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FACILE OXIDATION OF AROMATIC RINGS BY $Mn_2(SO_4)_3$

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The sulphate of manganese (III) is easily prepared from $KMnO_4$[1]. It is reasonably stable and a powerful one electron oxidant (E_0 = 1.51V in 7.5M sulphuric acid[2]). Its applications in synthetic organic chemistry are surprisingly little explored[2].

In continuation of our investigations[3-9] on the pathways in aromatic ring oxidation, we have found that quinones could be obtained in good yields from the parent hydrocarbons by oxidation with $Mn_2(SO_4)_3$ under mild conditions (Table I). This reagent seems to be superior to chromic acid[2] and ceric ammonium nitrate[10], but somewhat less efficient than ceric ammonium sulphate[7]. Whereas 2-methylnaphthalene is oxidised to 2-methyl 1,4-naphthoquinone (55%) and 6-methyl 1,4-naphthoquinone (10%), 1-methylnaphthalene gives a mixture of 1-naphthaldehyde (40%) and 1,4-naphthoquinone (10%).

We have also observed the formation of 2-bromo 1,4-naphthoquinone in the manganese (III) oxidation of 1-bromonaphthalene (Table I) through a 1,2-shift similar to the one observed earlier[8] by us in the oxidation of naphthalene derivatives by ceric ammonium sulphate. This 1,2-shift, while mechanistically distinct from the NIH shift[11], seems to be a general feature of the cation radical involvement[8,12].

Preparation of 1,4-naphthoquinone:

To a solution of $MnSO_4 \cdot 4H_2O$ (2 g) in 50 ml 6M sulphuric acid at 0°C, $KMnO_4$ (200 mg) in water (10 ml) was added dropwise with stirring (30 minutes). The resulting reddish pink solution was stirred for another hour at 25°C [the operation was carried out without being exposed to bright light to avoid disproportionation of Mn(III)].

The above solution (~6mmol in Mn(III) by titrimetry) was mixed with acetonitrile (20 ml) and naphthalene (128 mg, 1mmol) in acetonitrile (20 ml) was added with stirring during 1 hr at 25°C and further stirred for 3 hr at 25°C. The pale yellow solution was transferred to a separatory funnel and extracted with ether. 1,4-naphthoquinone (m.p. 123-124°C, lit.[10] 123-125°C) was obtained by preparative TLC over silica gel (benzene).

Table I. $Mn_2(SO_4)_3$ Oxidation of Polycyclic Aromatic Hydrocarbons.

Substrate	Reaction conditions Temp. (°C)	Time (hr)	Product[a]	Yield	m.p. (°C)	Lit. m.p. (°C)	Ref. No.
Naphthalene	25	4	1,4-Naphthoquinone	75	123-4	123-5	10
Phenanthrene	25	4	9,10-Phenanthrenequinone	32	205-6	205-7	10
			1,4-Phenanthrenequinone	19	147-8	148-9	13
Anthracene	50	3	9,10-Anthraquinone	80[b]	284-6	284-6	10
Fluoranthene	50	3	Fluoranthenequinone	71	187-8	188	14
2-Methylnaphthalene	25	4	2-Methyl 1,4-naphthoquinone	55	105-6	105-7	15
			6-Methyl 1,4-naphthoquinone	10	90-1	90-1	16
1-Methylnaphthalene	25	10	1-Naphthaldehyde	40			
			1,4-Naphthoquinone	10	123-4	123-5	10
1-Bromonaphthalene	50	3	4-Bromo 1,2-naphthoquinone	17	153-4	154	17
			2-Bromo 1,4-naphthoquinone	15	129-30	130-1	18
			1,4-Naphthoquinone	23	124-5	123-5	10

[a] Products isolated by preparative TLC (silica gel/benzene) and identified by their IR and NMR spectra.

[b] Isolated by crystallization in glacial acetic acid.

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