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The Oxidation of α- and β-Methylstyrenes by Manganese(III) Acetate

Akira Kasahara, Ryu-ichi Saito, and Taeko Izumi
Department of Applied Chemistry, Faculty of Engineering, Yamagata University, Yonezawa, Yamagata 992

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Earlier studies established that, in acetic acid at 135 °C, α-methylstyrene (I) and β-methylstyrene (II) reacted with manganese(III) acetate to give lactone (III and IV),[1] which could also be obtained with the same reactions in refluxing acetic acid–acetic anhydride.[2] Heiba *et al*[1] suggested that the $\cdot CH_2COOH$ radical is produced directly by the thermolysis of the complex and that the great selectivity of $\cdot CH_2COOH$ radical toward addition to the olefin over allylic hydrogen abstraction leads to high yields of lactones. On the other hand, Gilmore and Mellor[3] reported that, in the presence of potassium bromide, cyclohexene reacts with manganese(III) acetate at 70 °C in acetic acid, thus leading to the formation of cyclohexenyl acetate as the major product. The finding that the potassium bromide-catalyzed oxidation of cyclohexene proceeded *via* allylic hydrogen atom abstraction led us to examine the reactions of I and II under similar conditions.

At 80 °C in acetic acid, I reacted slowly with manganese(III) acetate, but the addition of potassium bromide led a rapid reaction and to the formation of β-phenylallyl acetate (V) as the major product (70%); no evidence for any lactone formation was obtained. Using this same set of conditions, from II cinnamyl acetate (VI) (62%) and α-phenylallyl acetate (VII) (10%) were obtained. These results indicate that potassium bromid-catalyzed oxidation of allylic olefin by manganese(III) acetate proceeds *via* allylic hydrogen abstraction rather than *via* $\cdot CH_2COOH$ radical addition to the olefin.

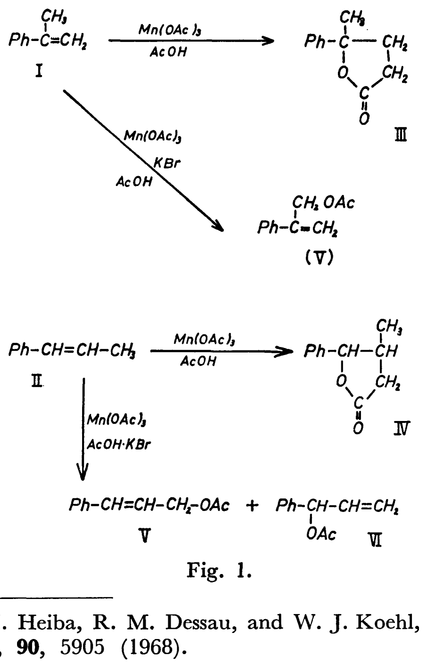

Fig. 1.

Experimental

Manganese(III) acetate was prepared by a modification of Christiansen's procedure.[3,4] β-Phenylallyl acetate (V) was prepared from α-methylstyrene by selenium dioxide oxidation;[5] bp 115—117 °C/7 mmHg (lit.[5] 112—113 °C/5 mmHg). Cinnamyl acetate (VI) was synthesized by esterifying cinnamyl alcohol with acetic anhydride (bp 124 °C/5 mmHg (lit.[6] bp 113 °C/2.4 mmHg)), while α-phenylallyl acetate (VII) was prepared by the esterification of the alcohol (from acrolein and phenylmagnesium bromide) with acetic anhydride (bp 106 °C/6 mmHg (lit.[6] bp 92 °C/2 mmHg)). Gas-chromatographic analyses were carried out on a column, silicon SE 30 (5% on celite), 1 m at 100 °C, with a Hitachi K-53 gas-chromatograph.

Oxidation of α-Methylstyrene (I). Manganese(III) acetate (5.0 g) in acetic acid (60 ml) was heated at 80 °C under nitrogen. To the stirred solution we then added I (1.2 g) and potassium bromide (0.25 g), and the solution was maintained at 80 °C until the color disappeared (*ca.* 6 hr). The reaction mixture was added to 500 ml of ether, which was then extracted four times with ice water. The ether layer was dried over anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator. The residual oil was distilled under reduced pressure, and the distillate was purified by gas-chromatography and identified as V (70% yields) by comparing the retention time on the gas-chromatogram and the infrared and NMR spectra with those of an authentic sample.

Oxidation of β-Methylstyrene (II). The oxidation of II was carried out in the manner described for I. On work-up, the reaction products contained VI (62% yields) and VII (10% yields), the infrared and NMR spectra and the retention time of which were identical with those of an authentic sample.

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