud. Surf. Sci. Catal.* **1997**, *110*, 151-175; c) Carvalho, W.A.; Varaldo, P.B.; Wallau, M.; Schuchardt, U. *Zeolites* **1997**, *18*, 408-416; d) Sheldon, R.A.; Wallau, M.; Arends, I.W.C.E.; Schuchardt, U. *Acc. Chem. Res.* **1998**, *31*, 485-493; e) Sheldon, R.A.; Arends, I.W.C.E.; Lempers, H.E.B. *Coll. Czech. Chem. Commun.* **1998**, *63*, 1724-1742.

7 Sharpless, K.B.; Akashi, K. *J. Am. Chem. Soc.* **1975**, *97*, 5927-5928.

8 a) Fieser, L.F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. I, pp 86-87. b) Roberts, D.L.; Heckman, R.A.; Hege, B.P.; Bellin, S.A. *J. Org. Chem.* **1968**, *33*, 3566-3569. c) Sheats, W.B.; Olli, L.K.; Stout, R.; Lundeen, J.T.; Justus, R.; Nigh, W.G. *J. Org. Chem.* **1979**, *44*, 4075-4078.

9 Oxidations by TBHP catalyzed by $(t\text{-BuO})_2CrO_2$ have been reported: Antunes, O.A.C.; Pinto, A.C.; Correia, C.R.D.; Rezende, C.M. *Rev. Univ. Rural, Sér. Cienc. Exatas e da Terra* **1995**, *17*, 15-19 and 21-25.

10 Talsi, E.P.; Chinakov, V.D.; Babenko, V.P.; Zamarev, K.I. *J. Mol. Catal.* **1993**, *81*, 235-254.

11 N'Aït Ajjou, A.; Aït-Mohand, S.; Muzart, J. *Unpublished work* 1989-1996.

12 Rothenberg, G.; Wiener, H.; Sasson, Y. *J. Mol. Catal.* **1998**, *136*, 253-262.

13 Note that $(HO)Cr^{VI}(OOCHR'_2)$[5a,14a] and $O{=}Cr^{VI}(OOCHR'_2)$[14b] have been proposed as intermediates for the catalysis by CrAPO-5 of the decomposition of secondary alkyl hydroperoxides (R'_2CHOOH). The subsequent hydrogen elimination which leads to R'_2CO would involve intramolecular decomposition of these intermediates while preserving the Cr(VI) oxidation state.[5a,14,15] Under these conditions, the decomposition of R'_2CHOOH "*via* homolytic, Haber-Weiss mechanism is apparently not significant".[15]

14 a) Lempers, H.E.B.; Chen, J.D.; Sheldon, R.A. *Stud. Surf. Sci. Catal.* **1995**, *94*, 705-712. b) Chen, J.D.; Lempers, H.E.B.; Sheldon, R.A. *Colloids Surf. A: Physicochem. Eng. Aspects* **1995**, *101*, 137-146.

15 Chen, J.D.; Dakka, J.; Sheldon, R.A. *Applied Catal. A: General* **1994**, *108*, L1-L6.

16 a) Cainelli, G.; Cardillo, G. *Chromium Oxidations in Organic Chemistry* Verlag: Berlin, 1984. b) Luzzio, F.A.; Guziec, F.S. *Org. Prep. Proced. Int.* **1988**, *20*, 533-584.

17 a) O'Neil, S.V.; Quickley, C.A.; Snider, B.B. *J. Org. Chem.* **1997**, *62*, 1970-1975. b) Guella, G.; Cavazza, M.; Guerriero, A.; Pietra, F. *Helv. Chim. Acta* **1984**, *67*, 1248-1253.

18 For the transposition of secondary and primary allylic alcohols catalyzed by high oxidation state transition metal oxo complexes, see also : a) Matsubara, S.; Okazoe, T.; Oshima, K.; Takai, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 844-849; b) Belgacem, J.; Kress, J.; Osborn, J.A. *J. Am. Chem. Soc.* **1992**, *114*, 1501-1502; c) Bellemin-Laponnaz, S.; Gisie, H.; Le Ny, J.-P.; Osborn, J.A. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 976-978; d) Jacob, J.; Espenson, J.H.; Jensen, J.H.; Gordon, M.S. *Organometallics* **1998**, *17*, 1835-1840. The transposition of tertiary allylic alcohols is more usual: a) refs 16 and 19; b) Chabardes, P.; Kuntz, E.; Varagnat, J. *Tetrahedron* **1977**, *33*, 1775-1783; b) Hosogai, T.; Fujita, Y.; Ninagawa, Y.; Nishida, T. *Chem. Lett.* **1982**, 357-360; c) Lorber, C.Y.; Pauls, I.; Osborn, J.A. *Bull. Soc. Chim. Fr.* **1996**, *133*, 755-758.

19 Dauben, W.G.; Michno, D.M. *J. Org. Chem.* **1977**, *42*, 682-685.

20 Corey, E.J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399-402.

21 a) Brown, S.B.; Jones, P.; Suggett, A. *Prog. Inorg. Chem.* **1970**, *13*, 159-204. b) Dickman, M.H.; Pope, M.T. *Chem. Rev.* **1994**, *94*, 569-584. c) Zhang, L.; Lay, P.A. *Inorg Chem.* **1998**, *37*, 1729-1733.

22 Muzart, J.; N'Aït Ajjou, A.; Aït-Mohand, S. *Tetrahedron Lett.* **1994**, *35*, 1989-1990.