

SYNTHETICALLY USEFUL OXIDATIONS AT SOLID SODIUM PERMANGANATE SURFACES

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Summary: Solid $\text{NaMnO}_4 \cdot \text{H}_2\text{O}$ is an efficient and selective oxidizing agent.

We recently reported the observation that alcohols in benzene can be oxidized to ketones by solid KMnO_4 ¹. Traces of water are critical to the reaction. Addition of $\text{CuSO}_4 \cdot (\text{H}_2\text{O})_5$ catalyzes the oxidation and permits high yields of product at room temperature. Easy work-up (filtration of excess permanganate and removal of solvent) constitutes a major advantage of the procedure. We now report that solid sodium permanganate monohydrate² oxidizes a variety of organic functionalities under mild conditions without the need of an additive (Table I). As seen from the table, the solid reagent manifests greater selectivity than that found with permanganate in solution^{3,4}. Thus, the heterogeneous oxidations proceed smoothly with alcohols, sulfides, aldehydes, etc., but not with alkenes, alkynes, epoxides, and amides. Allylic alcohols are oxidized more slowly than saturated alcohols (entries 1 and 9). This interesting reversal in reactivity cannot be exploited for selective synthetic purposes because 1-octen-3-ol was found to inhibit the oxidation of 2-octanol in hexane over solid NaMnO_4 (as if the allylic alcohol blocks productive binding sites on the crystal surface). In any event, the mildness, yield, easy work-up, and unusual selectivity of oxidations mediated by solid NaMnO_4 suggest that synthetic methodology based on crystal surfaces is a topic worthy of further research.

In a typical run, 0.39 g (3 mmol) of 2-octanol in 15 ml hexane was magnetically stirred with 1.92 g (12 mmol) of $\text{NaMnO}_4 \cdot \text{H}_2\text{O}$ at refluxing temperature for 2.5 hours. Analysis of the liquid phase by GLC indicated complete conversion of alcohol to ketone. After filtering the reaction mixture, the solvent was removed to give 2-octanone in 95% yield. Control experiments with oxidant dried over P_2O_5 at 50° and 0.3 mm for 24 hours gave only 9% yield; the reactivity could be restored with 2-3 drops of water added to the reaction mixture. Larger scale oxidations were carried out by adding every hour for 4 hours 8 g oxidant to 150 ml refluxing hexane

containing 6.5 g 2-octanol and then refluxing another 16 hours to secure 2-octanone of high purity in 84% isolated yield. Reactions were generally 3 times slower in methylene chloride than in hexane⁵.

Table I. OXIDATIONS BY SOLID SODIUM PERMANGANATE MONOHYDRATE^{a,b}

Substrate	Product	Solvent	Temp.(°C)	Time(h)	Yield(%)
1. 2-Octanol	2-Octanone	Hexane	69	2.5	95
2. Cyclohexanol	Cyclohexanone	Hexane	69	1.5	100
3. 5 α -Androstan-17 β -ol	5 α -Androstan-17-one	CH ₂ Cl ₂	41	24	84
4. 1-Octanol	Octanoic acid ^c	Hexane	69	5	67
5. Octyl aldehyde	Octanoic acid ^c	Hexane	69	4.5	77
6. Benzyl alcohol	Benzoic acid	Hexane	69	6	81
7. Benzaldehyde	Benzoid acid	Hexane	69	5	80
8. 2-Cyclohexen-1-ol	2-Cyclohexen-1-one	Hexane	69	24	47
9. 1-Octen-3-ol	1-Octen-3-one	Hexane	69	24	11
10. 1-Tridecene	Lauric acid ^c	Hexane	69	24	13
11. <u>trans</u> -Stilbene	Benzoic acid Benzaldehyde	CH ₂ Cl ₂	41	24	4 5
12. <u>n</u> -Butyl Sulfide	<u>n</u> -Butyl Sulfone	Hexane	69	24	91
13. <u>t</u> -Butylamine	2-Methyl-2-nitropropane	Hexane	69	24	76
14. Caproamide	No reaction	CH ₂ Cl ₂	41	24	-
15. 1-Decyne	No reaction	Hexane	69	24	-
16. 1,2-Epoxytridecane	No reaction	Hexane	69	24	-
17. <u>n</u> -Butylbenzene	No reaction	Hexane	69	24	-

^a Reactions were carried out using 3 mmol of substrate. ^b Except for runs 2 and 8, yields are based on weights of isolated product. ^c Work-up included an extraction of the hexane with dilute HCl/NaHSO₃.

References and Notes

1. F. M. Menger and C. Lee, J. Org. Chem., 44, 3446 (1979).
2. This material was used as obtained from the Carus Chemical Co., LaSalle, Illinois. We thank Carus for a free sample.
3. D. J. Sam and H. E. Simmons, J. Am. Chem. Soc., 94, 4024 (1972).
4. R. Stewart in "Oxidations in Organic Chemistry", K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, Part A, Chapter 1.
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