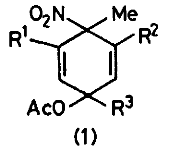
Electrophilic Aromatic Substitution. Part 20.[1,2] The Solvolyses in Aqueous Sulphuric Acid of 4-Methyl-4-nitrocyclohexa-2,5-dienyl Acetate and Some of its Homologues, and their Relevance to the Nitration of Methylbenzenes

By **Hugh W. Gibbs, Roy B. Moodie,** and **Kenneth Schofield,*** Department of Chemistry, University of Exeter, Exeter EX4 4QD

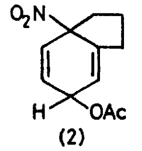
In aqueous sulphuric acid 4-methyl-, 3,4-dimethyl-, 1,4-dimethyl-, and 1,3,4-trimethyl-4-nitrocyclohexa-2,5-dienyl acetate, and 5-acetoxy-7a-nitro-5,7-dihydroindan are solvolysed too rapidly for the rates of reaction to be followed by conventional means. The products of solvolysis over a range of acidities have been determined quantitatively. In each case they can be accounted for by the occurrence of two competing reactions, *E*1 loss of nitrite and $A_{AL}1$ loss of acetic acid. From the secondary acetates the carbocation formed by loss of nitrite aromatises to an aryl acetate, and the nitro-W$_i^{Me}$ (Wheland intermediate) formed by loss of acetic acid can either be captured by water to give (after elimination of nitrous acid) a phenol or rearrange by 1,2-nitro-group migration to give a nitro-compound. The reactions of the corresponding intermediates from the tertiary acetates are more complicated; they include 1,2- and 1,3-acetate migration, and for the nitro-W$_i^{Me}$ rearrangement, capture by water, or reaction at a side-chain. The behaviour of the nitro-W$_i^{Me}$s formed in these solvolyses confirms the account given earlier of the results of nitrating methylbenzenes in aqueous sulphuric acid. It is confirmed that the positional reactivities in nitration are medium-dependent.

MYHRE'S recognition[3] of the ability of an *ipso*-Wheland intermediate, formed by attack of the nitronium ion at a nuclear carbon atom carrying a methyl group (W$_i^{Me}$), to generate nitro-compounds by 1,2-migration of the nitro-group has profound implications for the interpretation of the outcome of nitrations.[4] The results of nitrating toluene and some polymethylbenzenes in aqueous sulphuric acid of a range of concentrations have been intrepreted in terms of the partitioning of W$_i^{Me}$s between rearrangement of this kind and nucleophilic capture by water.[5] At any acidity other than that at which capture of W$_i^{Me}$ by water is complete, the yield of a nitro-compound in which the nitro-group is adjacent to a methyl group is made up of material formed by direct nitrodeprotonation and material formed by 1,2-rearrangement of W$_i^{Me}$. Given at that acidity a mass balance of products, and also an independent measure of the partitioning of W$_i^{Me}$ between capture and rearrangement, the amounts of initial attack at all the separate positions can be evaluated.

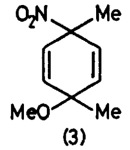
The independent measure of the partitioning of W$_i^{Me}$ between capture and rearrangement can be obtained, as Myhre showed,[3] by generating the W$_i^{Me}$ by acid-catalysed solvolysis of adducts of the type (1), and measuring at different acidities the yields of nitro-aromatic products obtained. Results of this sort have been reported for example (1b) relating to the nitration of *o*-xylene.[3,5] The importance of this kind of solvolysis for nitration studies made it desirable to study the mechanism in detail using appropriate examples of (1) from amongst the large variety available thanks to the studies of Fischer and his co-workers.[6] Whilst this work was in progress an excellent report on the solvolysis of (1d) was published.[7] We have studied the cases (1a—c and e) and (2).



(1)



(2)



(3)

a; R^1 = R^2 = R^3 = H
b; R^1 = R^3 = H, R^2 = Me
c; R^1 = R^2 = H, R^3 = Me
d; R^1 = R^2 = Me, R^3 = H
e; R^1 = H, R^2 = R^3 = Me

The published chemistry of nitrocyclohexadienyl acetates describes their thermolyses, and also some acid solvolyses other than those mentioned above. As regards the latter, the above adducts fall into two classes. Those derived from toluene (1a), *o*-xylene (1b), and indan (2), which are secondary acetates, eliminate nitrous acid to give the corresponding aryl acetate in weakly acidic solutions.[8-10]

In strongly acidic solutions the adducts lose the acetate group and, following 1,2-migration of the nitro-group, give nitro-aromatic compounds. The cases of (1b and d) have been most fully discussed, as mentioned above.

The adducts derived from *p*-xylene (1c)[11] and pseudo-

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[1] Part 19, R. B. Moodie, K. Schofield, and P. N. Thomas, *J.C.S. Perkin II*, 1978, 318.

[2] Preliminary report, H. W. Gibbs, R. B. Moodie, and K. Schofield, *J.C.S. Chem. Comm.*, 1976, 492.

[3] P. C. Myhre, *J. Amer. Chem. Soc.*, 1972, **94**, 7921.

[4] R. B. Moodie and K. Schofield, *Accounts Chem. Res.*, 1976, **9**, 287.

[5] J. W. Barnett, R. B. Moodie, K. Schofield, and J. B. Weston, *J.C.S. Perkin II*, 1975, 648.

[6] It is not possible to refer to all the relevant papers. Many are quoted in ref. 4, and the most recent one is A. Fischer and R. Röderer, *Canad. J. Chem.*, 1976, **54**, 3978.

[7] T. Banwell, C. S. Morse, P. C. Myhre, and A. Vollmar, *J. Amer. Chem. Soc.*, 1977, **99**, 3042.

[8] A. Fischer and J. N. Ramsay, *J.C.S. Perkin II*, 1973, 237.

[9] D. J. Blackstock, A Fischer, K. E. Richards, J. Vaughan, and G. J. Wright, *Chem. Comm.*, 1970, 641.

[10] A. Fischer, C. C. Greig, A. L. Wilkinson, and D. R. A. Leonard, *Canad. J. Chem.*, 1972, **50**, 2211.

[11] A. Fischer and J. N. Ramsay, *Canad. J. Chem.*, 1974, **52**, 3960.

cumene (1e)[12] are tertiary acetates, and exhibit a more varied chemistry. In aqueous acetic acid (1c) gives 2,5-dimethylphenyl acetate. In methanol containing a trace of sulphuric acid the acetoxy group is replaced by a methoxy group, giving (3), but in more acidic solutions there is extensive side-chain substitution. Thus, in chloroform containing nitric acid (1c) gave *p*-methylbenzyl nitrate and 2-nitro-*p*-xylene, whilst in chloroform containing sulphuric acid the products were nitro-*p*-tolylmethane, 2-nitro-*p*-xylene, *p*-methylbenzyl acetate, and *p*-tolualdehyde. Generally similar behaviour was shown by (1e).

EXPERIMENTAL

^{1}H N.m.r. spectra (60 and 100 MHz) were recorded on a Perkin-Elmer R10 and a JEOL MH100 spectrometer, respectively. U.v. spectra were recorded on Pye–Unicam SP 1800, SP 800, and SP 500 spectrophotometers. G.l.c. was done with a Pye 104 chromatograph fitted with a flame-ionisation detector and a Pye DP88 integrator to measure peak areas.

Materials.—Sulphuric acid, acetic anhydride, urea, and sulphamic acid were AnalaR reagents. Concentrations of aqueous sulphuric acid were determined by density measurements, and pure nitric acid was prepared as described in earlier Parts. Acetonitrile was refluxed over phosphorus pentaoxide, then distilled (b.p. 82 °C) and stored over molecular sieve 5A. Pentane and petroleum spirit (b.p. 60—80 °C) were distilled and stored over sodium. The fraction of petroleum spirit of b.p. 60—65 °C is referred to as petrol in the text.

Benzene, toluene, and nitrobenzene were AnalaR reagents, used without further purification. *o*-Xylene, b.p. 144 °C, *p*-xylene, b.p. 138 °C, indan, b.p. 176 °C, and pseudocumene, b.p. 168 °C, were reagent grade materials, and were distilled before use. *o*-, *m*-, and *p*-Nitrotoluene, 3- and 4-nitro-*o*-xylene, 2-nitro-*p*-xylene, 2-nitro-*m*-xylene, 5-nitropseudocumene, *p*-tolualdehyde, *p*-methylbenzyl alcohol, 3,4-dimethylbenzaldehyde, and 4-methyl-2-nitrophenol were obtained commercially, and checked for purity by g.l.c. 3- and 6-Nitropseudocumene were available from previous work.[5]

4- *and* 5-*Nitroindan*.—Indan (20 g) in acetic acid (66 ml) and acetic anhydride (15 ml) was treated slowly with fuming nitric acid (20 g) and the solution was stirred for 24 h and then poured onto ice (400 g). Extraction with ether, drying, and distillation gave an orange oil (15 g), b.p. 160 °C at 14 mmHg. 4- and 5-Nitroindan were separated from this mixture by preparative g.l.c. (Pye 105 instrument; 5 m; 15% SE30 on Chromasorb W column; oven temperature 170 °C). Both isomers were recrystallised from pentane to give 4-nitroindan, m.p. 44 °C, and 5-nitroindan, m.p. 39 °C, both as crystals, identified by n.m.r. spectroscopy.

3,4-Dimethylphenol, m.p. 65 °C (from pentane), 2,5-dimethylphenol, m.p. 70 °C (from EtOH), 5-hydroxyindan, m.p. 52 °C (from pentane), 3-hydroxypseudocumene, m.p. 63 °C (from EtOH), and 6-hydroxypseudocumene, m.p. 93 °C (from petrol) were commercial samples, which were purified by recrystallisation. *p*-Cresol was purified by vacuum sublimation.

5-*Hydroxypseudocumene*.—The amine was diazotised with sodium nitrite in sulphuric acid to give 5-hydroxypseudocumene which was separated by steam distillation and recrystallised from pentane to give crystals, m.p. 71 °C (lit.,[13] 70.5 °C); τ (60 MHz; $CDCl_3$) 3.3 (2 H, d, ArH), 5.2 (1 H, s, OH), and 7.9 (9 H, s, $ArCH_3$).

p-Tolyl acetate, 3,4-dimethylphenyl acetate, 2,5-dimethylphenyl acetate, and 3-, 5-, and 6-acetoxypseudocumenes were prepared by acetylating the corresponding phenols with acetic anhydride in alkaline solution. The purity of the acetates was checked by g.l.c.: *p*-tolyl acetate, b.p. 212 °C, τ 3.0 (4 H, m, ArH), 7.75 (3 H, s, $OCOCH_3$), and 7.85 (3 H, s, $ArCH_3$); 3,4-dimethylphenyl acetate, b.p. 220 °C, τ 3.1 (3 H, m, ArH), 7.8 (3 H, s, $OCOCH_3$), and 7.9 (6 H, s, $ArCH_3$); 2,5-dimethylphenyl acetate, b.p. 225 °C, τ 3.2 (3 H, m, ArH), 7.8 (3 H, s, $OCOCH_3$), and 7.95 (6 H, s, $ArCH_3$); 3-acetoxypseudocumene, b.p. 240 °C, τ 3.1 (2 H, s, ArH), 7.77 (3 H, s, $OCOCH_3$), 7.85 (3 H, s, 4-CH_3), and 8.0 (6 H, d, 1- and 2-CH_3); 5-acetoxypseudocumene, b.p. 246 °C, τ 3.18 (2 H, d, ArH), and 7.8 (12 H, m, $OCOCH_3$, $ArCH_3$); 6-acetoxypseudocumene, b.p. 242 °C, τ 3.25 (2 H, q, ArH), 7.8 (9 H, m, $OCOCH_3$, 1- and 2-CH_3), and 8.03 (3 H, s, 4-CH_3).

3,4-*Dimethyl*-2-*nitrophenol*.—3,4-Dimethylphenol (24 g) was dissolved in hot concentrated sulphuric acid (25 ml) to form the 6-sulphonic acid. Dilute sulphuric acid [concentrated acid (50 ml) in water (120 ml)] was added, and the solution was cooled to 0 °C. Concentrated nitric acid (20 g) was added slowly and the cooled solution was left for 1 h, and then poured into water (240 ml). The nitroxylenols were removed by filtration, and sodium chloride was added to the clear filtrate to 'salt out' the nitrosulphonic acid as an orange precipitate. Passage of steam through a solution of the nitrosulphonic acid in 70% H_2SO_4 produced orange crystals (3 g) of 3,4-dimethyl-2-nitrophenol, m.p. 71 °C (lit.,[13] 71.5 °C); τ (60 MHz; $CDCl_3$) 1.05 (1 H, s, OH), 3.1 (2 H, q, ArH), and 7.8 (6 H, d, $ArCH_3$).

4,5-*Dimethyl*-2-*nitrophenol*.—Fuming nitric acid (7.5 g) in acetic acid (30 ml) was added dropwise, with stirring, during 15 min to 3,4-dimethylphenol (5 g) in acetic acid (30 ml). The mixture was poured into water (500 ml) containing urea (5 g) and steam-distilled. The distillate was extracted with petrol (4 × 50 ml), and the extract was dried ($MgSO_4$). Removal of the solvent and recrystallisation from ethanol gave orange crystals (2.8 g) of 4,5-dimethyl-2-nitrophenol, m.p. 85 °C (lit.,[13] 87 °C); τ (60 MHz; $CDCl_3$) −0.8 (1 H, s, OH), 2.25 (1 H, s, ArH), 3.15 (1 H, s, ArH), and 7.8 (6 H, m, $ArCH_3$).

3,4-*Dimethyl*-2,6-*dinitrophenol*.—A solution of 4-amino-1,2-dimethylbenzene (1 g) in nitric acid [concentrated acid (2 g) in water (10 ml)] was treated at 0 °C with sodium nitrite (0.62 g) in water (5 ml), followed by concentrated nitric acid (7 g). When heated the mixture gave a red oil which solidified. Recrystallisation from ethanol gave yellow-orange needles of 3,4-dimethyl-2,6-dinitrophenol (0.35 g), m.p. 125 °C (lit.,[13] 125—126 °C).

Preparation of Nitrocyclohexadienyl Acetates.—Our methods are based essentially on those due to Fischer. Details are given only for cases concerning which the literature is not yet adequate. Generally, a solution of acetyl nitrate was prepared by slowly adding pure nitric acid (9.4 g) to acetic anhydride (25 ml), and allowing the solution to stand for 30 min at 0 °C. This solution was

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[12] A. Fischer and J. N. Ramsay, *J. Amer. Chem. Soc.*, 1974, **96**, 1614.

[13] Heilbron's Dictionary of Organic Compounds, Eyre and Spotiswoode, London, 1965.

slowly added, with stirring, to a solution of the aromatic (0.1 mol) in acetic anhydride (25 ml) at -70 °C. The mixture was allowed to warm to -30 °C and was maintained at this temperature, with stirring, until the ^1H n.m.r. spectrum of the solution showed that the reaction was complete. The mixture was then cooled to -70 °C, diethyl ether (100 ml) was added, and liquid ammonia (*ca.* 40 ml) was allowed to condense into the solution. More ether (100 ml) was then added, the mixture was allowed to warm to room temperature, and the ammonia was removed (water pump). The mixture was poured on to ice (500 g), the ether layer was removed, and the aqueous layer was extracted with ether (5×100 ml). The ether extract was washed with water (5×100 ml), and dried ($MgSO_4$). The ether was removed (water pump) to give a mixture of nitroaromatics and adducts which was stored at -10 °C. Chromatographic separation was carried out using an insulated, jacketted column, through which methanol was pumped from a Grant LB20 low temperature bath. The methanol also flowed through a double-surface condenser at the top of the column, through which the chromatographic solvent entered. The system could maintain a constant temperature of -27 °C in the column.

4-*Methyl*-4-*nitrocyclohexa*-2,5-*dienyl acetate* (1a). Toluene was nitrated on a scale ten times that described above. Reaction was complete in 45 min and ^1H n.m.r. spectroscopy indicated that the product, a red oil, contained *ca* 5%, of adducts. This oil (10 g) was chromatographed [8] at -25 °C on neutral alumina (400 g Brockman activity 1; deactivated with 10% of water). The adduct fraction (0.5 g) was *ca.* 90% pure. This material (2 g; obtained by repeating the process) was again chromatographed on alumina (150 g; deactivated with 5% of water). Petrol removed *p*-nitrotoluene and *p*-tolyl acetate, and ether–petrol (20 : 80) gave a 3 : 1 mixture of the *trans*- and *cis*-stereoisomers (1c) (0.85 g) as a yellow oil, τ (100 MHz; $CDCl_3$) 3.9 (4 H, m, 2-, 3-, 5-, 6-H), 4.4 (1 H, m, 1-H), 8.0 (3 H, s, $OCOCH_3$), 8.3 (s, 4-CH_3), and 8.36 (s, 4-CH_3).

3,4-*Dimethyl*-4-*nitrocyclohexa*-2,5-*dienyl acetate* (1b). *o*-Xylene was nitrated as described above to give an orange oil, which ^1H n.m.r. spectroscopy showed to contain *ca.* 50% of adducts. This material (4.5 g) was chromatographed on 10% deactivated alumina (150 g) at -25 °C. Elution with petrol gave the nitro-*o*-xylenes, ether–petrol (5 : 95) gave 3,4-dimethylphenyl acetate, and ether–petrol (10 : 90) a yellow oil (2.5 g) which contained *ca.* 95% of adducts. The procedure was repeated to give 5 g of this mixture of stereoisomers. We were not able to separate the isomers chromatographically. The mixture (5 g) was adsorbed on to 5% deactivated alumina (20 g) from a solution in ether, and allowed to stand at room temperature for 30 min, when brown fumes were evolved. The mixture was then chromatographed at -25 °C on 5% deactivated alumina (150 g). Petrol eluted 3,4-dimethylphenyl acetate, and ether–petrol (10 : 90) a yellow oil (1.1 g) which on cooling in an acetone–solid CO_2 bath gave crystals. They were recrystallised from pentane to yield *cis*-3,4-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate (0.45 g), m.p. 38—42 °C (decomp.); τ (100 MHz; $CDCl_3$) 3.95 [2 H, m, 5(6)-H], 4.16 (1 H, m, 2-H), 4.4 (1 H, m, 1-H), 7.92 (3 H, s, $OCOCH_3$), 8.16 (3 H, d, 3-CH_3), and 8.24 (3 H, s, 4-CH_3). This is in good agreement with the reported spectrum [9] although the m.p. is higher (lit., 25—30 °C).

1,4-*Dimethyl*-4-*nitrocyclohexa*-2,5-*dienyl acetate* (1c). *p*-Xylene was nitrated, as described above, for 30 min, to give a red oil containing *ca.* 80% of adducts. Chromatography of this material (20 g) according to Fischer *et al.*,[11] and crystallisation of the appropriate fraction from pentane gave crystals (1.08 g), m.p. 46 °C; τ (60 MHz; $CDCl_3$) 3.9 (4 H, s, 2-, 3-, 5-, 6-H), 8.05 (3 H, s, $OCOCH_3$), 8.23 (3 H, s, 4-CH_3), and 8.55 (3 H, s, 1-CH_3). This corresponds to the reported spectrum of *cis*-1,4-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate (lit., 47—49 °C).[11]

Further elution with petrol gave an oil which crystallised on cooling. Recrystallisation from pentane gave crystals (0.84 g), m.p. 57 °C; τ (60 MHz; $CDCl_3$) 3.8 (4 H, s, 2-, 3-, 5-, 6-H), 8.05 (3 H, s, $OCOCH_3$), 8.3 (4 H, s, 4-CH_3), and 8.5 (3 H, s, 1-CH_3). This corresponds to the spectrum reported for *trans*-1,4-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate (1c) (lit., 58—59 °C).[11]

5-*Acetoxy*-7a-*nitro*-5,7-*dihydroindan* (2). Indan was nitrated, using the method described above, for 10 min to give a red oil containing *ca.* 60% of adducts. This material (7 g) was chromatographed according to Fischer *et al.*[10] giving an orange oil which crystallised on cooling. Recrystallisation from pentane gave crystals (1.8 g), m.p. 46 °C; τ (60 MHz; $CDCl_3$) 3.7 (1 H, d, 7-H), 3.95 (2 H, m, 6-, 4-H), 4.5 (1 H, m, 5-H), 7.4, 8.2 (6 H, m, $CH_2CH_2CH_2$), and 8.0 (3 H, s, $OCOCH_3$). This corresponds to the spectrum reported for *cis*-(2) but the m.p. is low (lit., 61.5—62.5 °C).

1,3,4-*Trimethyl*-4-*nitrocyclohexa*-2,5-*dienyl acetate* (1e). Pseudocumene was nitrated, by the method described above, at -45 °C for 2 h, to give a deep red oil containing *ca.* 50% of adducts. This material (5 g) was chromatographed on 10% deactivated alumina (150 g) at -28 °C. Elution with petrol removed pseudocumene, followed by 5-nitropseudocumene. Ether–petrol (20 : 80) eluted acetoxypseudocumenes, followed by a red-orange oil (1.8 g) which ^1H n.m.r. spectroscopy showed to contain *ca.* 85% of adducts with *ca.* 15% of acetoxypseudocumenes. This oil was chromatographed on 5% deactivated alumina (150 g) at -28 °C. It was eluted with 500 ml fractions of petrol, ether–petrol (5 : 95), ether–petrol (10 : 90), ether–petrol (20 : 80), and ether–petrol (40 : 60). The material from ether–petrol (5 : 95) was recrystallised from pentane to yield crystals (0.3 g) of 1,3,4-trimethyl-4-nitrocyclohexa-2,5-dienyl acetate, m.p. 50 °C; τ (100 MHz; $CDCl_3$) 8.52 (3 H, s, 1-CH_3), 8.24 (6 H, s, 3-, 4-CH_3), and 8.06 (3 H, s, $OCOCH_3$). The low field signals resembled an ABC system, τ_A 5.96, τ_B 4.21, τ_C 4.19. The C absorption contained two additional peaks which could not be accounted for by simulated ABC spectra. They were evidently due to small amounts of impurity; the spectrum gave no indication of the presence of 2,3,5-trimethyl-2-nitrocyclohexa-3,5-dienyl acetate, and 1,2,4-trimethyl-4-nitrocyclohexa-2,5-dienyl acetate was not present (solvolysis at high acidities gave no 5-nitropseudocumene).

The ether–petrol (10 : 90) fraction was a yellow oil (1.1 g) which contained *ca.* 50% of this adduct, and 50% of a compound with a similar ^1H n.m.r. spectrum, probably the other diastereoisomer. No physical properties for these compounds were reported.[12]

Kinetic Measurements.—The aryl acetates were dissolved in acetonitrile and small volumes (*ca.* 5 μl) of these solutions were syringed into spectrophotometric cells containing sulphuric acid and urea (0.03M) at 25 °C, to give concentrations of the acetates of *ca.* 10^{-4} mol l^{-1}. The hydrolyses were followed by measuring the change with time of the u.v. absorption spectra. The cyclohexadienyl adducts were examined in the same way, but reacted too rapidly for rates to be determined by conventional methods.

Product Analyses.—A stock solution of an adduct (*ca.* 0.02 g) was prepared in acetonitrile (1 ml), and 100 μl of this solution was syringed into 100 ml of sulphuric acid at 25 °C, containing urea (0.03M). The solution was vigorously agitated, using a 'Vibro Mixer', for exactly 1 min, then poured into cold water (600—800 ml). A known amount of a reference standard was added, and the solution was extracted with dichloromethane (10 × 10 ml). The combined extracts were dried ($MgSO_4$), and most of the solvent was removed by careful fractional distillation (12 in × 0.5 in column, packed with glass helices) to leave a concentrated solution (2—3 ml) of products, which were then analysed by g.l.c. The response of the flame ionisation detector to the products and reference standard was determined by calibration. Solutions containing known concentrations of the products and reference standard were made up in dichloromethane and analysed. The ratios of the areas of the peaks for the products to the area of the peak for the reference standard were measured for each solution, and a calibration graph was then plotted of this area ratio against the mole ratios of products and reference standard, and the slope of the graph for each component was evaluated. This slope was used to convert measured peak area ratios into mole ratios. Since the concentration of the reference standard was known, the concentrations and yields of the products could then be evaluated. Details of the analytical conditions and reference standards are given in Table 1.

TABLE 1

G.l.c. analysis data

Adduct	Product or standard	R_t/s	Column (t/°C) [a]
(1a)	*p*-Tolyl acetate	400	10% polypropylene glycol (145)
	o-Nitrotoluene	500	
	p-Cresol	1 206	
	4-Methyl-2-nitrophenol	862	
	p-Nitrotoluene [b]	706	
(1b)	2,3-Dimethylnitrobenzene	878	15% SE30 (140)
	3,4-Dimethylnitrobenzene	1 227	
	3,4-Dimethylphenyl acetate	910	
	p-nitrotoluene [b]	610	
(1c)	2,5-Dimethylphenol	428	15% SE30 (145)
	2,5-Dimethylphenyl acetate	601	
	2,5-Dimethylnitrobenzene	714	
	Nitrobenzene [b]	318	
(1e)	3,4-Dimethylbenzaldehyde	565	15% SE30 (150)
	3-Hydroxypseudocumene	519	
	6-Hydroxypseudocumene	615	
	5-Hydroxypseudocumene	640	
	3-Nitropseudocumene	743	
	5-Nitropseudocumene	1 186	
	6-Nitropseudocumene	1 030	
	3-Acetoxypseudocumene	807	
	5-Acetoxypseudocumene	912	
	6-Acetoxypseudocumene	902	
	2-Nitro-*m*-xylene [b]	414	

[a] All on Chromosorb W, 6 ft, nitrogen as carrier gas, 40 ml min^{-1}, Pye 104 instrument, flame ionisation detector. [b] Standard.

The extraction procedure was tested using synthetic mixtures of products of known concentration. All products were extracted quantitatively, with the exception of certain phenols. The degree of extraction was found to be constant for these components, and so it was possible to make a correction for this when calculating the product yields.

RESULTS

Thermolysis of ipso-*Nitrocyclohexadienyl Acetates.*—In g.l.c. compounds (1a—c and e) and (2) behaved generally as reported by earlier workers except that in every case the parent aromatic hydrocarbon, formed by elimination of acetyl nitrate, was observed. Probably because of the g.l.c. conditions this reaction was missed in the early work, but noted for (1c) [11] and (1d).[7]

TABLE 2

First-order rate constants k_1 for the acidolysis of aryl acetates in sulphuric acid at 25 °C [a]

Ester	Wt. % H_2SO_4	$10^3k_1/s^{-1}$
p-Tolyl acetate	26.2	0.48
	31.2	0.64
	36.2	0.92
	39.3	1.07
	44.2	1.37
	48.9	1.84
	51.2	2.1
	53.4	2.4
	62.8	3.6
	68.0	4.4
	75.2	6.0
3,4-Dimethylphenyl acetate	26.2	0.51
	31.2	0.69
	36.2	0.97
	39.3	1.19
	48.9	2.0
	58.0	3.0
	73.2	5.1
2,5-Dimethylphenyl acetate	31.2	0.32
	39.3	0.49
	44.2	0.65
	51.2	1.01
	54.2	1.12
	58.4	1.39
	61.0	1.5
	70.9	1.55
	79.1	2.7

[a] Measurements at λ 275 nm.

Acidolysis of Aryl Acetates and ipso-*Nitrocyclohexadienyl Acetates.*—The first-order rate constants for the acidolysis of the aryl acetates in sulphuric acid are listed in Table 2. The profiles for the acidolysis of phenyl,[14] *p*-tolyl, and 3,4-dimethylphenyl acetate are very similar. This is to be expected as the rates of acidolysis of aryl acetates are very insensitive to substituents in the aryl ring. The profile is characteristic of an $A_{Ac}2$ solvolysis mechanism which changes to $A_{Ac}1$ at high acidities.[15] Perhaps for steric reasons the rate constants for the acidolysis of 2,5-dimethylphenyl acetate are somewhat smaller than those for the other acetates.

Solutions of the toluene adduct (1a) in water or dilute (<45%) sulphuric acid gave an initial u.v. spectrum identical with that of *p*-tolyl acetate. The spectrum changed in a kinetically first-order way to give a spectrum identical with that of *p*-cresol, and at a rate identical with that measured independently for the acidolysis of *p*-tolyl acetate to *p*-cresol. In 45—60% H_2SO_4 the initial spectrum of the solution prepared from (1a) became increasingly like that of *p*-cresol, the contribution from *p*-tolyl acetate decreasing with increasing acidity. In 60—85% H_2SO_4 the initial spectrum became increasingly like that of *o*-nitro-

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[14] K. Yates and R. A. McClelland, *J. Amer. Chem. Soc.*, 1967, **89**, 2686.

[15] K. Yates, *Accounts Chem. Res.*, 1971, **4**, 136.

toluene, the contribution of *p*-cresol decreasing with increasing acidity. Using a measured value for the extinction coefficient of *o*-nitrotoluene, it was calculated

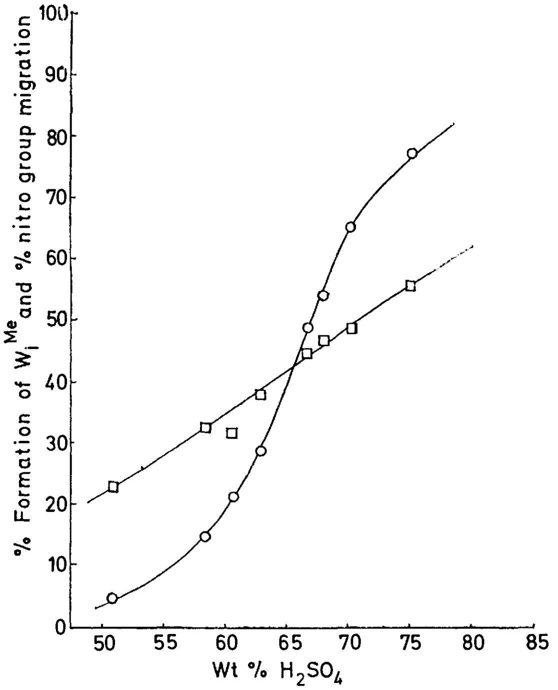


FIGURE 1 Solvolysis of toluene adduct (1a): % formation of W_i^{Me}, □; % migration of nitro-group, ○

that in 85% H_2SO_4 the W_i^{Me} formed gave *o*-nitrotoluene quantitatively.

The indan adduct (2) behaved in a similar manner, immediately decomposing to give 5-acetoxyindan at low acidities (<40% H_2SO_4), 5-hydroxyindan at intermediate acidities, and 4-nitroindan at high acidities, as indicated by u.v. spectroscopy.

In <40% H_2SO_4 the initial spectra of solutions prepared from the *o*-xylene adduct (1b) were identical with that of 3,4-dimethylphenyl acetate. They changed in a first-order way, and at the expected rate into the spectrum of 3,4-dimethylphenol. In 40—70% H_2SO_4 the spectrum showed an intense peak with $\lambda_{max.}$ 360 nm which was very rapidly formed and decayed slowly, both the rate of formation and decay decreasing rapidly with increasing acidity (Table 3). The intensity of the peak $\lambda_{max.}$ 360 nm increased rapidly with increasing acidity to reach a maximum at *ca.* 60% H_2SO_4. It then decreased rapidly, and no peak appeared in >70% H_2SO_4. The intensity of this peak, and its rates of formation and decay were unaffected by replacing urea by sulphamic acid as a nitrous acid ' trap ', or by carrying out the reaction in the absence of a ' trap '.

TABLE 3

Acidolysis of 3,4-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate in sulphuric acid at 25 °C. First-order rate constants for the formation and decay of the peak, $\lambda_{max.}$ 360 nm

Wt. % H_2SO_4	Formation $10^3 k/s^{-1}$	Decay $10^3k/s^{-1}$
44.2	61	1.67
48.9	101	1.72
53.4	105	1.43
54.4		1.44
57.9	90	
58.7		1.02
62.8	37	0.80
63.8		0.77
65.3	22	0.75
67.5	12.9	0.72
69.1	11.5	0.67

When nitrous acid was added to a solution of 3,4-dimethylphenol in 58% H_2SO_4 containing 0.03M-urea an intense peak, $\lambda_{max.}$ 360 nm, was quickly formed, and slowly decayed. Comparison with the spectrum obtained by acidolysis of (1b) showed the two to be identical. The rates of decay in the two cases were very similar. The reaction of nitrous acid with 3,4-dimethylphenol was shown by t.l.c. to produce a mixture of 4,5-dimethyl-2-nitrophenol with another, unidentified compound.

In >70% H_2SO_4 the initial spectra of solutions prepared from (1b) were identical with that of 2,3-dimethylnitrobenzene. The measured extinction coefficient of 2,3-dimethylnitrobenzene showed that in 85% H_2SO_4 (1b) gave this product quantitatively.

The adducts (1c and e), from *p*-xylene and pseudocumene respectively, behaved rather differently. The former, dissolved in <35% H_2SO_4, immediately gave a solution showing a spectrum identical with that of 2,5-dimethylphenol, whilst in >70% H_2SO_4 the initial spectrum was identical with that of 2-nitro-*p*-xylene. In intermediate regions the initial spectrum showed a very broad band between 260 and 330 nm, perhaps due to the formation of side-chain products. When the adduct was dissolved in water, the initial spectrum was identical with that of 2,5-dimethylphenyl acetate.

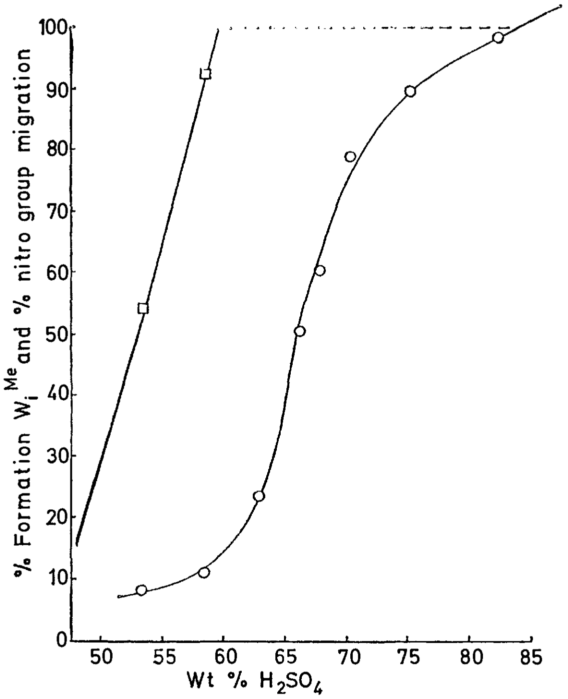


FIGURE 2 Solvolysis of *o*-xylene adduct (1b): % formation of W_i^{Me}, □; % migration of nitro-group, ○

The pseudocumene adduct (1e) behaved similarly. In water it immediately gave a spectrum similar to that of an acetoxypseudocumene, whilst in <30% H_2SO_4 the initial spectrum was similar to that of a hydroxypseudocumene. It was not possible to identify which acetate and phenol were formed, as the spectra of the possible isomeric acetates and phenols were very similar. In >75% H_2SO_4 the adduct gave solutions with initial spectra identical with that of 6-*nitro*pseudocumene. However, at intermediate acidities (35—75% H_2SO_4), the initial spectra were very complex, owing to the formation of side-chain products. It was not possible to identify any of these products on the basis of their u.v. spectra, but the u.v. spectrum of 3,4-dimethylbenzaldehyde is not inconsistent with its being present.

Products of Acidolysis of ipso-*Nitrocyclohexadienyl Acetates.*—The yields of products from the toluene adduct (1a), as they vary with acidity, are shown in Table 4. During the acidolysis some *p*-tolyl acetate is hydrolysed to *p*-cresol; the initial yields of acetate were calculated from its measured concentration at a known time and the rate constant for hydrolysis. The yield of *p*-cresol was corrected for this contribution from hydrolysis of the acetate, and also for the fact that of all the products it was the only one which could not be quantitatively extracted. The degrees of extraction over a wide acidity range were reproducible, and so the yields could be corrected to allow for incomplete extraction.

TABLE 4

Products of solvolysis of 4-methyl-4-nitrocyclohexa-2,5-dienyl acetate in sulphuric acid

	Yield (%)					
Wt. % H_2SO_4	*o*-Nitrotoluene	4-Methyl-2-nitrophenol	*p*-Tolyl acetate		*p*-Cresol	
85.3	58.0	2.8	*a*	*a*	39.2 [b]	*a*
75.2	42.8	4.2	21.1	44.5 [c]	31.9 [b]	12.7 [d]
70.2	31.5	3.7	26.1	51.4 [c]	38.7 [b]	16.1 [d]
68.0	25.1	1.4	31.5	53.3 [c]	42.0 [b]	21.6 [d]
66.5	21.6	1.7	34.3	55.4 [c]	42.4 [b]	23.0 [d]
62.8	10.7	1.3	40.2	62.3 [c]	47.8 [b]	27.0 [d]
60.7	6.6	1.0	43.2	68.6 [c]	49.2 [b]	24.8 [d]
58.4	4.7	1.8	48.0	67.7 [c]	45.5 [b]	27.6 [d]
51.2	1.0	2.1	56.6	77.2 [c]	40.3 [b]	21.8 [d]

[a] Any *p*-tolyl acetate formed would be hydrolysed to *p*-cresol. [b] Corrected for incomplete extraction. [c] Yields corrected for hydrolysis. [d] Yield corrected for formation of *p*-cresol by hydrolysis of *p*-tolyl acetate, and including yield of 4-methyl-2-nitrophenol.

The behaviour of the *o*-xylene adduct (1b) was similar, and yields are given in Table 5. The yields of 3-nitro-*o*-xylene agree well with earlier results.[3]

TABLE 5

Products of solvolysis of 3,4-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate in sulphuric acid

	Yield (%) [a]		
Wt. % H_2SO_4	2,3-Dimethyl-nitrobenzene	3,4-Dimethyl-phenol [b]	3,4-Dimethyl-phenyl acetate
82.4	98.4	1.6	
75.2	89.6	10.4	
70.2	78.8	21.2	
68.0	60.6	39.4	
66.5	50.9	49.1	
62.8	23.6	76.4	
58.4	10.1	82.1	7.8
53.4	4.0	50.0	46.0

[a] Yields corrected for acidolysis of 3,4-dimethylphenyl acetate and incomplete extraction of 3,4-dimethylphenol. [b] Includes *ca.* 1% of 4,5-dimethyl-2-nitrophenol.

Acidolysis of the *p*-xylene adduct (1c) gave 2-nitro-*p*-xylene quantitatively in >75% H_2SO_4. The yield decreased with decreasing acidity and five new products appeared in increasing amounts. Two of these were *p*-tolualdehyde and 2,5-dimethylphenol, the others presumably being side-chain substitution products. 2,5-Dimethylphenyl acetate was only obtained from (1c) in <45% H_2SO_4. The yields of products, corrected as in the previous cases are given in Table 6. In <50% H_2SO_4 approximately twelve products, other than 2,5-dimethylnitrobenzene, 2,5-dimethylphenol, and 2,5-dimethylphenyl acetate were seen. Amongst these were *p*-methylbenzyl alcohol, *p*-methylbenzyl acetate, and *p*-tolualdehyde, but no attempt was made to identify the others.

In >80% H_2SO_4 the pseudocumene adduct (1e) gave 6- and 3-nitropseudocumene quantitatively. The yields of these sharply decreased with decreasing acidity, and the yields of 3,4-dimethylbenzaldehyde and other side-chain substituted products increased. Below 65% H_2SO_4 the yield of side-chain substituted products decreased, and a corresponding increase in the yield of 6-hydroxypseudocumene was seen, reaching a maximum of 85.9% *in* 45% H_2SO_4. It then decreased with decreasing acidity, whilst the yields of 5-acetoxy-, 6-acetoxy-, and 5-hydroxy-pseudocumene increased. The yields of products, corrected in the same ways as those discussed above, are given in Table 7. Several products, which could not be identified uniquely by g.l.c. were found, and their yields are listed under ' Other products '. In >60% H_2SO_4 these products were probably 3,4-dimethylbenzyl alcohol and 3,4-dimethylbenzyl acetate,

TABLE 6

Products of solvolysis of 1,4-dimethyl-4-nitrocyclohexadienyl acetate in sulphuric acid

	Yield (%) [a]			
Wt. % H_2SO_4	2,5-Dimethyl-nitrobenzene	2,5-Dimethyl-phenol	2,5-Dimethyl-phenyl acetate	Other products [b]
85.3	101.2			
75.8	100.0			
69.3	89.9	5.3		4.6
66.5	69.9	8.3		21.8
63.6	53.7	10.5		33.8
61.0	42.3	14.5		43.2
57.1	30.0	25.0		45.0
55.0	23.1	29.4		47.5
51.5	14.3	31.7		55.0
45.3	5.8	51.3	1.2	42.7
26.2	4.0	75.4	20.5	
9.6	4.0	62.4	33.6	

[a] Yields corrected for acidolysis of 2,5-dimethylphenyl acetate and incomplete extraction of 2,5-dimethylphenol. [b] Including *p*-tolualdehyde, *p*-methylbenzyl alcohol, and *p*-methylbenzyl acetate.

and at lower acidities they were probably 3-acetoxy- and 3-hydroxy-pseudocumene.

TABLE 7

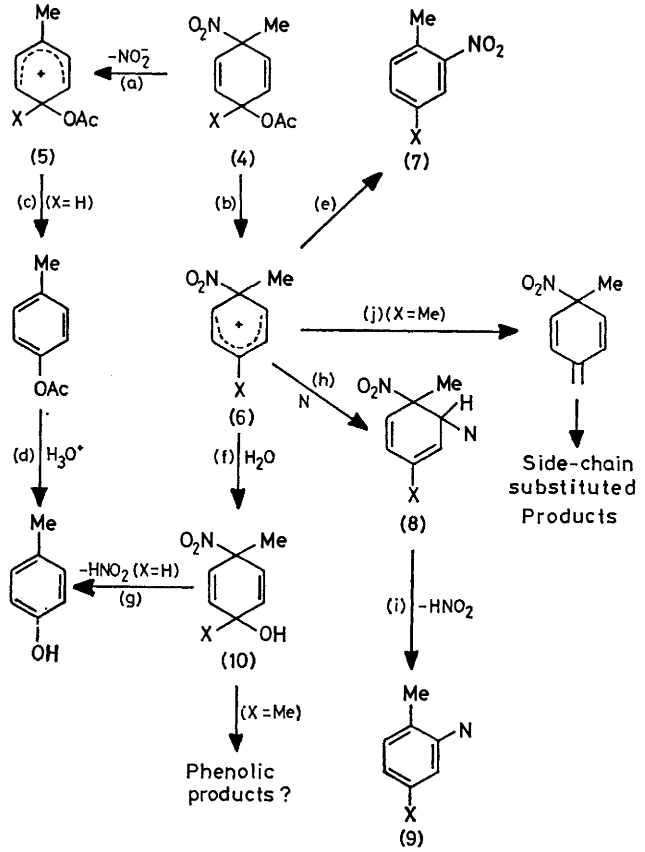
Products of solvolysis of 1,3,4-trimethyl-4-nitrocyclohexadienyl acetate in sulphuric acid

	Yield (%) [a]							
	Nitropseudocumenes		3,4-Dimethyl-benzaldehyde	Hydroxypseudocumenes		Acetoxypseudocumenes		Other products [b]
Wt. % H_2SO_4	6-	3-		6-	5-	6-	5-	
79.7	95.8	5.6						
75.8	91.0	5.2						3.8
72.3	67.4	3.0	6.2					23.4
69.3	36.8	2.7	24.8	2.4				33.3
66.5	24.0	1.8	45.8	19.3			<1.0	9.1
63.6	19.4	1.0	42.1	22.8			<1.0	14.7
61.0	11.8	<1.0	26.1	26.2			1.0	34.9
57.1	4.1		14.1	37.2			1.2	42.4
55.0	1.5		6.1	61.8	<1.0		2.3	27.4
51.5			3.2	81.5	3.7		3.1	8.5
45.3			<1.0	85.9	10.1		4.7	
40.1				80.4	14.7		6.9	
36.2				74.3	15.3	<1.0	8.1	1.4
31.2				52.3	21.0	1.0	11.8	13.9
26.2				40.6	26.3	2.5	15.8	14.8
9.6				7.3	36.9	11.2	28.3	16.3

[a] Yields corrected for acidolysis of acetoxypseudocumenes and incomplete extraction of hydroxypseudocumenes. [d] Including 3,4-dimethylbenzyl alcohol and 3,4-dimethylbenzyl acetate at high acidities, 3-acetoxy- and 3-hydroxy-pseudocumene at low acidities.

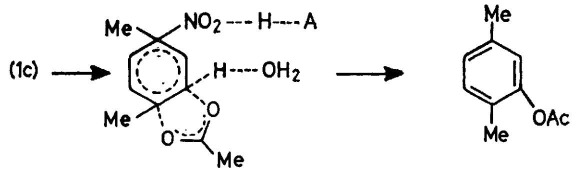
DISCUSSION

Scheme 1 will be used as a basis for discussing the behaviour of the *ipso*-nitrocyclohexadienyl acetates (for simplicity substituents other than the *ipso*-methyl group and the group occupying the *para*-position are omitted). In all cases the adducts (4) decompose by two competing reactions (a) and (b), both too rapid to be followed by conventional means. In one reaction (a) S_N1 heterolysis gives nitrite and the carbocation (5), whilst in the other (b) $A_{AL}1$ solvolysis gives the W_i^{Me} (6). In <30% H_2SO_4 path (a) was dominant for the secondary acetates (4; X = H). With increasing acidity path (b) competed more and more successfully. In >60% H_2SO_4 the path (4) $\xrightarrow{(b)}$ (6) $\xrightarrow{(e)}$ (7) was the main reaction, *i.e.* rearrangement of W_i^{Me} was more important than its capture.



SCHEME 1

Loss of Nitrite [*Path* (*a*)].—From the reactions of the adducts in sulphuric acid we could not identify the mechanism of loss of nitrite. This has been described[16] as a bimolecular 1,4-elimination (*E*2), the removal of the proton in (4; X = H) assisting the loss of the nitrite anion. However, very substantial evidence for the operation of the *E*1 mechanism has been obtained for the case (1d),[7] and we accept this as the mechanism of elimination of nitrous acid from the secondary acetates. For (1d) the rate of decomposition in aqueous ethanol was proportional to the solvent polarity parameter Y.[7] Extrapolation suggests that the decomposition would be rapid under our conditions.



The decomposition in dilute acids of the *p*-xylene (1c) and pseudocumene adduct (1e) was more complex; being tertiary esters they could not lose nitrous acid by 1,4-elimination. Earlier experiments[11] with (1c) in aqueous acetic acid gave 2,5-dimethylphenyl acetate as the main product. Since water strongly catalysed the reaction,

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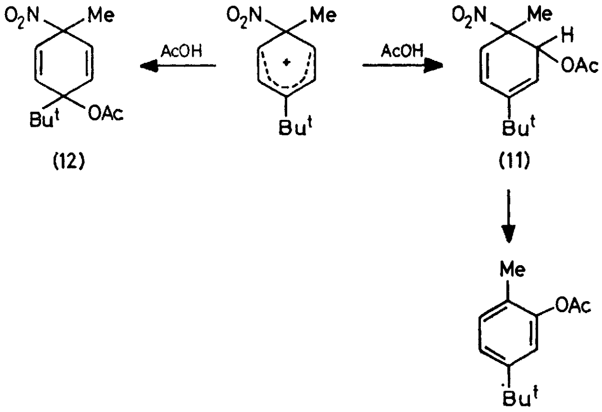
[16] A. Fischer, C. C. Greig, and R. Röderer, *Canad. J. Chem.*, 1975, **53**, 1570.

and propionate was not incorporated when propionic acid was used the reaction was represented as an acid-catalysed, intramolecular 1,2-acetate migration, concerted with loss of the nitro-group.

Our results relating to dilute sulphuric acid are not wholly in accord with this mechanism. In 9.6% H_2SO_4 only 33.6% of 2,5-dimethylphenyl acetate was found, with 62.4% of 2,5-dimethylphenol (yields corrected for acidolysis of the aryl acetate). Clearly the phenol must arise from a pathway other than that of hydrolysis of its acetate [route (a) ⟶ (c) ⟶ (d)]. Tertiary acetates react readily by the $A_{AL}1$ mechanism even at low acidities,[15] and it is possible that (1c) gives W_i^{Me} (6; X = Me) even at acidities as low as 9.6% H_2SO_4. The W_i^{Me} may be recaptured by water to give the 1,2-adduct (8; X = Me, N = OH), and thence the phenol (9; X = Me, N = OH). The same route [(b) ⟶ (h) ⟶ (i); N = OAc] could also provide the acetate, but (6; X = Me) would have to capture acetic acid before it left the solvent shell in which (6; X = Me) and acetic acid were formed from the adduct, *i.e.* the two would have to react at or near to the diffusion rate. This seems improbable, and furthermore this mechanism would not explain the decrease in yield of acetate with increasing acidity (Figure 3).

1,2-Capture of nitro-W_i^{Me}s is uncommon, but not unknown. Thus, in the nitration of *p*-t-butyltoluene both the 1,2- (11) and the 1,4-adduct (12) are formed and the latter can lose nitrous acid to give the aryl acetate.[17]

Professor Myhre has pointed out to us the possibility that at low acidities (5; X = Me, OH in place of OAc), formed from (10; X = Me), could rearrange by methyl group migration to give 2,4-dimethylphenol. We have not been able to prove the presence or absence of this compound in the phenolic product formed in our experiments. Under our g.l.c. conditions the elution times of 2,5- and 2,4-dimethylphenol differed by only 10 s, and whilst we are confident that the 2,5-isomer was present, we could not exclude the possibility that some of the 2,4-isomer was also formed.



The case of *p*-t-butyltoluene would seem to provide precedent for the kind of capture process mentioned above as the possible source of 2,5-dimethylphenol and its acetate. However, the symmetry of *p*-xylene makes it impossible in this case to distinguish amongst a 1,2-acetate migration, an $A_{AL}1$ solvolysis followed by 1,2-acetate capture by the W_i^{Me}, or any other process as the true source of 2,5-dimethylphenyl acetate. As regards the source of both the phenol and the acetate, clarification comes from the behaviour of the pseudocumene adduct (1e), in which the symmetry is lacking.

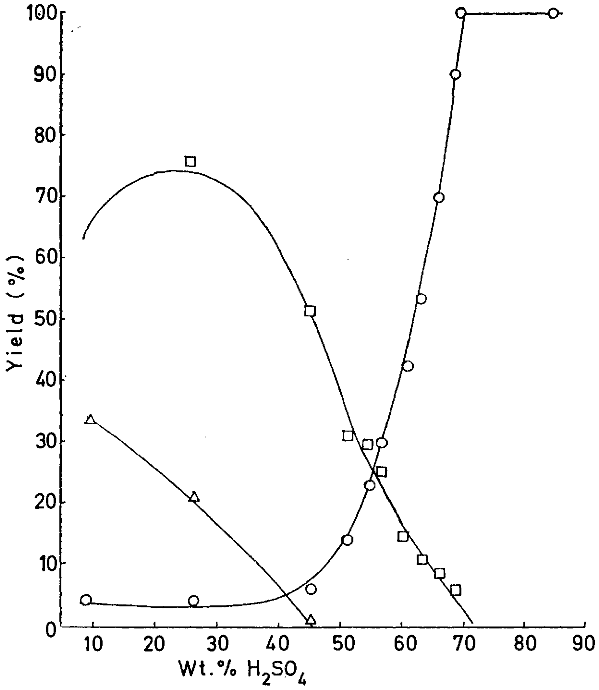


FIGURE 3 Solvolysis of *p*-xylene adduct (1c): % yield of 2,5-dimethylnitrobenzene, ○; % yield of 2,5-dimethylphenol, □; % yield of 2,5-dimethylphenyl acetate, △

In 9.6% H_2SO_4 (1e) gave 7.3% of 6-hydroxy-, 11.2% of 6-acetoxy-, 36.9% of 5-hydroxy-, and 28.3% of 5-acetoxy-pseudocumene. As Figure 4 shows, the yield of 6-hydroxypseudocumene rose with increasing acidity, reaching a maximum at *ca.* 42% H_2SO_4, and then decreasing. In contrast the yields of 6-acetoxy-, 5-acetoxy-, and 5-hydroxy-pseudocumene all declined with increasing acidity. These acidity dependences are the main clues to mechanism.

As regards 6-hydroxypseudocumene the acidity dependence is wholly consistent with its being formed from (13) (Scheme 2) by 1,2-recapture by water, followed by loss of nitrous acid [route (b) ⟶ (h) ⟶ (i) in Scheme 1]; increasingly successful competition at higher acidities from routes (b) ⟶ (j), giving 3,4-dimethylbenzaldehyde, and (b) ⟶ (e), giving nitropseudocumenes (see below), accounts for the eventual decline in yield of the acetate.

The fact that production of 5-hydroxypseudocumene does not benefit from increasing acidity suggests strongly that it is produced by route (b) ⟶ (f), *ipso*-recapture of the nitro-W_i^{Me} (13) by water evidently being im-

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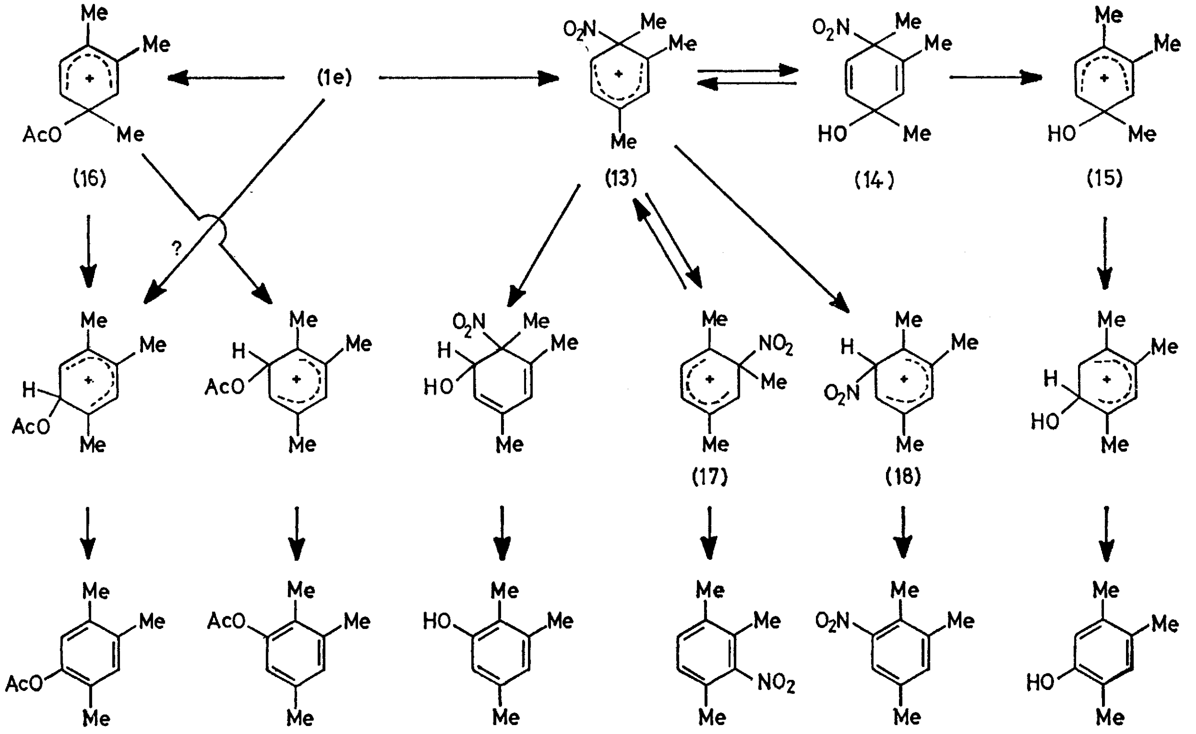
[17] A. Fischer and R. Röderer, *Canad. J. Chem.*, 1976, **54**, 3978.

portant (see below); loss of nitrite from (14) and 1,2-migration of *either* the methyl *or* hydroxy group in (15) would give 5-hydroxypseudocumene. Rising acidity would reduce the importance of this reaction by increasingly favouring (13) over (14) in the equilibrium between them. Similarly, 5-acetoxypseudocumene most probably arises by 1,2-migration of acetoxy in the acetoxy-W_i^{Me} (16), or by synchronous loss of nitrite and 1,2-migration of acetoxy in (1e). In either case there are no grounds here for invoking acid catalysis as in the form of 1,2-migration of acetoxy proposed by Fischer and Röderer[17] (see above). 1,3-Migration of acetoxy in (16) (in effect an allylic rearrangement) is the likely source of 6-acetoxypseudocumene. Such a rearrangement was proposed by Fischer and Röderer[17] to account for the formation of 2-methyl-5-t-butylphenyl acetate from (12).



Scheme 2

The solvolysis of (1e) in 9.6% H_2SO_4 probably produces some 3-hydroxypseudocumene and some of its acetate (Table 7). Supposing that half the yield of ‘ Other products ’ can be ascribed to each of these compounds, then at this acidity the loss of nitrite [process (a), perhaps including some synchronous loss of nitrite and 1,3-migration of acetoxy] and process (b) account for 48 and 52% of the fate of (1e), respectively. The same processes, at work in the solvolysis of (1c) cannot be separated on available evidence.

Loss of Acetate [*Path* (*b*)].—The acetate group is lost by $A_{AL}1$ cleavage to give the W_i^{Me} and acetic acid. That the solvolysis was for all adducts too fast to follow kinetically supports this view, for the alternative $A_{Ac}2$ pathway is insensitive to the nature of the alkyl group, and for other acetates proceeds at a rate convenient for kinetic study under our conditions.[15] The tertiary acetates (1c and e) would be expected to react by the $A_{AL}1$ route more quickly than do the secondary acetates (1a and b), and (2). The slower reaction of the latter compounds, whilst it is still too fast to follow kinetically, brings more readily into competition the alternative elimination of nitrous acid to give the aryl acetates. The yield of aryl acetate from the secondary acetates is equal to the proportion of the adduct which eliminates nitrous acid. The remainder of the adduct must eliminate acetic acid to give the nitro-W_i^{Me}.

The percentage formation of the W_i^{Me}, as it varies with acidity, is shown in Figure 1 for (1a) and in Figure 2 for (1b). Also shown are the yields of the nitro-compounds formed by rearrangements of the W_i^{Me}s calculated as a percentage of the adduct which follows path (b). These yields, representing the partitioning of the W_i^{Me}s between rearrangement and capture [path (b) → (e) *versus* path (b) → (f) or (h)], are given in Table 8. The product yields from the *p*-xylene and pseudocumene adducts are shown in Figures 3 and 4.

The toluene and *o*-xylene adducts differ considerably with respect to the degree of formation of the W_i^{Me}s. With the former there is a slow change from elimination of nitrous acid [path (a)] to elimination of acetic acid [path (b)] as the major reaction over the range 50—85% H_2SO_4. For the *o*-xylene adduct the change occurs rapidly over the range 50—60% H_2SO_4. This implies that the dependence upon acidity of the rate constants for either the $A_{AL}1$ cleavage of the acetates, or for the elimination of nitrous acid, or both of these, are different for the two compounds. Since both reactions were too fast for kinetic study, it is not possible to resolve this problem at present.

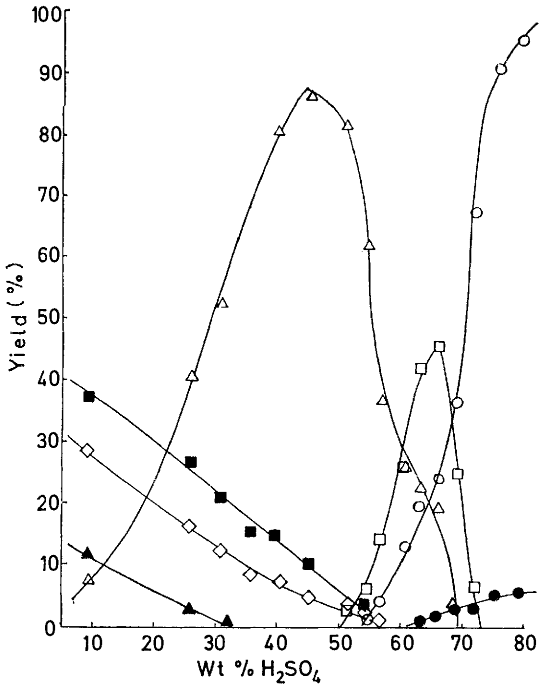


FIGURE 4 Solvolysis of pseudocumene adduct (1e): % yield of 5-nitropseudocumene, ○; % yield of 3-nitropseudocumene, ●; % yield of 3,4-dimethylbenzaldehyde, □; % yield of 6-hydroxypseudocumene, △; % yield of 6-acetoxypseudocumene, ▲; % yield of 5-hydroxypseudocumene ■; % yield of 5-acetoxypseudocumene, ◇

TABLE 8

The extent of formation and the fate of W_i^{Me}s from the solvolyses of 4-methyl- (A) and 3,4-dimethyl-4-nitrocyclohexadienyl acetate (B) in sulphuric acid

Substrate	Wt. % H SO_4	% Formation of W_i^{Me}	Fate of W_i^{Me} % Capture	Fate of W_i^{Me} % Migration
(A)	75.2	55.5	22.9	77.1
	70.2	48.6	35.0	65.0
	68.0	46.7	46.3	53.7
	66.5	44.6	51.6	48.5
	62.8	37.7	71.6	28.4
	60.7	31.4	79.0	21.0
	58.4	32.3	85.4	14.6
	51.1	22.8	95.6	4.4
(B)	82.4	100	1.6	98.4
	75.2	100	10.4	89.6
	70.2	100	21.2	78.8
	68.0	100	39.4	60.6
	66.5	100	49.1	50.5
	62.8	100	76.4	23.6
	58.4	92.2	88.9	11.1
	53.4	54.0	92.0	8.0

In organic solvents the diastereoisomeric secondary *ipso*-nitrocyclohexadiene acetates (1d) from hemimellitene eliminate nitrite at different rates.[7] If this difference were maintained in sulphuric acid diastereoisomers would give different product distributions; our results show this not to be so for the tertiary *p*-xylene adducts (1c). Either the two stereoisomers lose nitrite at more nearly the same rate in this case, or if there is a significant difference it is compensated for by an opposing difference in the two rates of $A_{AL}1$ solvolysis.

From (1d) no aryl acetate was obtained in the range 50—70% H_2SO_4.[7] It was supposed that reaction (b) was much faster than reaction (a). In the lower part of the acidity range this may not have been true, and acetate may not have been found because in the time of the experiment it was hydrolysed to the phenol.

Capture of Nitro-W_i^{Me}*s*.—All of the adducts studied gave phenolic products in the range 40—65% H_2SO_4. For the secondary acetates (1a and b) and (2) the yields of phenols reached maxima in *ca.* 60% H_2SO_4, as the proportion of the adduct forming the W_i^{Me} increased. The yields then rapidly decreased with increasing acidity, and nitro-migration became dominant. The mechanism of capture is presumably attack on the W_i^{Me} by water to give a dienol (10) [path (f)]. Loss of nitrous acid from (10) probably occurs in a manner analogous to its loss from the dienyl acetate (*E*1).[7] Acetate (1a) gave a small amount (*ca.* 1%) of 4-methyl-2-nitrophenol, presumably by nitrosation of the *p*-cresol formed by the elimination of nitrous acid and subsequent oxidation. Neither urea nor sulphamic acid were able to stop the formation of this product, suggesting that the eliminated nitrous acid does not diffuse away from the solvent cage before nitrosating the phenol, or that neither urea nor sulphamic acid compete successfully with the phenol.

That the intense peak, $\lambda_{max.}$ 360 nm, seen during the decomposition of the *o*-xylene adduct in 40—70% H_2SO_4 could also be produced by treating 3,4-dimethylphenol with sodium nitrite suggested that the peak is evidence of nitrosation, or some related reaction, and indeed small yields (*ca.* 2%) of 2-nitro-4,5-dimethylphenol were observed during the decomposition of the adduct. Intense, transient colours have been reported in other nitrosations.[18] Since the rates of formation and decay, and the intensity of the peak were unaffected by the addition of urea or sulphamic acid, it is presumably caused by reaction of the nitrous acid immediately it is eliminated from the dienol. Similar peaks were not seen during the decomposition of the other adducts, and attempts to produce them by the reaction of sodium nitrite with the corresponding phenols also failed.

Nitro-group Migration [*Path* (*e*)].—All the adducts gave good yields of nitroaromatics when solvolysed at high acidities. Acetate (1a) gave only *o*-nitrotoluene, (1b) only 3-nitro-*o*-xylene (as already stressed [3,5]), (1c) gave 2-nitro-*p*-xylene, (2) gave only 4-nitroindan, and (1e) gave only 6-nitro- (95%) and 3-nitro-pseudocumene (5%). To account for these products it is only necessary to postulate that nitroaromatics arise by 1,2-migration to an unsubstituted position followed by deprotonation, or by successive 1,2-shifts from one methylated position

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[18] A. R. Butler and A. P. Sanderson, *J.C.S. Perkin II*, 1974, 1671.

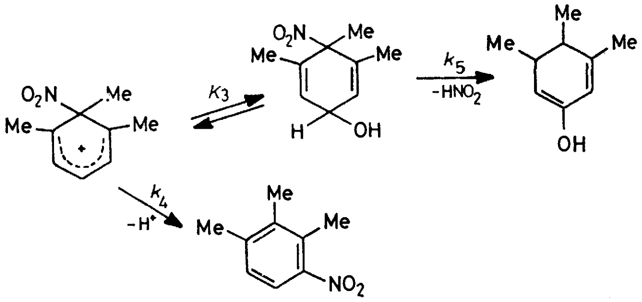
to another followed by movement to an unsubstituted position (or return to the first *etc.*) and deprotonation. Direct 1,3-shifts, or migration across unsubstituted positions need not be postulated.

Myhre[7] found that for the W_i^{Me} from *o*-xylene, the direct 1,2-shift producing 3-nitro-*o*-xylene and the repeated 1,2-shifts through the alternative *ipso*-position occur at comparable rates, a result implying that the migration from C-1 to -2 occurs considerably more readily than that from C-1 to -6. The situation with the 1-nitro-W_i^{Me} from pseudocumene is noticeably different, the single 1,2-migration (C-1 ⟶ C-6) being markedly preferred over the repeated shift (C-1 ⟶ C-2 ⟶ C-3). This is in line with the account of the solvolysis of (1e) given above, which supposes that the *ipso*-capture of (13) to give (14) is important. Were it not so the source of 5-hydroxypseudocumene might have been supposed to be the isomerisation of (13) to (17), followed by capture of (17) by water, and loss of nitrous acid. The factors controlling the relative rates of competing rearrangement such as (13) ⟶ (17) and (13) ⟶ (18) are not understood.

Attempts have been made[5] to compare, for various nitro-W_i^{Me}s, the relative ease of nitro migration and nucleophilic capture by noting for each case the acidity at which 50% of each nitro-W_i^{Me} rearranges, low acidity indicating relatively easier migration. For nitro-W_i^{Me}s such as those generated from (1c and e) this comparison is not very significant, for over a considerable range of acidity a substantial proportion of each reacts in a third way (generating side-chain products) which is not open to the nitro-W_i^{Me}s from secondary acetates. Even if allowance were made for the fraction of reaction occurring in the side-chains the comparison would be being made between capture at positions adjacent to *ipso*-positions and at substituted *para*-positions on the one hand, with capture at *para*-CH positions on the other; the requirements of these various processes might be quite different. The simple comparison between the W_i^{Me} from the toluene adduct and that from the *o*-xylene adduct shows little difference between them; both rearrange to the extent of 50% in *ca.* 67% H_2SO_4. This observation, is based on the solvolysis of adducts, more reliable, particularly in the case of toluene, than that based on nitration results.[5] Clearly, the simple treatment ascribing partitioning between rearrangement and capture to the 'downhill' or 'uphill' nature of the rearrangement is unsatisfactory; in the case of toluene migration occurs from a less reactive to a more reactive position whilst for *o*-xylene the opposite is true.

Myhre[7] found that the solvolysis of the secondary acetate (1d) in 50—75% H_2SO_4 gave 4-nitrohemimellitene and 5-hydroxyhemimellitene, and, assuming that in these conditions process (a) was much slower than (b) (see comment above), analysed the results in terms of the following reactions.

If the ionisation equilibrium of the carbinol follows H_R, and activity coefficients cancel then $\log[\% \text{ 4-nitro}/(100 - \% \text{ 4-nitro})] = -H_R + \log(k_4/k_5K_3)$. A good linear correlation of $\log \%[\text{4-nitro}/(100 - \% \text{ 4-nitro})]$ and H_R was found (though not with a slope of unity). We have treated our results for (1a and b) similarly, plotting log (% nitro migration/% capture) *versus* $-H_R$. They cover a rather larger range of acidity than those for (1d), and it could not be assumed that process (a) was negligible by comparison with (b). Over most of their length the plots for (1a and b) (Figure 5) were linear with slopes of 0.7 and 1.00, respectively. The argument assumes that either the rate constants for loss of nitrous acid from the carbinol and for formation of nitroaromatic from W_i^{Me} are independent of acidity or vary with it in the same way; neither assumption is likely to be strictly true. The assumption that K_3 relates to a pre-equilibrium, *i.e.* that the carbinol ionises faster than it loses nitrous acid, is also questionable.



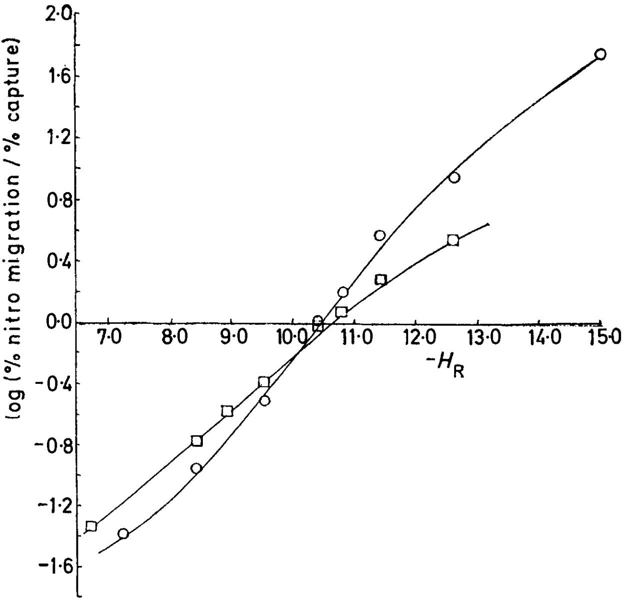


FIGURE 5 The relationship between the fates of W_i^{Me}s and acidity: W_i^{Me} from *o*-xylene, ○; W_i^{Me} from toluene, □

The more complicated processes occurring with the W_i^{Me}s corresponding to *p*-xylene and pseudocumene prevent a similar analysis of their performances.

Side-chain Substitution.—Side-chain substitution products were only found on decomposition of the *p*-xylene

(1c) and pseudocumene adduct (1e), in agreement with Fischer's[11] findings that only methylbenzenes with methyl groups *para* to each other form side-chain derivatives, and that the methyl group substituted is the one *para* to the *ipso*-nitro group.

The aldehyde was the major product from both adducts, although small amounts of other products, including the side-chain acetate and alcohol were also formed. With (1c and e) the yields of these products reached maxima at 51% H_2SO_4 and 63% H_2SO_4, respectively.

It is commonly assumed,[4,19] without direct evidence, that side-chain reactions involve the pathway (b) $\longrightarrow$ (j), the triene then being attacked by a nucleophile. In terms of such a pathway it would not be surprising that the yield of side-chain products varied with acidity as found. The acetate formed in step (b) is obviously the source of the side-chain acetate, which itself could give the alcohol, or the latter could be formed by reaction of the triene with water. The aldehyde could arise by nitrite oxidation of the alcohol, presumably through the formation of the nitrite ester. Alternatively, the triene could lose nitrite, giving an ion-pair from which recombination generated the benzyl nitrite, and thence the aldehyde.[19,20]

Relevance of Adduct Solvolysis to Nitration.—The changes in the yields of nitroaromatics with acidity during the nitration of methylbenzenes in sulphuric acid were interpreted in terms of the behaviour of W_i^{Me}s.[5] This interpretation is confirmed by the present studies of the behaviour of W_i^{Me}s formed by adduct solvolysis.

The small proportion of *ipso*-attack in toluene (*ca.* 5%), and ' medium effects ' on the isomer ratios make this case the most difficult for which to relate the nitration results to the results obtained from solvolysis. We can, however, note that both the 5% increase in yield of nitrated products in the nitration of toluene on going from 55 to 65% H_2SO_4, and the presence of 4.2% 4-methyl-2-nitrophenol in the nitration products in 55% H_2SO_4, may be accounted for in terms of the observed reactions of the W_i^{Me}.

In nitration the yield of 3-nitro-*o*-xylene increases from 11 to 57% in the range 55—75% H_2SO_4. This exactly follows the increase in 3-nitro-*o*-xylene formed by 1,2-nitro migration in the W_i^{Me} formed by solvolysis over the same acidity range. The increasing yields of 2,5-dimethylnitrobenzene, and 6-nitropseudocumene found during the nitration of *p*-xylene and pseudocumene, also exactly follow the increasing formation of these products by 1,2-nitro migration from their W_i^{Me}s. It seems clear that the chemistry exhibited by the W_i^{Me} is identical, whether they are formed directly during nitration or by solvolysis.

During nitration, the phenolic ' capture ' products and side-chain substituted products formed from the W_i^{Me}s may be nitrated or oxidised to give products which are difficult to isolate, and are not identified in many reports in the literature. These products from the W_i^{Me}s generated by adduct solvolysis do not undergo such extensive further reaction, as no nitric acid is present, and so it is possible to identify them. It has been noted that the yield of ' by-products ' during aromatic nitration decreases with increasing acidity, and only those aromatics prone to *ipso*-substitution give ' by-products '.[21]

The view has been expressed[2] that the solvolyses are only relevant to the nitrations when the adduct generates the W_i^{Me} in a known yield, by elimination of acetic acid. The results obtained in dilute acids, when the adduct eliminates nitrous acid to give the aryl acetate, are not relevant, as the W_i^{Me} is not formed. This view has been criticised[7] because the elimination of nitrous acid from the adduct provides a good model for the elimination of nitrous acid from the dienol formed by capture of the W_i^{Me} by water. The difference is one of stress; our original interest was in the primary chemistry of nitro-W_i^{Me}s, that is in their partitioning between capture and rearrangement.

For each W_i^{Me} there is an acidity at which and below which it is quantitatively captured by water, and an acidity at which and above which it rearranges by quantitative 1,2-migration of the nitro group. If the parent aromatic of the W_i^{Me} is nitrated at each of these acidities the difference in yields of the nitro-aromatics will be equal to the proportion of *ipso*-attack in the aromatic. This has also been obtained by nitrating the aromatic in acetic anhydride, measuring the yield of aryl acetates isolated on work-up, and taking this to be equal to the yield of the W_i^{Me}.[22] This assumes that capture of the W_i^{Me} is complete in acetic anhydride. Table 9 shows the amount of *ipso*-attack for several polymethylbenzenes calculated using both of these approaches, together with the amount of adduct formation during low temperature nitration in acetic anhydride, measured by ^1H n.m.r. spectroscopy of the nitration solution. The broadly similar performance of the different media strengthens the view that complete capture has been achieved in both media.[5]

TABLE 9

Extent of *ipso*-attack in aqueous sulphuric acid and in acetic anhydride

Substrate	% *ipso*-attack (Wt. % H_2SO_4)[5]	% Formation of aryl acetates from reaction products in acetic anhydride[22]	% Formation of adducts in acetic anhydride[a]
Toluene	5 (54.9)	3	5
o-Xylene	65 (54)	59	50
p-Xylene		75	80
Pseudocumene	60 (51)	60	50
Hemimellitene	49 (54)	46	46

[a] This work. ^1H n.m.r. analysis (± 5%).

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[19] H. Suzuki, *Synthesis*, 1977, 217.

[20] R. G. Gillis, *J. Org. Chem.*, 1956, **21**, 805; S. D. Ross, E. R. Coburn, and M. Finklestein, *ibid.*, 1968, **33**, 585.

[21] C. Hanson, T. Kaghazchi, and M. W. Pratt, ' Industrial and Laboratory Nitrations ', eds. L. F. Albright and C. Hanson, American Chemical Society Symposium Series, 1975, vol. 22.

[22] A. Fischer and G. J. Wright, *Austral. J. Chem.*, 1974, **27**, 217.

The evidence adduced below that the degree of *ipso*-attack is to some extent medium dependent makes it necessary to stress that precise coincidence of performance between dilute sulphuric acid and acetic anhydride is not to be expected. Further, the degrees of *ipso*-attack indicated by the results in Table 9 are not necessarily the largest which can be attained.

Positional Reactivities in the Nitration of Methylbenzenes.—By combining the nitration results with the solvolysis results it is possible to calculate the degree of attack at a given position, and to examine the possibility that positional reactivities vary with acidity.[5] The assumption made is that any loss of mass balance in the nitration yields is to be attributed to nucleophilic capture of W_i^{Me}. The results for *o*-xylene have been recalculated and differ quantitatively from those given earlier,[5] whilst qualitatively showing the same trends (Table 10). To reduce errors arising from interpolations we restricted our calculations to acidities at which yields of 3- and 4-nitro-*o*-xylene have been determined,[5] and at which the loss of mass balance is significant. Calculations for pseudocumene could not be made because we have solvolysis results for only one of the possible *ipso*-nitrocyclohexadienyl acetates. For *p*-xylene the nitration results [5] are inadequate to warrant treatment; qualitatively they do suggest variation with acidity of positional reactivities, C-2 becoming more, and C-1 less reactive.

The calculations for *o*-xylene (Table 10) indicate, even after due account is taken of errors, that there is a significant decrease in the degree of attack at the *ipso*-position with increasing acidity, accompanying the experimentally established increase in the degree of attack at C-4. Errors preclude a conclusion about the dependence upon acidity of the degree of attack at C-3, but this is clearly the least reactive position.

The more general dependence of relative positional reactivities upon medium [23] strengthens the above conclusions. It is clear that the methods which we have so far used are not accurate enough to evaluate this dependence precisely.

TABLE 10

Positional reactivities in *o*-xylene [a]

Wt. % H_2SO_4	% *ipso*-Attack [b]	% Attack at C-3	% Attack at C-4
54.2	71 (±6)	6 (±6)	23 (±2)
63.5	53 (±5)	16 (±5)	31 (±2)
67.1	50 (±8)	15 (±8)	35 (±2)

[a] Errors were calculated by assigning each yield, expressed as a percentage, an error of ±2, and then using standard formulae for the propagation of errors.[24] [b] Calculated as the percentage departure from quantitative yield of nitro-products in the nitration of *o*-xylene,[5] divided by the percentage of W_i^{Me} which is captured. (See Figure 2 and text).

[7/2121 *Received, 5th December,* 1977]

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[23] H. W. Gibbs, unpublished results.

[24] J. Topping, ' Errors of Observation and Their Treatment ', Institute of Physics, Bristol, 1963.