Nitration of alkylbenzenes catalysed by mercury(II), thallium(III) and lead(IV)

Michael W. Greenop and C. Barry Thomas *
Department of Chemistry, University of York, Heslington, York, UK YO1 5DD

The nitration of alkylbenzenes, catalysed by mercury(II), has been studied in a range of solvents. Using toluene as a model, catalysis, accompanied by a corresponding change in isomer ratio, is observed in a nitric acid–acetic acid system and also when dilute nitric acid is employed as the solvent. The results are consistent with a mercuration–nitrosodemercuration sequence occurring on the aromatic ring. Under more forcing nitrating conditions catalysis is not observed. With other alkylbenzenes there is little evidence of catalysis though a complication, with compounds possessing benzylic hydrogen atoms, is that reaction occurs on the side chain. This may remove nitrosating species from the system. Thallium(III) and lead(IV), which are isoelectronic with mercury(II), catalyse nitration without affecting the isomer distribution.

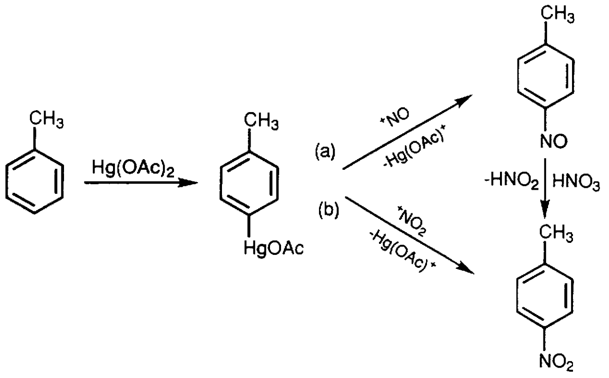
A frequent problem in electrophilic aromatic substitution is that a mix of isomers is obtained. Not only does this reduce the yield of a desired product but it also has a considerable impact on the ease and cost of purification of that material. Any means by which isomer distribution can be controlled and a particular isomer favoured has obvious synthetic advantages. As a part of our studies of selective aromatic substitution we have re-examined the nitration of alkylbenzenes with particular emphasis on the use of added metal salts to control isomer ratios.

That mercury can exert a catalytic effect on the nitration of benzene was first demonstrated as long ago as 1908.[1] Subsequently, the effect of a number of other metal additives has been examined[2,3] but only mercury salts were found to have a catalytic effect. Extension of this work to alkylbenzenes showed, not only the acceleration of the reaction, but also that there is a marked influence on the isomer ratio.[4]

In their definitive work on the nitration of toluene in the presence of mercury(II) salts, Stock and Wright demonstrated that the role of the electrophilic mercury salt is to compete with a nitronium ion, present under normal nitrating conditions, to give an arylmercury compound.[5] This then undergoes rapid nitrosodemercuration and the resultant nitrosotoluenes are oxidised to nitrotoluenes (Scheme 1, for the *para*-isomer). It is perhaps surprising that the mercury group is displaced by a nitrosonium ion rather than the more powerful nitronium electrophile. Indeed Olah suggests that nitrodemercuration must also be occurring (Scheme 1, path b) under these conditions.[6] However, the suppression of the catalytic reaction by the addition of urea and the results of a study of the reactions of arylmercury compounds with nitronium and nitrosonium salts[5] all suggest that nitrosodemercuration is far and away the dominant process.

The isomer distribution of nitrotoluenes corresponds closely to the ratio of tolylmercury compounds obtained on mercuration of toluene under similar conditions[7] consistent with mercuration being the first step in the overall conversion. However, whilst the mercury(II) catalysed rate favours production of the *para* isomer (typically the *ortho*:*meta*:*para* ratio is 36:13:51) compared to direct nitration of toluene in acetic acid (typical ratio 58:3:39), there are still very large quantities of the other two components.

Two other metal ions resemble mercury(II) in their organic chemistry.[8] Thallium(III) and lead(IV) are both iso-electronic with mercury(II) and both have been shown to metalate aromatic rings under relatively mild conditions.[9,10] In addition it has been shown that thallium substituents can be displaced from a benzene ring by sources of the nitrosonium ion[11] and a 'one-pot' production of nitroalkylbenzenes using thallium(III) to control isomer distribution has been described.[†,12] What is more, thalliation[13] and plumbylation[6,10,14] are very much more selective for substitution in the *para* position than is mercuration. In this paper we examine the potential for increasing further the selectivity in nitration by using catalytic amounts of these heavy metal salts.



Scheme 1

Results and discussion

Repeating the experiments of Stock and Wright[5] under both mercury(II) catalysed and uncatalysed conditions gave results in good agreement with those reported earlier other than somewhat different overall yields of nitrotoluenes (Table 1, experiments 1 and 2). Two extra products, benzaldehyde and benzyl acetate, were found but in trivial amounts (0.1% and 0.2%, respectively).

Increasing the amount of catalyst further leads initially to higher conversions but eventually the yield of nitrotoluenes falls, possibly because of problems of dimercuration. The essentially constant isomer ratio suggests that mercuration of toluene competes very effectively with the classical nitration route involving a nitronium ion.

A mixed nitric acid–sulfuric acid medium is more commonly

[†] In this paper the mechanism of this process was said to involve nitrodethalliation. In the light of more recent work it would seem more likely that nitrosodethalliation is occurring.

Table 1 Catalytic effect of mercury(II) on the nitration of toluene in acetic acid at 80 °C[a]

Expt.	$PhCH_3:Hg^{2+}$ [b]	*ortho*:*meta*:*para*[c]	Yield[c] (%)
d	—	58:3:39	7
1	—	55:4:41	15
d	1:0.016	36:12:52	64
2	1:0.016	37:11:52	44
3	1:0.032	36:11:53	61
4	1:0.125	38:11:51	51

[a] Experiments were carried out by heating the toluene–nitric acid–acetic acid mixture (mol ratio 1:1:5) at 80 °C for 2 h in the presence, or absence, of mercury(II) acetate. [b] Mol ratio. [c] Nitrotoluenes. [d] Results from the work of Stock and Wright.[5]

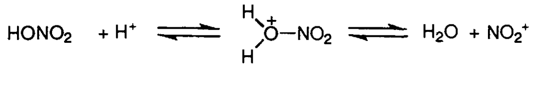
Table 2 Products from the mercury(II) catalysed nitration of toluene in aqueous nitric acid at 80 °C[a]

Expt.	$HNO_3:H_2O$[b]	*ortho*:*meta*:*para*[c]	Yield[c] (%)
5	1:0.36	55:5:40	93
6	1:1.25	46:6:48	77
7	1:2.5	40:6:54	41
8	1:5.0	30:6:64	19
9	1:5.0[d]	31:7:62	47
10	1:10	28:9:63	8
11	1:10[e]	54:5:41	0.5

[a] Experiments carried out by stirring toluene, nitric acid and water (mol ratio toluene:nitric acid 1:2.4) at 80 °C in the presence of mercury (II) acetate for 2 h. [b] Mol ratio. [c] Nitrotoluenes. [d] Reaction time 8 h. [e] Mercury(II) acetate omitted.

used[15,16] for nitration than the acetic acid solvent employed above. However, attempts to catalyse such a system proved unsuccessful.‡ Not only was the isomer distribution unchanged by inclusion of mercury(II) but the yield of nitrotoluenes fell. Lower temperature and reduced amounts of sulfuric acid only decreased the yield of nitrotoluenes further with no change in isomer distribution. In addition, substantial quantities of 2,4- and 2,6-dinitrotoluene were produced even at 30 °C.

The sulfuric acid serves to ensure a high concentration of nitronium ion (Scheme 2).[15] Using nitric acid alone will reduce



$$HONO_2 + H^+ \rightleftharpoons H_2\overset{+}{O}{-}NO_2 \rightleftharpoons H_2O + NO_2^+$$

Scheme 2

substantially that concentration and perhaps allow mercuration to compete. However, the effect of mercury(II) on product distribution was still very limited. Diluting the nitric acid with water to displace the equilibrium in Scheme 2 to the left proved more successful (Table 2), the isomer distribution showing considerable modification.

Despite the claim that direct nitrosation of an aromatic ring is confined to highly activated substrates such as phenols and amines[16] there is a report of a kinetic study of the supposed nitrosation of toluene though products were not identified.[17] We therefore checked that the results of experiment 10 did not stem simply from nitrosodeprotonation, a process favoured by dilute acid. Omitting the mercury(II) salt gave some nitrotoluenes (experiment 11) though in very low yield and the isomer ratio was similar to that obtained in more concentrated acid. Either direct nitration can still occur or nitrosation, followed by oxidation, has a very similar selectivity for the three positions.

The requirement for mercury(II) catalysed nitration seems to be a solvent system in which nitronium ion concentration is kept low enough for mercuration to be competitive yet one in which there is sufficient nitrosonium ion present to displace a mercury substituent. Diluting the nitric acid slows down the rate of the conversion though this can be offset (experiment 9) by longer reaction times.

We also employed an acetic anhydride–nitric acid medium for nitration. Whilst good yields of nitrotoluenes were obtained (70% after 2 h at 0 °C) inclusion of mercury(II) acetate in the system had almost no effect. Trifluoroacetic acid was also investigated as a potential solvent. This strong acid has the advantage, not only that nitric acid can be formed *in situ* if sodium nitrate is added to the solvent, but that ligand exchange on the mercury results in a more powerful and hence more competitive metal electrophile. Stirring sodium nitrate and toluene in trifluoroacetic acid at 80 °C gave a reasonable yield of nitrotoluenes with an isomer ratio typical of normal nitration (experiment 12, Table 3). Addition of mercury(II) acetate resulted in a small change to that ratio (experiment 13) but a large reduction in the yield of nitrotoluenes, in part, at least, through the formation of a black tar. The NMR spectrum of the tar shows the presence of methyl groups bonded to aromatic rings but nothing else is apparent. We suspect that polymerisation of toluene occurs through an electron-transfer process similar to those reported with thallium(III)[18] and lead(IV)[19] in trifluoroacetic acid.

Since mercury(II) catalysed nitration appears to require the presence of nitrosonium ions in the system we also looked at the behaviour of toluene in a solution of sodium nitrite in trifluoroacetic acid. Alone (experiment 14) these reagents gave a low yield of nitrotoluenes though the isomer distribution differs somewhat from that obtained by direct nitration (*cf.* experiment 12). Perhaps this ratio is that of initial nitrosoation followed by oxidation. Unexpectedly there was a significant formation of benzaldehyde which we believe to be due to interaction between nitrogen oxides and the alkyl side-chain (*vide infra*). A catalytic amount of mercury(II) acetate had a major effect on product distribution. Nitrotoluene yields were not enhanced but benzaldehyde production was virtually eliminated and the isomer ratio changed substantially.

One drawback to mercury(II) catalysis is that the isomer ratio of mercuration dictates the ratio of the nitrotoluenes[5] and this reaction is frequently reversible. The result is thermodynamic rather than kinetic control with substantial amounts of *ortho*- and *meta*-isomers being formed. The reactions of the isoelectronic thallium(III) and lead(IV) salts tend to be much more selective for the *para*-position.[13,14] We thus investigated whether these metal ions could influence product distribution.

Replacing mercury(II) with lead(IV) or thallium(III) acetate under the conditions in Table 1 showed that both metal ions catalyse the production of nitrotoluenes by a factor of about four but have no influence on the isomer distribution. At least in the case of thallium(III), it does not seem to matter how much catalyst is present. Varying the toluene:catalyst ratio from 1:0.06 down to 1:0.001 04 gave essentially the same yield and isomer distribution. The isomer ratio suggests that substitution occurs by nitrodeprotonation and we suspect that catalysis stems from an increase in the effective nitronium ion concentration. A possible explanation is that rapid ligand exchange on the metal[14,20] leads to a labile metal nitrate complex from which nitronium ion is formed (Scheme 3). The complex itself is unlikely to be the effective nitrating agent as

---

‡ Full details of these, and some of the other, experiments are deposited as supplementary material at the British Library [Supp. Pub. No. 57099 (3 pp.)]. For details of the deposition scheme, see 'Instructions for Authors (1955)', *J. Chem. Soc., Perkin Trans. 2*, 1995, issue 1.

Table 3 Products from the nitration of toluene in trifluoroacetic acid in the presence of sodium nitrate and sodium nitrite[a]

Expt.	Additive	$PhCH_3:Hg^{2+}$	*ortho*:*meta*:*para*[b]	Nitrotoluenes[c] (%)	Benzaldehyde[c] (%)
12	$NaNO_3$	—	56:2:42	61	—
13	$NaNO_3$	1:0.016	46:6:48	13	—
14	$NaNO_2$	—	41:8:51	7	4
15	$NaNO_2$	1:0.016	21:14:65	5	1

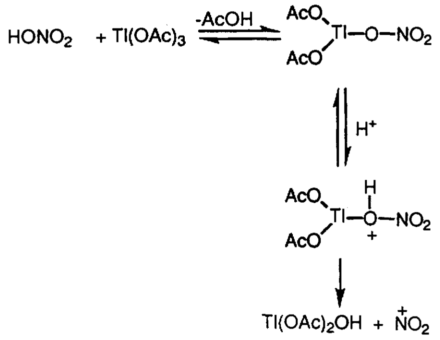
[a] Reactions carried out by heating toluene, trifluoroacetic acid and the appropriate sodium salt (mol ratio 1:5:1) at 80 °C for 4 h. [b] Nitrotoluenes. [c] Yield.

Table 4 Products from oxidation of alkylbenzenes (PhR) in dilute nitric acid[a] and in acetic acid–nitric acid[b] at 80 °C

Expt.	R	Solvent	*ortho*:*meta*:*para*[c]	Alkylnitrobenzenes[d] (%)	Other products (%)
16	C_2H_5	H_2O	44:7:49	31	$PhCH(CH_3)NO_2$ (7)[f]
17	C_2H_5	H_2O[e]	39:7:54	27	$PhCH(CH_3)NO_2$ (6)[f]
18	$CH(CH_3)_2$	H_2O	27:7:66	8	$PhCOCH_3$ (16), $PhC(Me){=}CHNO_2$ (12)[f]
19	$CH(CH_3)_2$	H_2O[e]	24:8:68	8	$PhCOCH_3$ (8), $PhC(Me){=}CHNO_2$ (6)[f]
20	$C(CH_3)_3$	H_2O	16:13:71	36	—
21	$C(CH_3)_3$	H_2O[e]	12:15:73	50	—
22	$C(CH_3)_3$	CH_3CO_2H	14:9:77	52	—
23	$C(CH_3)_3$	CH_3CO_2H[e]	12:11:77	57	—

[a] Mol ratio alkylbenzene:nitric acid:water 1:3:9. [b] Mol ratio alkylbenzene:nitric acid:acetic acid 1:1:5. [c] Alkylnitrobenzenes. [d] Yield. [e] $Hg(OAc)_2$ present: ratio alkylbenzene:$Hg(OAc)_2$ 1:0.0125. [f] Polymeric material also present.

steric factors would undoubtedly influence isomer distribution to disfavour the *ortho*-isomer.

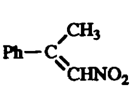


Scheme 3

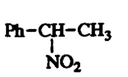
Finally we looked to see whether the mercury(II) catalysis of the nitration of toluene can be extended to other alkylbenzenes choosing ethylbenzene, cumene and *tert*-butylbenzene as examples. Mercuration for all three substrates is highly selective for *para*-substitution when mercury(II) trifluoroacetate is used as the electrophile.[6]

Oxidising ethylbenzene in dilute nitric acid at 80 °C for 2 h gave the three isomeric ethylnitrobenzenes in reasonable yield (Table 4). Adding mercury(II) acetate did not affect the overall conversion but did alter the isomer ratio slightly. In addition, besides unreacted starting material, GC showed the presence of one other component (*vide infra*).§ Cumene gave similar results: in dilute nitric acid a low yield of the three nitrocumenes was obtained, mercury(II) having very little effect on the conversion or the isomer ratio. In addition two other products were seen by GC. One was identified by GC–MS as acetophenone and the second appears to be the nitro-α-methylstyrene (**1**).

Nitration of *tert*-butylbenzene in aqueous nitric acid and in nitric acid–acetic acid followed a broadly similar pattern. Substantial yields of nitrated products were obtained and addition of mercury(II) acetate had only a limited effect on the isomer ratio or the yield. In contrast to ethylbenzene and cumene no other products were detected and overall accountability was high (> 90%).

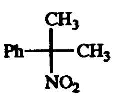


1



$$Ph{-}\underset{NO_2}{CH}{-}CH_3$$

2



$$Ph{-}\overset{CH_3}{\underset{NO_2}{C}}{-}CH_3$$

3

When ethylbenzene and cumene were nitrated, unlike toluene and *tert*-butylbenzene, polymeric materials were formed and extra components were observed on the GC trace. Attack on the side chains of alkylbenzenes has been noted in two related studies. Stock and Wright found 1,2-dimethylbenzene to undergo reactions on the side-chain though this process was effectively suppressed by the presence of mercury(II),[5] whilst Olah, observed the formation of acetophenone from ethylbenzene.[6] We believe our extra component in the ethylbenzene system to be 1-nitro-1-phenylethane (**2**). It is a minor component when the solvent is dilute nitric acid but when acetic acid–nitric acid was employed it made up some 70% of the product. We were unable to isolate it in a pure state nor to prepare an authentic sample,¶ but its ^1H and ^{13}C NMR and mass spectra are consistent with the structure and in good agreement with reported spectra.[21] Substitution in the side-chain appears to be due to a radical process involving nitrogen oxides. Addition of urea, to destroy any nitrous acid, and the removal of nitrogen oxides by passing air through the solution eliminated reactions on the alkyl group.

The suppression of side-chain attack by mercury(II), observed previously with 1,2-dimethylbenzene,[5] can be attributed to mercuration occurring easily on that substrate and nitroso-demercuration mopping up any nitrogen oxides and nitrous

---

§ Overall accountability was significantly reduced in experiments 16–19 by the formation of a polymer believed to be polystyrenes.

¶ The compound was unstable which may explain the polystyrene formation during nitration. Styrene formed by elimination from **2**, would polymerise easily under the reaction conditions. Attempts to synthesise **2** by reaction of 1-bromo-1-phenylethane with sodium nitrite gave the same compound as was obtained from nitration but in a complex mixture of products from which isolation did not prove possible.

acid. With ethylbenzene mercuration appears unable to compete with direct nitration allowing side-chain substitution to occur.

The analogous compound **3** was not found from cumene possibly because it decomposes to α-methylstyrene extremely readily. The formation of **1** can then result from attack on the double bond by the nitronium ion. Reaction of α-methylstyrene with dilute nitric acid under the same conditions gave both acetophenone (30%) and **1** (21%) together with a substantial amount of a yellow polymeric solid.

In a radical substitution on the side-chain it is the benzylic site we would expect to be the most reactive. It is thus no surprise that *tert*-butylbenzene, which lacks an appropriate hydrogen, substitutes only in the ring. It is somewhat unexpected therefore that the methyl group in toluene is unreactive. However, in a sodium nitrite–trifluoroacetic acid medium, which one would anticipate being rich in nitrosating species, toluene does behave consistently. Benzaldehyde is produced in significant amounts and its formation is suppressed by the addition of mercury(II) to the system.

This work has demonstrated that the mercury(II) catalysed nitration of toluene can occur under other conditions, *e.g.* dilute nitric acid, in which a significant amount of nitrosating species is present. Reaction does not proceed rapidly in dilute nitric acid but *para* substitution is favoured. The iso-electronic electrophiles, thallium(III) and lead(IV) have no effect on the isomer ratio though both do accelerate nitration, most plausibly by increasing the concentration of nitronium ion. The catalytic effect on alkylbenzenes with longer side-chains than methyl is scarcely noticeable. In cases where benzylic hydrogen is present side-chain substitution can be a complication.

Experimental

Analyses

GC analyses were carried out on a Philips PU 4500 chromatograph fitted with a flame ionisation detector. Two 2.7 m × 0.2 cm columns were employed for the separations. One was packed with 10% diethylene glycol adipate (DEGA) absorbed on 100–120 mesh Gas Chrom Q (analysis of toluene products), the second with 10% Carbowax 20M absorbed on the same material (analyses of products from other alkylbenzenes). Mass spectra were recorded on a Kratos MS3074 spectrometer coupled, *via* a jet separator, to a Pye 104 GC. ^1H and ^{13}C NMR spectra were recorded as solutions in deuteriochloroform on a JEOL FX90Q spectrometer.

Materials

Toluene (Fisons AnalaR grade), ethylbenzene (Fisons), cumene (Fisons), *tert*-butylbenzene (Aldrich) and α-methylstyrene (Aldrich) were commercial samples which were checked for purity before use. Commercial samples of 2-, 3- and 4-nitrotoluenes, 2- and 4-nitroethylbenzenes and 4-*tert*-butylnitrobenzene were used as reference materials. The other nitroalkylbenzenes were identified on the basis of their mass spectra.[22] Mercury(II) acetate (Fisons), thallium(III) acetate (Aldrich) and lead(IV) acetate (Fisons) were commercial reagents and were used without purification. Nitric acid (S.G. 1.5), sulfuric acid (S.G. 1.84) and acetic acid (AnalaR grade) were obtained from Fisons.

Nitrations

A typical reaction in acetic acid was carried out as follows. Toluene (0.02 mol), acetic acid (0.1 mol) and, where appropriate, mercury(II) acetate (0.000 32 mol) were weighed into a flask, nitric acid (0.02 mol) added, and the resultant mixture heated at 80 °C. After 2 h the mixture was poured into water (50 cm^3), sodium hydrogen carbonate was added to neutralise the acids and the solution was extracted with diethyl ether (2 × 20 cm^3). After drying ($MgSO_4$) the solvent was removed and the resultant liquid analysed by GC using acetophenone as an internal standard.

When reactions were carried out in mixed sulfuric–nitric acids the nitrating mixture was made up using nitric acid (0.02 mol) and sulfuric acid (0.02 mol) and the mixture was added cautiously to toluene (0.02 mol) containing an appropriate amount of mercury(II) acetate. After heating at 30 °C for 2 h work-up was as for ethanoic acid solutions. Similar procedures were used for reactions in nitric acid and in nitric acid–water mixtures.

In some instances acetic anhydride was employed as solvent. In these cases nitric acid (0.02 mol) was cautiously added to ethanoic anhydride (0.03 mol) cooled in ice and the nitrating mixture added to cooled toluene (0.02 mol). After stirring at 0 °C for 2 h the mixture was poured into water, stirred for 10 min to ensure complete hydrolysis of the anhydride and then worked-up in the usual way.

In the nitrations of ethylbenzene a fourth product was present. This was identified as 1-nitro-1-phenylethane on the basis of NMR and mass spectra of the crude product: δ_H 1.85 (3 H, d, *J* 7.0 Hz, CH_3), 5.65 (1 H, q, *J* 7.0 Hz, CH) and 7.2–7.5 (5 H, m, ArH); δ_C 18.6 (CH_3), 85.5 (CH), 125.8, 127.2, 127.5 and 144.1 (aromatic C); *m/z* 105 (100, M − NO_2), 104 (24, M − NO_2 − H), 103 (22, M − NO_2 − H_2), 79 (25, $C_6H_7^+$), 77 (33, $C_6H_5^+$) and 51 (20, $C_4H_3^+$), *cf.* ref. 21.

Nitration of cumene gave, besides the expected nitrocumenes, acetophenone and a fifth component which was isolated as a yellowish liquid by repeated column chromatography using first 80% dichloromethane and 20% hexane and then pure hexane as eluents. This, whilst giving a single GC peak, appeared to be a mixture of (*E*)- (major) and (*Z*)- (minor) 1-nitro-2-phenylpropane; δ_H 2.19 (d, *J* 1.2 Hz, CH_3 minor isomer), 2.63 (d, *J* 1.6 Hz, CH_3 major isomer), 7.29 (q, *J* 1.6, $CHNO_2$ major component) and 7.44 (br s, C_6H_5); *m/z* 163 (11%, $M^{\cdot +}$), 133 (33, M − NO), 117 (61, M − NO_2), 115 (100, M − NO_2 − H_2) 91 (75, $C_7H_7^+$), 77 (46, $C_6H_5^+$) and 51 (42, $C_4H_3^+$).

Acknowledgements

We thank the SERC and A. H. Marks Ltd for financial support to M. W. G.

References

1 R. Wolffenstein and O. Boeters, German Pat., 194 883; *Chem. Abstr.*, 1908, **2**, 1861.

2 S. Tsutsumi and E. Iwata, *J. Chem. Soc. Jpn., Pure Chem. Sect.*, 1951, **72**, 141.

3 T. Osawa, T. Yoshida and U. Namba, *Kogyo Kagaku Kyokaishi*, 1966, **27**, 162.

4 H. Komoto, F. Hayano, T. Takami and S. Yamato, *J. Polym., Sci. Part A-1*, 1971, **9**, 2983.

5 L. M. Stock and T. L. Wright, *J. Org. Chem.*, 1977, **42**, 2875.

6 G. A. Olah, V. V. Krishnamurthy and S. C. Narany, *J. Org. Chem.*, 1982, **47**, 596.

7 H. C. Brown and C. W. McGary, *J. Am. Chem. Soc.*, 1955, **77**, 2300.

8 A. Lethbridge, R. O. C. Norman and C. B. Thomas, *J. Chem. Soc., Perkin Trans. 1*, 1974, 1930; 1975, 231.

9 For a review, see S. Uemura in J. S. Pizey, *Synthetic Reagents*, Ellis Horwood, Chichester, 1983, vol. 5, p. 165.

10 L. M. Stock and T. L. Wright, *J. Org. Chem.*, 1980, **45**, 4645.

11 E. C. Taylor, R. H. Danforth and A. McKillop, *J. Org. Chem.*, 1973, **38**, 2088.

12 B. Davies and C. B. Thomas, *J. Chem. Soc., Perkin Trans. 1*, 1975, 65.

13 E. C. Taylor, F. Kienzle, R. L. Robey, A. McKillop and J. D. Hunt, *J. Am. Chem. Soc.*, 1971, **93**, 4845; P. Y. Kwok, L. M. Stock and T. L. Wright, *J. Org. Chem.*, 1979, **44**, 2309.

14 D. De Vos, W. A. A. van Barneveld, D. C. van Becklen, H. P. van

der Kooi, J. Wolters and A. van der Gen, *Recl. Trav. Chim. Pays-Bas*, 1975, **94**, 97, H. C. Bell, J. R. Kelman, J. T. Pinhey and S. Sternhell, *Aust. J. Chem.*, 1979, **32**, 1521.

15 See, R. Taylor, *Electrophilic Aromatic Substitution*, Wiley, Chichester, 1990, p. 263.

16 G. A. Olah, R. Malhotra and S. C. Narong, *Nitration, Methods and Mechanism*, VCH, New York, 1989.

17 B. C. Challis, R. J. Higgins and A. J. Lawson, *J. Chem. Soc., Perkin Trans. 2*, 1972, 1831.

18 A. McKillop, A. G. Turrell, D. W. Young and E. C. Taylor, *J. Am. Chem. Soc.*, 1980, **102**, 6504.

19 R. O. C. Norman, C. B. Thomas and J. S. Willson, *J. Chem. Soc., Perkin Trans. 1*, 1973, 325.

20 D. de Vos, F. E. H. Boschman, J. Wolters and A. van der Gen, *Recl. Trav. Chim. Pays-Bas*, 1973, **92**, 467; H. C. Bell, J. R. Kalman, G. L. May, J. T. Pinhey and S. Sternhell, *Aust. J. Chem.*, 1979, **32**, 1531.

21 R. P. Kozyrod and J. T. Pinhey, *Aust. J. Chem.*, 1985, **38**, 713.

22 A. R. Butcher and C. B. Thomas, *Org. Mass Spectrom.*, 1979, **14**, 48.

Paper 5/01836F
Received 22nd *March* 1995
Accepted 10th *May* 1995