Tetrahedron Letters No. 22, pp 1939 - 1942, 1977. Pergamon Press. Printed in Great Britain.

ALLYLIC OXIDATION WITH CHROMIUM(VI)

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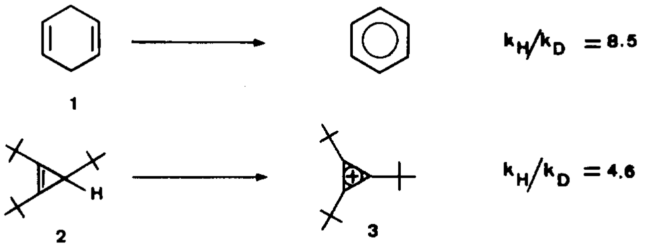
(Received in UK 21 March 1977; accepted for publication 15 April 1977)

Chromic acid oxidizes alkenes by reacting with the double bonds as well as with the allylic positions.[1] The reaction at the double bond is due to attack of chromium(VI).[2] Oxidation of the allylic CH bonds, however, is believed to involve an intermediate valence state of chromium, presumably Cr(IV).[3]

In the absence of double bonds Cr(VI) also reacts with CH bonds. Alkanes[4] and aryl alkanes[5] are oxidized by hydrogen transfer to Cr(VI) with concurrent formation of an organic radical.

Although Cr(VI) shows a strong preference for double bond in comparison to allylic oxidation, we have found two alkenes, 1,4-cyclohexadiene (1) and 1,2,3-tri-*t*-butylcyclopropene[6] (2) reacting at the allylic CH bonds. Furthermore, although Cr(VI) usually oxidizes CH bonds by hydrogen abstraction, our results suggest that these reactions are two-electron transfer processes involving hydride transfer from the substrate to the oxidant.

1,4-Cyclohexadiene (1) was oxidized at room temperature for 16 hours in 80% acetic acid with one equivalent of CrO_3. GC analysis after work-up revealed the presence of a single product in the organic phase, namely benzene in 85% yield. The reaction of 2 with one eq. of CrO_3 was investigated in 80-90% CD_3COOD/D_2O. After 24 hours a peak appeared in the NMR at δ 1.56 ppm, characteristic for the tri-*t*-butylcyclopropenium cation (3).[6] Addition of authentic 3 to the reaction mixture produced no additional peaks. The reactivity of 1 and 2 with respect to chromic acid was investigated under pseudo first-order conditions with excess substrate. The disappearance of Cr(VI) was monitored by measuring the absorbance at 350 nm.[7] Under these conditions Cr(VI) is the only kinetically relevant Cr



species, and the reaction rates therefore refer to Cr(VI) alone. The results of the reactivity study are summarized in the table.

Table. *Rate Constants for Reaction of Alkenes with Chromic Acid*[a]

Substrate	10^4k 80% AcOH[b]	10^3k 90% AcOH[c]	10^3k 95% AcOH[d]	k_{rel}
1,4-Cyclohexadiene (1)	24.3	18.9		5200
1,4-Cyclohexadiene-d_8	2.89			610
Cyclohexene	0.99	0.76	11.00	210
Tri-*t*-butylcyclopropene (2)		54.6		15100
Tri-*t*-butylcyclopropene-d_1		11.7		3200
Tri-*t*-butylcyclopropenium perchlorate (3)		0.61		170
Triphenylmethane			5.2	1.0
Ethylbenzene			2.1[e]	0.4
Toluene			0.65[e]	0.1

[a] Rate constants in $M^{-1}s^{-1}$; [b] 10^{-2}N H_2SO_4, 25°; [c] 10^{-2}N H_2SO_4, 25°; [d] 0.2N H_2SO_4, 30°; [e] 0.1M $HClO_4$, ref. 5.

Both 1 and 2 are oxidized with a primary kinetic isotope effect indicating CH bond cleavage in the rate-limiting step. The value of k_H/k_D = 4.6 for 2 is in the normal range for hydrocarbon oxidation (6.4 for diphenylmethane[5] and 2.5 for 3-methylheptane[4]), while that of 8.5 for 1 appears abnormally high (see below).

The preference of 1 and 2 to react by CH cleavage instead of by oxidation at the double bonds is unique. Even more surprising is the high reactivity of these compounds. Although they react only 20-75 times faster than a typical alkene, i.e. cyclohexene (reacting at the double bond), their oxidation rates are accelerated by 5000 and 15000, respectively over that of triphenylmethane, the latter compound representing a typically activated substrate. In comparison with less activated hydrocarbons, the rate enhancement is event more important.

We believe that these results are best explained with a change in mechanism from hydrogen to hydride transfer to Cr(VI) due to aromatic stabilization of the transition state. Hydrogen abstraction from 2 would lead to a cyclopropenyl radical. The tri-*t*-butylcyclopropenyl radical is a σ radical,[8] and for radicals of this type no particular (aromatic) stabilization is possible.[9] We may expect reactions leading to such radicals to proceed at moderate rates. This is indeed the case. Methyl radicals abstract hydrogen from triphenylcyclopropene 6 times slower than from triphenylmethane.[10] Even in a more "polar" radical generating reaction such as perester pyrolysis, the di-*n*-propylcyclopropenyl radical forms only 20 times faster than diphenylmethyl.[11] On the other hand, hydride transfer from cyclopropenes leads to an aromatic cyclopropenium ion,[12] the stability of which is reflected in the transition state of the reaction and leads to impressive rate enhancement. For example, triphenylcyclopropene reacts with triphenylmethylfluoroborate or 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) 10^3 to 10^5 times faster than with simple model compounds.[13] The rate acceleration in the oxidation of 2 with chromic acid suggests that this reaction proceeds also by a hydride mechanism leading to 3 in a single oxidation step. The same mechanism has been proposed for the exothermic reaction of 2 with *m*-chloroperoxybenzoic acid. Similarly, dehydrogenation of 1 with DDQ or triphenylmethylfluoroborate proceeds at rates comparable to hydride transfer from cycloheptatriene or triphenylcyclopropene.[13] A mechanism involving simultaneous transfer of two *cis* hydrogens in a two-electron process was proposed for the reaction, and the high rate of 1 was explained by a transition state reflecting in part the aromatic stabilization of the product, benzene. The same effect must be responsible for the high rate of 1 with chromic acid. An additional parallel between the reaction of 1 with DDQ and chromic acid is found in the magnitude of the kinetic isotope effect. The simultaneous breaking of two CH bonds results in an unusually high isotope effect of 10.0 with DDQ.[13] With chromic acid the effect is less impressive, namely 8.5, however this value is still above the usual range.

While for oxidation of CH bonds with Cr(VI) one-electron (hydrogen) transfer seems to be the general rule, the two-electron (hydride) mechanism is not without precedent. Wiberg[5] suggested the same pathway for the oxidation of *p*-methoxydiphenylmethanes. It appears therefore that the possibility to form a highly stabilized carbenium ion in a single oxidation step can provoke a mechanistic change from hydrogen to hydride transfer to Cr(VI).

Acknowledgement. This work was financially supported by the *Swiss National Science Foundation* (Grants No 2.128.74 and 2.522-0.76).

REFERENCES AND NOTES

1) For a review on chromic acid oxidations see: K.B. Wiberg, ed., "Oxidation in Organic Chemistry, Part A", Academic Press, New York, 1965.

2) A.K. Awasthy & J. Rocek, *J. Amer. Chem. Soc.* 91, 991 (1969).

3) P. Müller & J. Rocek, *J. Amer. Chem. Soc.* 96, 2836 (1974); J. Rocek & J.C. Drozd, *ibid.* 92, 6668 (1970).

4) K.B. Wiberg & G. Foster, *J. Amer. Chem. Soc.* 83, 423 (1961); J. Rocek, *Tetrahedron Letters* 1962, 135.

5) K.B. Wiberg & R.J. Evans, *Tetrahedron* 8, 313 (1960).

6) J. Ciabattoni & E.C. Nathan, *J. Amer. Chem. Soc.* 91, 4766 (1969).

7) Details of the method have been described; cf. P. Müller & J.C. Perlberger, *Helv. Chim. Acta* 57, 1943 (1974).

8) K. Schreiner & A. Berndt, *Angew. Chem.* 88, 764 (1976).

9) N.C. Baird, *J. Org. Chem.* 40, 624 (1975).

10) P. Gal, Ph.D. Thesis, Columbia University, Diss. Abstr. 13, 2693 (1963).

11) C. Rüchardt, *Fortschritte Chem. Forsch.* 6, 251 (1966).

12) R. Breslow, *Chem. Eng. News* 43, (26) 90 (1965); *Angew. Chem. Intern. Ed. Engl.* 7, 565 (1968).

13) P. Müller, *Helv. Chim. Acta* 56, 1243 (1973); J. Rocek & P. Müller, *J. Amer. Chem. Soc.* 94, 2716 (1972); F. Stoos & J. Rocek, *ibid.* 94, 2719 (1972).

14) P.J. Kociensky & J. Ciabattoni, *J. Org. Chem.* 39, 388 (1974).