

Nitromethylation of Aromatic Hydrocarbons with Nitromethane–Manganese(III) Acetate

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Summary Treatment of aromatic hydrocarbons with nitromethane and manganese(III) acetate produces aryl nitromethanes by way of homolytic aromatic substitution involving the $\cdot\text{CH}_2\text{NO}_2$ radical.

THE direct introduction of certain α -substituted alkyl radicals (*e.g.*, carboxymethyl radicals) onto aromatic rings has been accomplished both by photochemical methods¹ and by the influence of certain metal salt oxidants.² Generally these processes either lead to low yields or suffer from competing side reactions.

We report that manganese(III) acetate can be used to promote the substitution of nitromethyl radicals onto aromatic rings [equation (1)] in a clean reaction leading to reasonably high yields. The Table shows the yields of the resulting aryl nitromethanes from a series of aromatic hydrocarbons, together with their relative rates of substitution obtained from competitive experiments.

Typically the reactions were performed by dissolving manganese(III) acetate³ (0.01 mol) in acetic acid (25 ml), adding to this a mixture of the appropriate hydrocarbon

(25 ml) and nitromethane (25 ml), and either refluxing or heating the mixture at constant temperature under nitrogen

TABLE

Nitromethylation of aromatic hydrocarbons with nitromethane–manganese(III) acetate^a

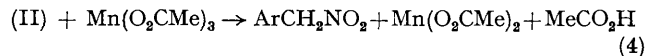
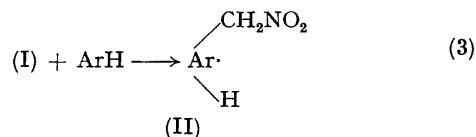
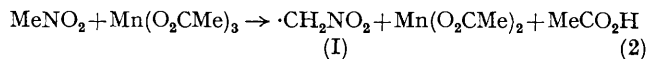
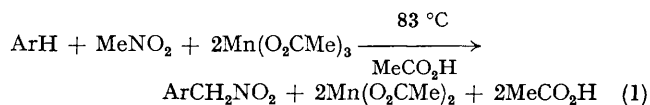
Hydrocarbon	ArCH ₂ NO ₂ / % ^b	Relative rate of substitution
C ₆ H ₆	78	1
PhMe	77 ^{c,d}	3.5
PhOMe	77 ^c	13.9
PhCl	20 ^c	0.37
PhNO ₂	0	—

^a At 83 °C with an excess of aromatic hydrocarbon and nitromethane in acetic acid solution. ^b Yields are based on manganese(III) acetate as limiting reagent and stoichiometry shown in equation (1). ^c Mixture of *o*- (60–70%) and *m*- and *p*- (30–40%) isomers. ^d Isolated yield 66%.

until the dark brown colour due to the manganese(III) salt changed to light yellow (typically 0.5–2 h). Removal of the salt by washing, and removal of solvent and excess of

reactants by evaporation yielded the crude aryl nitromethane directly.

Based on similarity to previously studied manganese(III) acetate systems² a free radical substitution mechanism is proposed [equations (2)—(4)]. The relative rates and the failure of this substitution with nitrobenzene suggest that the nitromethyl radical (I) exhibits appreciable electrophilic properties.



This reaction might well provide an alternative route to obtaining aryl nitromethanes which are generally synthesized by side chain substitutions on benzyl halides⁴ or nitriles.⁵

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