

Nitromethylation of Benzene Using Electrochemically Generated Manganese(III)

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The electrochemical oxidation of manganese(II) acetate in acetic acid containing 0.1 M lithium fluoroborate proceeds with high current efficiency at both graphite and platinum anodes, and the resulting solution of manganese(III) acetate, on admixture with nitromethane and benzene, produces phenylnitromethane with a current yield of 76 %. Potassium acetate (0.1 M) is also an excellent electrolyte, but is incompatible with the nitromethylation reaction; it may however be used in other applications of manganese(III).

The procedure recently reported by Kurz and Chen¹ for the nitromethylation of aromatic compounds, using a solution of manganese(III) acetate in a mixture of acetic acid, nitromethane and the aromatic compound, gives a more direct route to aryl nitromethanes than either of the two existing general methods,² both of which involve functional group modification. Unfortunately, attempts to regenerate manganese(III) from the manganese(II) formed during the reaction, or to initially generate manganese(III) *in situ* using a variety of oxidants *viz.* oxygen, ozone, potassium permanganate, thereby increasing the convenience of the reaction, were unsuccessful.¹ In this paper we report conditions which allow the manganese(III) to be generated electrochemically from manganese(II) acetate, and which are compatible with the subsequent use of the manganese(III) in the nitromethylation of benzene.

The preparation of phenylnitromethane by the nitromethylation of benzene using manganese(III) acetate is both simple and reliable.

* This investigation was carried out at the University of Lund, Sweden.

However, it appeared to us that in certain situations, *e. g.*, repeated synthesis or larger scale, it would be more convenient if the manganese(III) acetate could be generated *in situ* electrochemically from the more readily available manganese(II) acetate. Furthermore, since manganese(II) acetate separates out from the reaction medium during the nitromethylation reaction, it should be recoverable and recyclable in these situations. The electrochemical generation of manganese(III) from manganese(II) acetate in acetic acid containing potassium acetate as an electrolyte has been reported³ in a process for the manufacture of γ -butyrolactones from alkenes, but, as shown below, potassium acetate is incompatible with the nitromethylation reaction.

We selected a temperature at or above 83 °C for these studies, since Kurz and Chen had shown that this appeared to be the optimum temperature for the reaction. At 83 °C, a 0.1 M solution of manganese(II) acetate in acetic acid has a rather low conductivity and the presence of a good supporting electrolyte is essential to obtain an acceptable current density and electrolysis time. For convenience, a single compartment, jacketed beaker cell was used and the electrolyses were performed under constant current conditions. To minimize reduction of manganese(III) at the cathode, the area of the latter was very small compared to that of the anode. Both platinum and graphite anodes were used. Table 1 gives the electrolysis conditions and current efficiencies as a function of theoretical conversion (up to 60 %) for the generation of manganese(III) from manganese(II) acetate in the presence of a variety of readily

Table 1. Electrogeneration of manganese(III) from manganese(II) in acetic acid ^a

Added electrolyte/ concentration	Electrode material	Overall current efficiency /% (current efficiency per 2×10^{-3} F)		
		No. of F ($\times 10^3$) 2.0 (20 %)	(% of theoretical maximum) 4.0 (40 %)	6.0 (60 %)
LiBF ₄ /0.1 M	Pt	84	80(77)	79(77)
	C	94	91(87)	88(84)
KOAc/0.1 M	Pt	88	78(69)	72(58)
	C	93	87(82)	83(74)
Et ₄ NBF ₄ /0.02 M	Pt	87	80(72)	73(59)
	C	89	82(75)	76(65)
Et ₄ NNO ₃ /0.02 M	Pt	86	81(77)	70(47)
	C	92	83(74)	77(65)
NH ₄ NO ₃ /0.1 M	Pt	238	180(122)	132(35)
	Pt ^b		61	
None	C ^c		59	

^a Mn(OCOCH₃)₂·4H₂O (10 mmol) in CH₃CO₂H (100 ml); current density 4 mA cm⁻²; temperature 85–115 °C. ^b 1 mA cm⁻² at 250 V; ^c 2 mA cm⁻² at 250 V.

available supporting electrolytes, each of which was soluble up to 0.1 M. The current efficiencies in every case were very good, with in most cases a graphite anode giving a slightly higher value than a platinum anode. The anomalously high value for ammonium nitrate arises because this electrolyte can oxidise manganese(II) to manganese(III) (see Experimental). Both the nitrate ion and the ammonium ion appear to be necessary before this chemical oxidation occurs to any significant extent, since 0.1 M tetraethylammonium nitrate was much less reactive. The ability of the nitrate ion to oxidise manganese(II) has been used to prepare anhydrous manganese(III) acetate.⁴ Both tetraethylammonium fluoroborate and nitrate gave satisfactory results at a concentration of 0.02 M, but produced some manganese(IV), which does not promote nitromethylation, at a concentration of 0.1 M.

Having tested the suitability of several electrolytes for the electrolysis stage, we then examined the compatibility of these and other electrolytes with the nitromethylation reaction using manganese(III) acetate prepared chemically; the corresponding yields of phenylnitromethane are given in Table 2. While most conditions gave yields comparable to that obtained in the absence of added electrolyte (76 %), 0.1 M lithium fluoroborate and 0.1 M ammonium nitrate gave extremely high yields

(97 and 98 %, respectively), and 0.1 M potassium acetate gave an extremely low yield (8 %). If the nitromethylation reaction follows the mechanism suggested in Ref. 1, then replacement of acetate by the nitromethyl anion in the manganese(III) coordination may be necessary before nitromethylation can occur, and increasing the acetate ion concentration, e.g. potassium acetate, would probably inhibit such an exchange, and hence the reaction. The

Table 2. Nitromethylation of benzene using manganese(III) acetate ^a

Added electrolyte	Conc. /M	Yield of PhCH ₂ NO ₂ /%
None	—	76
LiBF ₄	0.02	73
	0.1	97
NH ₄ BF ₄	0.02	63
	0.1	72
Et ₄ NBF ₄	0.02	66
	0.02	26
Et ₄ NNO ₃	0.02	55
	0.1	98
LiNO ₃	0.02	55
	0.1	66
KOAc	0.1	8

^a Mn(O·CO·CH₃)₂·2H₂O (2.0 mmol) in CH₃CO₂H (50 ml), CH₃NO₂ (50 ml) and C₆H₆ (40 ml) at 83 °C in the presence of various electrolytes.

reason for the beneficial effect of lithium fluoroborate while lithium nitrate and ammonium fluoroborate have little effect is less obvious, and since the detailed mechanism of the reaction is unknown, we prefer not to speculate further. Since the high yield with ammonium nitrate is due to reoxidation of manganese(II) by nitrate ion* we selected 0.1 M lithium fluoroborate for the combined electrochemical-chemical procedure.

For the preparation of phenylnitromethane, the electrochemical generation of manganese(III) was taken to 40 % theoretical conversion, with current efficiencies of 93 and 84 % for graphite and platinum anodes, respectively. After removing the electrodes, nitromethane and benzene were added and the temperature was maintained at 83 °C for 3 h; in most cases the dark colour had disappeared after 1 h. The current yield of phenylnitromethane was 76 % in both cases. Using 0.1 M potassium acetate and a graphite anode, the current yield was 4 %.

Our attempts to generate manganese(III) electrochemically in a mixture of acetic acid, nitromethane and benzene, in the absence of added electrolyte, were disappointing. The maximum current was very low (0.3 mA cm⁻²) and the phenylnitromethane produced (33 %) was contaminated by other products. A similar result was obtained in the presence of 0.02 M tetraethylammonium fluoroborate.

The electrogeneration of manganese(III) in the presence of 0.1 M lithium fluoroborate for subsequent use in the nitromethylation of benzene is thus a satisfactory alternative to using manganese(III) acetate prepared chemically. The other electrolytes, although less satisfactory for the nitromethylation reaction, may be compatible with other reactions utilising manganese(III), e.g. the synthesis of γ -butyrolactones from alkenes,^{3,5,6} of dihydrofurans from alkenes and 1,3-dicarbonyl compounds,⁷ of 1,4-diketones from enolisable ketones and enol esters,⁸ and allylic acetates from cycloalkenes,⁹ particularly potassium acetate which is frequently used to raise the boiling point of solutions of manganese(III) acetate in acetic acid,^{3,5} and which has already been used³ in

the electrochemical generation of manganese(III). We are currently extending the present work on the nitromethylation reaction to other aromatic compounds, and exploring the wider utility of electrogenerated manganese(III).

EXPERIMENTAL

The power supply for the electrolyses was a Philips PE1213 unit operating in the controlled current mode (maximum voltage 250 V). GLC analyses were performed on a Hewlett-Packard 5830A gas chromatograph with a 18850 g.c. terminal, using a 3 m column packed with 5 % OV17 on Chrom. W (80–100 mesh) and a temperature of 150 °C.

Procedure for the electrochemical generation and analysis of manganese(III). Manganese(II) acetate tetrahydrate (2.45 g, 10 mmol) and the supporting electrolyte (see Table 1) in acetic acid (100 ml) were heated with stirring in a jacketed beaker-type cell, using boiling 1,2-dichloroethane to maintain the temperature at or above 83 °C. The anode was either a half-cylindrical platinum sheet (ca. 50 cm²) or a planar graphite plate (ca. 25 cm²) and the cathode was a platinum wire positioned 1–2 cm from the anode. The electrolyses were performed at a constant current density of ca. 4 mA cm⁻², except when no supporting electrolyte was present when only 1 and 2 mA cm⁻², for platinum and graphite anodes, respectively, could be achieved using the maximum voltage of the power supply. Normally the applied voltage was 67–96 V for a platinum anode and 37–77 V for a graphite anode, and the temperature was 85–115 °C, both depending upon the supporting electrolyte being used.

The electrolysis was stopped periodically (0.2, 0.4, 0.6 F mol⁻¹) and duplicate 5.0 ml samples were removed for titration. (The pipette was filled twice with the hot solution and discharged back into the cell before the two samples were withdrawn). The samples were discharged into a solution of potassium iodide (1.0 g) in 0.5 M sulfuric acid (20 ml) and the liberated iodine was titrated with 0.02 M sodium thiosulfate solution using starch indicator.

Separate tests, using acetic acid only, showed that the sample withdrawn from acetic acid at 83 °C using the above procedure was 4.8 % lower (by weight) than a sample withdrawn from acetic acid at 22 °C, due largely to the change in density of the acetic acid. The analytical results given for manganese(III) are not corrected for this sampling error and are probably low by about 5 %.

The current efficiencies for the generation of manganese(III) from manganese(II) in the presence of a range of supporting electrolytes, as well as in the absence of any added elec-

* A 73 % yield of phenylnitromethane was obtained when manganese(II) was used with 0.1 M ammonium nitrate.

trolyte, as a function of the number of Faradays passed, are given in Table 1.

The above electrolysis conditions were found to be unsatisfactory for the generation of manganese(III) in the presence of 0.1 M Et_4NBF_4 and 0.1 M Et_4NNO_3 . In both of these cases, the liberation of iodine in the analytical procedure was accompanied by the formation of a fine solid suspension which also reacted, albeit rather slowly, with thiosulfate. This behaviour is typical of the formation of manganese dioxide.

In the presence of 0.1 M NH_4NO_3 , manganese(III) was generated without electrolysis, thus accounting for the current efficiency exceeding 100% in the presence of this electrolyte. At 83°C, the yield of manganese(III) was 18, 26, 34 and 43% (based on available manganese) after 0.5, 1, 2, and 3 h, respectively. The same result was obtained when the control was performed under nitrogen. In the presence of 0.1 M Et_4NNO_3 , the generation of manganese(III) was only 4.5% complete after 2 h.

Electrolysis in the presence of 0.1 M potassium acetate and using a graphite anode at higher current densities caused the solution to boil, but high current efficiencies appeared to be maintained, *viz.* 90 and 86% for 8 and 16 mA cm^{-2} , respectively, at 0.2 F mol^{-1} , *cf.* 93% for 4 mA cm^{-2} (94°C).

Manganese(III) acetate dihydrate. This was prepared by a literature procedure¹⁰ (using manganese(II) acetate and potassium permanganate) and was dried over solid potassium hydroxide. Iodometric determination of the manganese(III) content gave 20.1–21.4%; $\text{Mn}(\text{O}(\text{COCH}_3)_2 \cdot 2\text{H}_2\text{O})$ requires 20.5% Mn.

Nitromethylation of benzene using manganese(III) acetate. Manganese(III) acetate dihydrate (0.536 g, 2 mmol) and the added electrolyte (see Table 2) were dissolved by heating in acetic acid (50 ml), and then nitromethane (50 ml) and benzene (40 ml) were added. The solution was maintained at 83°C for 3 h, but in most cases the solution became light brown after 0.5 h. The GLC standard, 1,2,3-trimethoxybenzene (1.00 mmol), was added as a solution in nitromethane (2.00 ml), to the cooled mixture. The yields of phenylnitromethane produced in the presence of various electrolytes, and in the absence of added electrolyte, are given in Table 2. For comparability to the electrolytic generation of manganese(III), the concentration of added electrolyte relates to the solution in acetic acid only.

When manganese(II) acetate was used instead of manganese(III) acetate in a 0.1 M NH_4NO_3 solution, the yield of phenylnitromethane, based on manganese, was 73%.

Nitromethylation of benzene using electrochemically generated manganese(III). A solution of manganese(II) acetate tetrahydrate (1.47 g, 6 mmol) and the supporting electrolyte in acetic acid (60 ml) was heated to 83°C and electrolysed as described above at 4 mA cm^{-2}

until 2.4×10^{-3} F had passed (40% conversion). Two 5.0 ml samples were withdrawn and analysed iodometrically. The electrodes were removed, nitromethane (50 ml) and benzene (40 ml) were added, and heating was continued for 3 h. The mixture was analysed for phenylnitromethane as described above.

(a) 0.1 M Lithium fluoroborate and graphite anode: current efficiency for generation of Mn(III) 93%, current yield of phenylnitromethane 76% [82% yield based on Mn(III) analysis].

(b) 0.1 M Lithium fluoroborate and platinum anode: current efficiency 84%, current yield 76% [90% yield based on Mn(III) analysis]. The product also contained an impurity (4.5%) of shorter retention time than phenylnitromethane.

(c) 0.1 M Potassium acetate and graphite anode: current efficiency 85%, current yield 4% [5% yield based on Mn(III) analysis].

Attempts to generate manganese(III) by electrolysis of manganese(II) in acetic acid containing nitromethane and benzene, and in the absence of an additional electrolyte, were largely unsuccessful. The solution had a very low conductivity and the maximum current was 15 mA at an applied voltage of 250 V for a 50 cm^2 platinum anode. Electrolysis under these conditions for 6 h produced phenylnitromethane with a current yield of 33%; the product also contained two significant impurities, phenyl acetate and most probably phenol. When 0.02 M tetraethylammonium fluoroborate was included, solid separated when the benzene was added and results similar to those obtained in the absence of electrolyte were obtained.

Phenylnitromethane. The method of Kornblum *et al.*¹¹ as modified by Cameron and Hildyard¹² was used. Benzyl bromide (8.6 g) was added to a solution of sodium nitrite (7.2 g), urea (13.7 g) and phloroglucinol (13.4 g) (all dried *in vacuo* at 100°C) in dry dimethylformamide (175 ml) at -15°C, and the solution was kept at 0°C for 4 h. After pouring into ice-water (600 ml), the product was extracted with ether (150, 100 and 100 ml) and the combined extracts were shaken with 15% aqueous potassium hydroxide (250 ml) for 15 h. The aqueous layer was removed and the ether layer was shaken with more 15% aqueous potassium hydroxide (250 ml) for a further 6 h. The aqueous extracts were combined, carefully neutralized with cooling by acetic acid, and the resulting suspension was extracted into ether (200, 200 and 100 ml). After drying, the extract was concentrated and the residue, which contained some acetic acid, was distilled b.p. 67–71°C/0.1 mmHg (lit.¹¹ b.p. 76°C/2 mmHg) to give phenylnitromethane (96.5% pure by GLC), δ (CCl_4) 5.24 (s, CH_2NO_2) and 7.34 (C_6H_5).

Acknowledgements. The author wishes to thank the Ciba-Geigy Fellowship Trust for the award of a Senior Fellowship, Professor L.

Eberson, University of Lund, Sweden, for his hospitality, and the University of Edinburgh for leave of absence.

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Received November 29, 1978.