Tetrahedron Letters No.24, pp. 2835-2840, 1968. Pergamon Press. Printed in Great Britain.

CHROMIC ACID OXIDATION OF 1-METHYLCYCLOBUTANOL: THE FIRST EXAMPLE OF A DIRECT OXIDATION OF A TERTIARY ALCOHOL.

Jan Rocek* and Annette Radkowsky
Department of Chemistry, The Catholic University of America,
Washington, D.C.

(Received in USA 4 March 1968; received in UK for publication 15 March 1968)

Tertiary alcohols are in general very unreactive towards direct oxidation. Except for cobaltic salts (1) no clearly documented example of a direct oxidation of a tertiary alcohol seems to be available. The chromic acid oxidation of a number of tertiary alcohols has been studied (2-8) and even though direct oxidation was originally postulated in some cases, kinetic studies later revealed (9,10) that the oxidation is preceded by an olefin-forming elimination of a water molecule. Thus, the substrate undergoing oxidation is an olefin and not the alcohol itself.** In this communication we wish to report what we believe is the first example of an unambiguously demonstrated direct oxidation of a tertiary alcohol by hexavalent chromium.

1-Methylcyclobutanol is a tertiary alcohol very reluctant to undergo dehydration. Studies by Riesz, Taft and Boyd (12) indicated that 1-methylcyclobutanol is dehydrated (in aqueous solution at 30°)

---

[*] To whom inquiries should be directed at the Dept. of Chemistry University of Illinois at Chicago Circle, Illinois 60680.

[**] Two tertiary alcohols incapable of undergoing simple dehydration have been investigated (6,11). However, no kinetic data allowing to draw conclusions about the mechanisms is available.

at least 300 times slower than tertiary-butanol and 10^5 times slower than 1-methylcyclopentanol. The low dehydration rate would make the oxidation of this alcohol by the normal route, i.e. by way of the olefin, very slow and thus improves the chance of detecting a direct oxidation. Further, the large ring strain existing in the cyclobutane system should aid any reaction involving ring cleavage in the rate limiting step. As it is reasonable to assume that a direct oxidation of a tertiary alcohol would proceed by carbon-carbon bond cleavage, this factor should also favor a direct oxidation of tertiary alkylcyclobutanols.

We found that the oxidation of 1-methylcyclobutanol in 1M aqueous perchloric acid at 30° proceeds at a relatively slow (220 times slower than cyclobutanol) but still a well measurable rate indicating a first order dependence on the concentration of chromic acid. A more detailed investigation was carried out in aqueous acid solutions. Table 1 summarizes the results obtained in determining oxidation rates for

TABLE 1

Oxidation of 1-Methylcyclobutanol in 90% Acetic Acid at 30°.
Concentrations: $HClO_4$ - 0.4M, 1-methylcyclobutanol - 0.1M.

$[CrO_3]$, 10^3M	10^2k, M^{-1}, s^{-1}
0.22	0.94
0.32	0.92
0.44	0.93
0.68	0.95
0.70	0.98
0.70	0.94
1.31	1.09
2.15	0.86
2.83	1.13
3.13	0.96
5.61	1.09
5.68	1.04
8.52	1.19
11.57	1.26
13.80	1.37

1-methylcyclobutanol in 90% acetic acid over a 50 fold concentration range of chromic acid. It is evident from the data in the table that the reaction is first order in the oxidant.*

The rate of dehydration of 1-methylcyclobutanol under these conditions is too slow to be measured (no noticeable reaction during 16 hours), but can be studied in 99% acetic acid.** The results together with measurements of dehydration rates of tertiary-butanol and of 1-methylcyclohexanol are given in Table 2. The rate of dehydration of 1-methylcyclobutanol is about 160 times slower that that of tertiary-butanol and 1,500 times slower than of 1-methylcyclohexanol. The dehydration of 1% of methylcyclobutanol would thus require about 140 minutes, whereas the oxidation of the alcohol under comparable conditions with a 110:1 ratio of alcohol:chromium(VI) proceeded with a half-life of less than 3 minutes. It is thus clear that the oxidation of 1-methylcyclobutanol cannot be preceded by a dehydration reaction and that the oxidation of 1-methylcyclobutanol thus represents a genuine example of a direct oxidation of a tertiary alcohol by chromium(VI).

The chromic acid oxidation of 1-methylcyclobutanol differs from the oxidation of secondary alcohols in two respects. One, the typical decrease in the second order rate constant observed in the oxidation of secondary alcohols (14) as well as of aldehydes (15, 16), and

---

* A slight increase in the second order rate constants at very high chromium(VI) concentrations may be due to further oxidation of primary reaction products. This oxidation of products formed from the tertiary alcohol will obviously grow in importance with increasing the chromium(VI):alcohol ratio.

** The measurements were carried out spectrophotometrically by determining the rate of the uptake of bromine present in the solution at 450 mμ; good zero order plots were obtained in all cases. The method was tested by including 1-methylcyclohexanol for which the rates of dehydration have been previously determined using a classical bromometric procedure (13).

TABLE 2

Dehydration Rates in Acetic Acid Solutions

Alcohol	Conditions	Acid,M	$Br_2, 10^{-3}M$	10^4k, sec^{-1}
1-Methylcyclohexanol	A	0.4	2.7	0.66
	B	0.3	4.5	1.65[a]
Tert.-Butanol	B	0.3	5.2	0.23
	B	0.3	8.9	0.18
	B	0.9	5.2	2.00
1-Methylcyclobutanol	A	0.4	2.7	----[b]
	B	0.9	5.2	0.12

A: $HClO_4$ in 90% Acetic Acid at 30°.

B: H_2SO_4 in 99% Acetic Acid at 20°.

[a] By a different method a value of $k = 1.25 \times 10^{-4}$ sec^{-1} was obtained previously (13).

[b] No observable reaction in 16 hours.

connected with the $HCrO_4^- \rightleftarrows Cr_2O_7^=$ equilibrium is missing in the present case. Second, the oxidation of the tertiary alcohol increases less steeply when the solvent is changed from water to acetic acid than is usual for secondary alcohols (17,18). This results in the relative rate of oxidation of cyclobutanol to 1-methylcyclobutanol increasing from 200 in water to 2400 in 90% acetic acid and to 3100 in 99% acetic acid.

The oxidation of 1-methylcyclobutanol results in an extensive degradation probably all the way to carboxylic acids, dicarboxylic acids and carbon dioxide. No carbonyl compounds, which should be formed earlier in the oxidation, could be detected. In the absence of sufficient information about the nature of the reaction products, the interpretation of the mechanism would be premature. It is hoped that now that direct oxidation has been demonstrated on one example, other tertiary alcohols reacting directly with chromic acid will be found and that their study will supply the information needed for a detailed understanding of the mechanism of the reaction.

Acknowledgement. Acknowledge is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, and to the U.S. Army Research Office-Durham, for generous support of this research.

References

1. D. G. Hoare and W. A. Waters, *J. Chem. Soc.*, 965(1962) and 2552(1964).
2. P. Barbier and R. Locquin, *Comt. Rend.*, **156**, 1443(1913).
3. H. Wieland, O. Schlichting, and R. Jacobi, *Z.Physiol. Chem.*, **161**, 80(1926).
4. J. R. Bielleter and K. Miescher, *Helv. Chim. Acta*, **30**, 1409(1947).
5. L. F. Fieser and J. Szmuszkovic, *J. Am. Chem. Soc.*, **70**, 3352(1948).
6. H. H. Zeiss, *J. Am. Chem. Soc.*, **70**, 858(1948).
7. H. H. Zeiss and D. A. Pease, Jr., *J. Am. Chem. Soc.*, **78**, 3182(1956).
8. H. H. Zeiss and F. R. Zwanzig, *J. Am. Chem. Soc.*, **79**, 1733(1957).
9. W. F. Sager, *J. Am. Chem. Soc.*, **78**, 4970(1956).
10. J. Rocek, *Collection Czech. Chem. Communs.*, **23**, 833(1958).
11. M. L. Huber, M. S. Thesis, University of Delaware, 1947.
12. P. Riesz, R. W. Taft, Jr., R. H. Boyd, *J. Am. Chem. Soc.*, **79**, 3724(1957).
13. J. Roček, *Collection Czech. Chem. Communs.*, **25**, 275(1957).
14. F. H. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506(1943).
15. G.T.E. Graham and F. H. Westheimer, *J. Am. Chem. Soc.*, **80**, 3030(1958).
16. K. B. Wiberg and T. Mill, *J. Am. Chem. Soc.*, **80**, 3022(1958).
17. M. Cohen and F. H. Westheimer, *J. Am. Chem. Soc.*, **74**, 4387(1952).

References (Cont'd)

18. J. Roček, F. H. Westheimer, A. Eschenmoser, L. Moldovanyi and J. Schrieber, Helv. Chim. Acta, 45, 2554(1962).