CHEMISTRY LETTERS, pp. 2131 - 2134, 1984. © The Chemical Society of Japan 1984

HIGHLY SELECTIVE OXIDATION OF BENZYLIC ALCOHOLS WITH CETYLTRIMETHYLAMMONIUM PERMANGANATE

R. RATHORE, VIDYA BHUSHAN, and S. CHANDRASEKARAN*
Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India

Cetyltrimethylammonium permanganate (CTAP) has been found to be a mild and highly selective reagent for the oxidation of benzylic alcohols to the corresponding aldehydes or ketones.

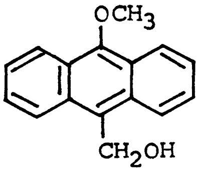
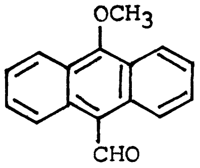
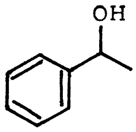
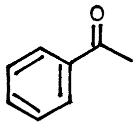
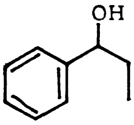
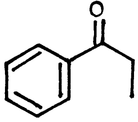
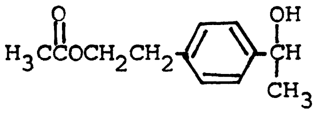
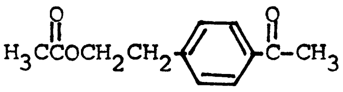
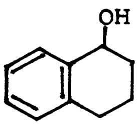
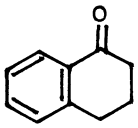
Although there are a number of reagents available for the oxidation of alcohols to carbonyl compounds, there are only a very few reagents which are known to oxidise benzylic and allylic alcohols selectively. Active maganese dioxide is a well known oxidant for effecting this transformation.[1,2) Recently, 4-dimethylaminopyridinium chlorochromate[3) and bipyridinesilver permanganate[4) have been shown to have moderate selectivity in the oxidation of allylic and benzylic alcohols in the presence of other primary and secondary alcohols.

In the course of our studies on cis-hydroxylation of olefins with CTAP,[5) it was found that treatment of diphenylacetylene with CTAP afforded benzil in good yield. This result was surprising because we had observed that a number of primary and secondary alcohols and diols (products of cis-hydroxylation) did not undergo further oxidation with excess of CTAP. It was, therefore, apparent that although simple primary and secondary alcohols were inert towards this reagent, benzylic alcohols would undergo a facile oxidation.

Herein, we report our results on the highly selective oxidation of benzylic alcohols with cetyltrimethylammonium permanganate. Treatment of a wide range of benzylic alcohols with one mole equivalent of CTAP in dichloromethane at room temperature gave excellent yields of the corresponding carbonyl compounds in a very short time. In a typical reaction, to a solution of the substrate (2 mmol) in dichloromethane (5 ml) was added a solution of CTAP (2 mmol) in dichloromethane (4 ml) and the resulting mixture was stirred at 28-30 °C for 0.25-1.5 h. It was then diluted with ether (30 ml) and filtered through a pad of celite and anhydrous magnesium sulphate. The filtrate was evaporated and the residue was purified by chromatography on silica gel. The results of these oxidations are summarised in Table 1.

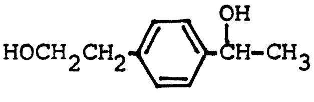
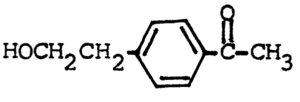
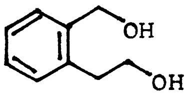
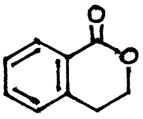
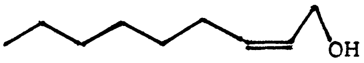
Three important features of this methodology are worth mentioning: (i) Aldehydes which are the oxidation products of primary benzylic alcohols (entries 1-6 in Table 1) do not undergo further oxidation under the reaction conditions. However, aldehydes when treated separately with CTAP get converted to carboxylic acids.[5)

Table 1. Oxidation of benzylic alcohols with CTAP

Entry	Substrate	Mole eq. of CTAP	Time / h	Product[a)]	Yield[b)] / %
1	Benzyl alcohol	1	1.0	Benzaldehyde	97
2	p-Nitrobenzyl alcohol	1	1.0	p-Nitrobenzaldehyde	97
3	m-Methoxy benzyl-alcohol	1	1.0	m-Methoxy benzaldehyde	96
4	m-Chlorobenzyl alcohol	1	1.0	m-Chlorobenzaldehyde	90
5	Furfuryl alcohol	1	0.5	Furfural	90
6		1	1.0		92
7	Benzoin	1	0.15	Benzil	98
8	Benzhydrol	1	0.25	Benzophenone	98
9		1	1.5		94
10		1	1.5		95
11		1	1.0		90
12		1	1.0		94

....contd.

Table 1 (contd.)

Entry	Substrate	Mole eq. of CTAB	Time / h	Product[a)]	Yield[b)] / %
13		2	1.5		90
14		2	1.5		65
15		1	72	No reaction	
16		1	72	No reaction	
17	Ph-CH=CH-CH_2OH	1	48	No reaction	

a) Products were characterized by comparison with authentic samples (IR spectrum, TLC and mp).

b) All yields refer to isolated products.

(ii) The remarkably selective oxidation of benzylic alcohols (entries 13 and 14) in the presence of other hydroxyl groups in the substrate with excess of CTAP is particularly noteworthy.[6)] In both these cases not even a trace of products derived by oxidation of non-benzylic hydroxyl groups could be detected.

(iii) Unlike manganese dioxide[1)] and 4-dimethylaminopyridinium chlorochromate,[3)] CTAP does not oxidise allylic alcohols. Neither hydroxylation of the double bond nor oxidation of the allylic alcohol (entries 15-17) was observed with CTAP even after prolonged reaction time.

Sala and Sargent have shown that tetra-n-butylammonium permanganate in pyridine is a mild oxidant for a variety of organic substrates but high selectivity of the type shown by CTAP has not been reported.[7)]

Thus, it is evident that CTAP is an extremely mild and highly selective reagent for the oxidation of benzylic alcohols even in the presence of other hydroxyl groups including allylic alcohols. The ease of preparation and relative stability of CTAP8) would thus make it a valuable addition to the presently available reagents and add to the arsenal of the synthetic organic chemist. Investigations into the reasons for the observed selectivity and into the usefulness in organic synthesis are currently in progress.

We are thankful to Professor M.V. George, Department of Chemistry, I.I.T., Kanpur for encouragement and for extending his spectral facilities for our use.

References

1) H.O. House, "Modern Synthetic Reactions," 2nd ed, W.A. Benjamin, New York (1972), pp. 265-267.

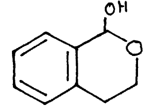
2) A.J. Fatiadi, Synthesis, 1976, 65, 133.

3) F.S. Guziec Jr. and F.A. Luzzio, J. Org. Chem., 47, 1787 (1982).

4) H. Firouzabadi, B. Vessal, and M. Naderi, Tetrahedron Lett., 23, 1847 (1982).

5) R. Rathore and S. Chandrasekaran (unpublished results).

6) Since the direct oxidation of primary alcohol to carboxylic acid is not very facile, the diol (entry 14) probably goes to the lactone via



7) T. Sala and M.V. Sargent, Chem. Commun., 1978, 253.

8) Vidya Bhushan, R. Rathore, and S. Chandrasekaran, Synthesis, 1984, 431.

(Received October 17, 1984)