Electrophilic Aromatic Substitution. Part 29.[1] The Kinetics and Products of the Solvolyses in Aqueous Sulphuric Acids of 2-Cyano-3,4-dimethyl-4-nitrocyclohexa-2,5-dienyl Acetate: the Non-occurrence of an Intramolecular 1,3-Migration of the Nitro-group in the Solvolytic Reactions of the Diene. The Kinetics and Products of Nitration of 2,3- and 3,4-Dimethylbenzonitrile

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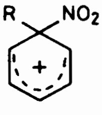
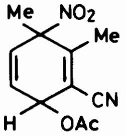
The kinetics in 61.8—79.5% H_2SO_4 and the products formed in 61.8—84.3% H_2SO_4 for the solvolyses of the above-named diene have been determined. The reactions are interpreted as involving concurrent elimination of nitrous acid and $A_{AL}1$ generation of the same *ipso*-intermediate as arises in the nitration of 2,3-dimethylbenzonitrile. This intermediate reacts by intermolecular rearrangement (as is proved by the isolation from the solvolyses of 2,3-dimethylbenzonitrile and the trapping of nitronium ion by reaction with 4-fluorophenol), by nucleophilic capture by water, and by 1,2-intramolecular rearrangement to 2,3-dimethyl-4-nitrobenzonitrile. The results permit the partitioning of the overall solvolytic rate coefficient and the demonstration that the derived coefficient for the reaction competing with the elimination depends on acidity as would be expected for an $A_{AL}1$ reaction. The elimination of nitrous acid is also acid-catalysed and may not be a simple $E1$ reaction. The solvolytic reactions of the diene do not lead to a 1,3-intramolecular rearrangement of the nitro-group and the observed 1,3-rearrangement of the diene to give 2,3-dimethyl-5-nitrobenzonitrile under non-solvolytic conditions appears to be a thermal reaction of the diene molecule. By combining the solvolysis results with those for the nitration of 2,3-dimethylbenzonitrile in 70.4—82.5% H_2SO_4 it is shown that the major primary consequence of the nitration is *ipso*-attack and that it is possible to determine the positional reactivities in the nitrile.

The rearrangements of *ipso*-Wheland intermediates (1) to give aromatic nitro-compounds have been classified as intra-, extra-, and inter-molecular.[2] In intramolecular migration the nitro-group does not become free of the carbon skeleton and 1,2-migration occurs. If the nitro-group does become free of the carbon skeleton as a nitronium ion two kinds of case arise; in one the residual aromatic compound and the nitronium ion react at the encounter rate and in the other they react below the encounter rate. In the first case, described as extramolecular rearrangement, the nitronium ion and the residual aromatic molecule do not escape from the solvent cage and nitration occurs but not necessarily at the *ortho*-position. In the second case, intermolecular rearrangement, the nitronium ion and the aromatic molecule may escape from the solvent cage, and the nitronium ion may nitrate an aromatic molecule other than its initial partner. Extra- and inter-molecular migration of the nitro-group have been demonstrated with *p*-cresol derivatives.[1,2]

When 2-cyano-3,4-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate (2) was thermolysed, or heated with acetic acid, 2,3-dimethylbenzonitrile, and 2,3-dimethyl-5-nitrobenzonitrile resulted.[3] That the nitro-group migration was an intramolecular 1,3-migration rather than a merely formal 1,3-migration was thought to be demonstrated by two observations. First, no nitro-compounds other than the 5-nitro-isomer were formed; they would have been expected if a process of dissociation and re-nitration were involved [nitration of 2,3-dimethylbenzonitrile with nitric acid–acetic anhydride gave (2), and 2,3-dimethyl-4-, -5-, and -6-nitrobenzonitrile]. Second, the decomposition of (2) in boiling mesitylene gave 2,3-dimethyl-5-nitrobenzonitrile and no nitromesitylene. The formation of 2,3-dimethyl-5-nitrobenzonitrile in these reactions was viewed as involving the formation from (2) of (3), and rearrangement of (3); since 2,3-dimethyl-4-nitrobenzonitrile was not also formed that rearrangement could not occur by two consecutive shifts of the nitro-group, but must be a 1,3-intramolecular rearrangement.



(1)



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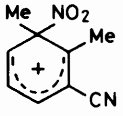


(3)

The results outlined above, and similar ones for the isomeric 2-cyano-4,5-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate, are not readily compared with others for the acid solvolyses of nitro-acetates similar to (2).[2,4,5] The experimental conditions were unusual, and the supposed intramolecular 1,3-rearrangement of (3) is difficult to accept. Other intramolecular rearrangements of structures of type (1) involve 1,2-shifts, single or, when the 2-position is substituted, repeated.[2] Accordingly, we have re-examined the solvolysis of (2) in aqueous sulphuric acid of a range of concentrations. The retarding effect of the cyano-group made possible the study of both the kinetics and the products of the reactions. Related studies of the kinetics and products of nitration in aqueous sulphuric acid of 2,3-dimethylbenzonitrile (and of the 3,4-isomer) have also been carried out.

Experimental

Materials.—Sulphuric acid and sulphanilic acid were AnalaR reagents. Sulphuric acid concentrations were determined by density measurements. Nitric acid was prepared by vacuum distillation from a mixture of fuming nitric acid and an equal volume of concentrated sulphuric acid, and stored at −10 °C. A commercial sample of 2,3-dimethylbenzonitrile was purified by distillation, b.p. 100—102 °C at 4 mmHg.

2,3-*Dimethylnitrobenzonitriles.*—2,3-Dimethylbenzonitrile (15 ml) was added to 98% sulphuric acid (60 ml) containing

Table 1. G.c. conditions for products and standards [a]

Compound	R_t/s	Response factor [b]	Column
For the solvolysis of (2)			
4-Fluorophenol	220		10% Dexsil 400 GC on Chromasorb WAW; nitrogen flow rate 40 ml min^{-1}; 130 °C
4-Fluoro-2-nitrophenol [c]	380		
2-Nitrotoluene [d]	600		
2,3-Dimethylbenzonitrile	820	1.277	
Above four compounds	<300		As above, but at 180 °C
6-Hydroxy-2,3-dimethylbenzonitrile	390	<0.01	
Pentachlorobenzene [d]	560		
6-Acetoxy-2,3-dimethylbenzonitrile	680	1.390	
2,3-Dimethyl-4-nitrobenzonitrile	780	1.344	
2,3-Dimethyl-5-nitrobenzonitrile	1 220	1.345	
For the nitrations			
2,3-Dimethylbenzonitrile	120	0.947	As above, but at 205 °C
2,3-Dimethyl-4-nitrobenzonitrile	340	0.748	
2,3-Dimethyl-5-nitrobenzonitrile	500	0.875	
1-Bromo-2-methoxynaphthalene [d]	655		
2,3-Dimethyl-6-nitrobenzonitrile	890	0.830	
3,4-Dimethylbenzonitrile	135	0.662	As above, but at 205 °C
3,4-Dimethyl-5-nitrobenzonitrile	430	0.624	
3,4-Dimethyl-2-nitrobenzonitrile	590	0.614	
1,3-Diphenylpropan-1-one [d]	830		
3,4-Dimethyl-6-nitrobenzonitrile [e]	1 020		

[a] Pye 104 instrument with flame ionization detector and computing integrator (Datalab 308). [b] (Area ratio/mol ratio), both for (compound/ref. standard). [c] The response factor (y) and the area ratio (x) were related by the equation, $y = -1.981x^4 + 4.342x^3 - 3.735x^2 + 1.718x + 0.1667$, ($0 \leqslant x \leqslant 0.8$). [d] Reference standard. [e] The response factor (y) and the area ratio (x) were related by the equation, $y = 0.979x^3 - 1.631x^2 + 0.980x + 0.347$, ($0.05 \leqslant x \leqslant 0.8$).

fuming nitric acid (30 ml). After 1 h at 0 °C the mixture was poured onto ice. Extraction with ether and removal of this solvent after washing with saturated sodium carbonate solution and water, and drying ($MgSO_4$), gave a mixture of nitro-compounds (21 g). The isomers were separated by chromatography of the mixture (7.5 g) in five portions on silica (230—400 mesh, 4 × 20 cm). Elution with 40 : 60 ether–ligroin (b.p. 30—40 °C) gave, in order of appearance, the 4-, 5-, and 6-nitro-compounds, together with intermediate mixtures. The 5- and 6-nitro-compounds were obtained substantially pure, but were crystallised from ether–ligroin (b.p. 60—80 °C): 2,3-dimethyl-5-nitrobenzonitrile (2.3 g), needles, m.p. 129—130 °C; 2,3-dimethyl-6-nitrobenzonitrile (1.8 g), pale yellow needles, m.p. 110—110.5 °C. The 4-nitro-compound (0.2 g) contained *ca.* 4% of the 5-nitro-isomer; this mixture was used without further purification for g.c. calibration. Additional quantities of the 4-nitro-compound were obtained from chromatography of 2-cyano-3,4-dimethyl-4-nitrocyclohexa-2,4-dienyl acetate (see below) and from combined samples a pure specimen was obtained by recrystallisation from ether–ligroin (b.p. 60—80 °C) as fawn crystals, m.p. 90—91 °C. The ^1H n.m.r. spectra of the three nitro-compounds were identical with those reported, and the mass spectra differed only in that in each case a peak with *m*/*e* 160 was present.[3]

2-Cyano-3,4-dimethyl-4-nitrocyclohexa-2,5-dienyl Acetate.—Nitric acid (9.6 ml) was added to acetic anhydride (24 ml) at 0 °C and the mixture was kept at that temperature for 40 min. The solution was added to 2,3-dimethylbenzonitrile (6.1 g) in acetic anhydride (14 ml) at 12 °C and the mixture was kept at 12 °C for 21 h. Worked up as described [3] the reaction gave a dark red oil (7.8 g). The impure diene (2.2 g) was obtained by chromatography [−10 °C; 160 g of 230—400 mesh silica; 40 : 60 ether–ligroin (b.p. 30—40 °C)]. G.c. showed this material to contain diene (65%) and 2,3-dimethyl-6-nitrobenzonitrile (35%). It was subjected to further chromatography at −10 °C on neutral alumina (140 g); 2,3-dimethyl-5-nitro- (from decomposition of the diene), and 2,3-dimethyl-6-nitro-benzonitrile, and the diene were separated by 35 : 65, 35 : 65—40 : 60, and 50 : 50 ether–ligroin, respectively. The diene crystallised from tetrachloromethane as cubes (0.23 g), m.p. 98—98.5 °C, δ ($CDCl_3$) 1.807 (3 H, s, Me-4), 2.169 (s, Me-3) and 2.191 (s, MeCO) (6 H together), 5.843br (m), and 5.976 (s), 6.08 (d), and 6.16 (dd) (3 H together) (J_{15} 1.2, J_{16} 3.25, $J_{Me\text{-}3\text{-}1}$ 1.6, J_{56} 9.9 Hz). The spectrum was analysed by use of a shift reagent, and subjected to computer simulation as described,[3] but differs in some respects from that already reported,[3] *m*/*e* 190(1%), 148(20), 147(4), 122(9), 121(75), 120(25), 117(10), 116(100), 104(10), and 103(18).

In g.c. (10% Dexsil on Chromosorb WAW; 200 °C; injector temp. 250 °C) the diene gave 2,3-dimethylbenzonitrile (*ca.* 80%), 2,3-dimethyl-5-nitrobenzonitrile (*ca.* 20%), and a trace of 6-acetoxy-2,3-dimethylbenzonitrile.

Solutions of the diene in acetonitrile at −10 °C were stable over long periods, and for kinetic purposes and for product studies the diene was stored in this way. The spectrum of such a solution at ambient temperatures in a cell in a u.v. spectrophotometer did not change during a week.

6-Hydroxy-2,3-dimethylbenzonitrile.—A specimen of this compound, needed for characterisation, was obtained from solvolysis of the diene just described. The crude diene (17 g) from initial chromatography was stirred vigorously in acetonitrile (120 ml) and 14.5% H_2SO_4 (9 l) for 42 h at 25 °C. The heterogeneous mixture was cooled and extracted with dichloromethane. Recovery of the product after drying ($MgSO_4$) and fractional crystallisation from dichloromethane gave needles of the phenol (2.2 g), m.p. 137.5—138 °C, δ (hexadeuterioacetone) 2.21 (3 H, s), 2.39 (3 H, s), 5.58 (1 H, s), 6.77 (1 H, d), and 7.21 (1 H, d) (J_{45} 9 Hz), *m/e* 147(96%), 146(33), 132(100), 118(18), and 104(18). Conventional acetylation gave crystals of 6-acetoxy-2,3-dimethylbenzonitrile, m.p. 74—75 °C, δ ($CDCl_3$) 2.28 (3 H, s), 2.36 (3 H, s), 2.46 (3 H, s), 6.95 (1 H, d), and 7.36 (1 H, d) (J_{45} 9.5 Hz), *m/e* 189(10%), 148(6), 147(100), 146(6), and 132(32).

3,4-*Dimethylnitrobenzonitriles*.—3,4-Dimethylbenzonitrile (6.0 g), m.p. 67—67.5 °C, obtained from 3,4-dimethylaniline in 47% yield,[6] in acetic acid (30 ml) was nitrated as described for the 2,3-dimethyl compound. The crude mixture of products (6.7 g) was separated in four equal batches by chromatography [230—400 mesh silica (160 g); 63 : 35 ether–ligroin (b.p. 60—80 °C)] giving, in order of elution, 3,4-dimethyl-5-nitrobenzonitrile (1.8 g) forming, by recrystallisation from ethanol, needles, m.p. 118—119 °C, δ ($CDCl_3$) 2.38 (3 H, s), 2.40 (3 H, s), 7.68 (1 H, d), 7.94 (1 H, d) (J_{26} 2.0 Hz), *m/e* 176(25%), 160(16), 159(100), 132(16), 131(50), 130(16), 116(12), 114(92), 113(50), 112(16), and 87(62) and a mixture of the other isomers. Fractional crystallisation of the mixture from ether–ligroin (b.p. 60—80 °C) gave the 6-nitro-isomer as needles, m.p. 179—180 °C, δ ($CDCl_3$) 2.39 (3 H, s), 2.43 (3 H, s), 7.60 (1 H, s), and 8.14 (1 H, s), *m/e* 177(9%), 176(100), 160(32), 147(7), 146(88), 145(46), 130(56), 118(16), 116(14), 104(35), 91(28), and 77(60). The 2-nitro-isomer was isolated as a mixture containing some of the 6-nitro-compound (*ca.* 5%), which could be used for g.c. calibrations and stability studies.

Thermal Reactions of 2-*Cyano*-3,4-*dimethyl*-4-*nitrocyclohexa*-2,5-*dienyl Acetate* (2).—A solution (48 μl; 1.0 × 10^{-3}M) of the diene in acetonitrile was added to mesitylene (3 ml) and the mixture was heated at 100 °C. The u.v. spectrum of the solution changed fairly quickly over the first 4—5 h, and then much more slowly. After heating had continued overnight the final spectrum was not identical with that of a solution of nitromesitylene of equivalent concentration. Analysis by g.c. under the conditions of Table 1, but at 150 and 180 °C, detected 2,3-dimethylbenzonitrile and 2,3-dimethyl-5-nitrobenzonitrile in the ratio 3 : 2. No nitromesitylene was found.

Direct injection of the diene on to the g.c. column at 150 °C gave 2,3-dimethylbenzonitrile, 2,3-dimethyl-5-nitrobenzonitrile, and 6-acetoxy-2,3-dimethylbenzonitrile in the ratios 17 : 7 : 1. None of the 6-nitro-isomer was detected.

Kinetic Measurements and Product Yields.—(a) *Nitration*. The kinetic methods used have been described in several papers in this series. The measurements for 3,4-dimethylbenzonitrile were complicated by the fact that the hydrolysis of one of the nitration products, 3,4-dimethyl-2-nitrobenzonitrile, proceeded at rates large enough (Table 3) to be significant by comparison with the rates of nitration. The difficulty was avoided by following the nitration at 300 nm, almost coincident with an isosbestic point (298 nm) involving the faster of the two hydrolysis steps. Rate coefficients for nitrations are in Table 4.

The method of determining yields of nitro-compounds (Table 5) by recovery in dichloromethane and assay by g.c. has also been described several times in this series. G.c. conditions are given in Table 1. The reproducible yields of products recoverable by extraction are given in Table 2. Hydrolysis of 3,4-dimethyl-2-nitrobenzonitrile made a correction for this reaction necessary.

(b) *Solvolysis of* 2-*cyano*-3,4-*dimethyl*-4-*nitrocyclohexa*-2,5-*dienyl acetate*. Portions of the stock solution of the diene in acetonitrile were syringed into sulphuric acid mixtures containing sulphanilic acid. Solvolysis was followed by measuring the increase in absorbance at 300 nm (below 290 nm sulphanilic acid absorption interfered) using a Pye-Unicam SP 500 instrument fitted with a Gifford photomultiplier and linked to a PET computer. The cell compartment was flushed with dry nitrogen during measurements at 5.0 ± 0.1 °C. It was also necessary to know rate coefficients for acid hydrolyses of 6-acetoxy-2,3-dimethylbenzonitrile; these were measured by conventional methods and are given in Table 6. Above 74% H_2SO_4 an unidentified reaction interfered with the hydrolysis.

Product measurements (g.c.) were carried out on reactions run in darkened flasks and worked up by extraction in the usual way. Results for reactions both with and without added 4-fluorophenol are given in Table 9, and for reactions run for shorter times in the presence of 4-fluorophenol in Table 10.

Table 2. Recovery of aromatic compounds, by extraction with dichloromethane after dilution, from solution in aqueous sulphuric acids at 25.0 ± 0.1 °C

Compound	H_2SO_4 (%)	Recovery (%)[a]
2,3-Dimethylbenzonitrile	70.4	100
	82.5	100.5
2,3-Dimethyl-4-nitrobenzonitrile	70.4	96.6
	74.3	95.5
	82.5	97.5
2,3-Dimethyl-5-nitrobenzonitrile	70.4	98.3
	74.3	98.5
	82.5	97.0
2,3-Dimethyl-6-nitrobenzonitrile	70.4	101
	74.3	103
	82.5	100
3,4-Dimethylbenzonitrile[b]	70.4	100
	82.5	100
3,4-Dimethyl-5-nitrobenzonitrile	70.4	77.1
	74.3	82.9
	76.8	86.6
	80.6	91.5
	82.5	91.0
3,4-Dimethyl-6-nitrobenzonitrile	70.4	100
	74.3	102
	76.8	99.7
	80.6	100
	82.5	102
3,4-Dimethyl-2-nitrobenzonitrile[b]	70.4	81.9
	74.3	81.6
	76.8	83.6 ± 2
	80.6	90.9 ± 5
	82.5	101 ± 15

[a] Solutions in sulphuric acid kept for 10 half-lives of nitration of the parent compound. [b] Yields corrected for hydrolysis of stated aromatic (Table 3). Errors are given when estimated to be > ±2%.

Results

Nitrations.—Amongst the products of nitration of the dimethylbenzonitriles, 3,4-dimethyl-2-nitrobenzonitrile was noteworthy for being hydrolysed rapidly enough, by comparison with the rate of nitration of its parent, to necessitate a correction for this fact in calculating product yields (Tables 3 and 5). In the related kinetic studies possible difficulties caused by the hydrolysis could be avoided (see Experimental section). 2,3-Dimethylbenzonitrile is *ca.* 2.3 times more reactive than its 3,4-isomer (Table 4), and of reactivity similar to that of 2,3-dimethylnitrobenzene.[7]

From 2,3-dimethylbenzonitrile the aggregate yield of nitro-compound above *ca.* 76% H_2SO_4 was quantitative. At lower acidities the aggregate yield and the yield of each isomer fell, the overall loss reaching 26—27% in 70.4% H_2SO_4 (Table 5, Figure 1). The results were not dependent on the concentration

Table 3. Hydrolyses of 3,4-dimethyl- and 3,4-dimethyl-2-nitrobenzonitrile, and of 3,4-dimethyl-2-nitrobenzamide in aqueous sulphuric acids at 25.0 ± 0.1 °C

Compound	H_2SO_4 (%)	10^5k_1/ s^{-1}
3,4-Dimethylbenzonitrile [a]	72.3	0.23
	74.3	0.38
	76.8	0.75
	78.4	1.33
	81.6	2.7
	82.5	2.3
	83.6	3.6
	86.7	6.7
	90.7	6.9
	92.4	4.6
	94.6	4.2
3,4-Dimethyl-2-nitrobenzonitrile [b,c]	76.8	2.3 [d]
	78.4	8.0, 8.7 [d]
	80.6	70 [f]
	82.5	240 [f]
	83.6	430 [g]
3,4-Dimethyl-2-nitrobenzamide [b,e]	83.6	27 [h]
	84.3	32 [i]
	86.7	51 [i]

[a] [Ar] 6.75 × 10^{-5}M. λ 270 nm. The product (amide or acid) was not identified. [b] [Ar] 8 × 10^{-5}M. [c] The hydrolysis occurred in two stages, presumably giving the amide and then the acid. [d] λ 345 nm. [e] The second stage of the hydrolysis of 3,4-dimethyl-2-nitrobenzonitrile. [f] λ 313 nm. [g] λ 312 nm. [h] λ 298 nm. [i] λ 296 nm.

Table 4. Rate coefficients for the nitration of 2,3- and 3,4-dimethylbenzonitrile in aqueous sulphuric acids at 25.0 ± 0.1 °C

		$k_{2obs.}$/dm^3 mol^{-1} s^{-1}	
Acid (%)	$10^2[HNO_3]$/ M	2,3-Dimethylbenzonitrile [a,b]	3,4-Dimethylbenzonitrile [a,c]
70.4	19.3	8.9×10^{-4}	3.5×10^{-4}
74.3	9.7	1.73×10^{-2}	7.2×10^{-3}
76.8	8.9	0.106	4.95×10^{-2}
80.6	1.20	3.9	1.64
82.5	0.96	19.0 [d]	8.5 [e]

[a] Reaction followed at λ 300 nm. [Sulphanilic acid] 1—2 × 10^{-2}M. [b] [Ar] 6.7 × 10^{-5}M. [c] [Ar] 1.15 × 10^{-4}M. [d] [Ar] 6.0 × 10^{-5}M. [e] [Ar] 5.06 × 10^{-6}M.

Table 5. Yields of products formed in the nitrations of 2,3- and 3,4-dimethylbenzonitrile in aqueous sulphuric acids at 25.0 ± 0.1 °C

H_2SO_4 (%)	10^2-$[HNO_3]$/ M	Nitro-compound (%)			Aggregate yield (%)
		(4) [d]	(5) [e]	(6)	
2,3-Dimethylbenzonitrile [a,b]					
70.4	9.95	8.6	37.6	27.4	73.6
	19.9	9.5	38.6	25.9	74.0
72.3	10.2	9.8	42.0	28.9	80.7
74.3	4.89	9.7	44.6	31.8	86.1
	10.0	10.7	44.9	30.5	86.1
76.8	2.22	11.5	54.3	34.5	100
80.6	0.558	9.8	55.6	34.1	99.5
82.5	0.222	8.7	56.9	38.1	104
3,4-Dimethylbenzonitrile [a,c]					
		(2) [e]	(5) [d]	(6)	
70.4	19.9	35.6	33.6	18.5	87.7
74.3	10.0	36.1	41.2	22.5	99.7
76.8	2.22	34.9 ± 3	43.1	24.6	103 ± 3
80.6	0.558	37.4 ± 10	44.3	26.9	109 ± 10
82.5	0.222	38.4 ± 15	45.2	27.2	111 ± 15

[a] All reactions ran for 10 half-lives of nitration. No starting material was detected in reaction products. [Sulphanilic acid] 1—3 × 10^{-2}M. [b] [Ar] 1.993 × 10^{-4}M. [c] [Ar] 1.995 × 10^{-4}M. [d] Yields corrected for incomplete extraction (Table 2). [e] Yields corrected for incomplete extraction (Table 2), and hydrolysis of product (Table 3). Combined errors where > ±2% are indicated.

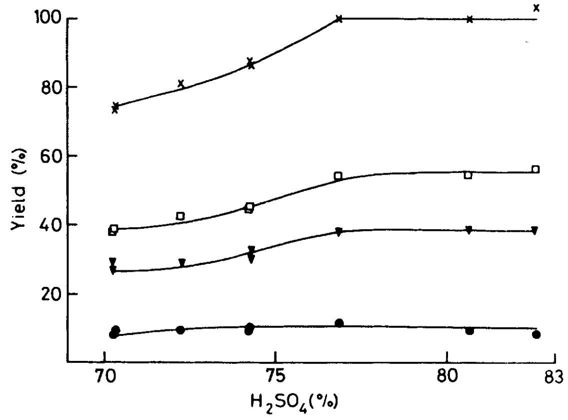


Figure 1. Yields of products from the nitration of 2,3-dimethylbenzonitrile in sulphuric acid at 25 °C: ×, aggregate yield; □, 2,3-dimethyl-5-nitrobenzonitrile; ▼, 2,3-dimethyl-6-nitrobenzonitrile; ●, 2,3-dimethyl-4-nitrobenzonitrile

of nitric acid used (Table 5). The products which might have been formed if nitrodecyanation had occurred were absent. The losses in yield in the range 76.8—70.4% H_2SO_4 indicated by the figures in Table 5 are 25, 31, and 21% for the 4-, 5-, and 6-nitro-compounds, respectively, which, bearing in mind the errors involved, are very similar.

The aggregate yield of nitro-compounds from 3,4-dimethylbenzonitrile, quantitative at high acidities, shows the same characteristic of falling off at lower acidities. The explanation is presumably the same as that given below for the case of 2,3-dimethylbenzonitrile. However, the measured yields (Table 5) are, because of the corrections which had to be made, much less accurate, and will not be discussed further.

Solvolyses of 2-Cyano-3,4-dimethyl-4-nitrocyclohexa-2,5-dienyl Acetate.—Good first-order kinetics were observed in these solvolyses (Table 8). The products isolated from solvolyses run for relatively long times were 2,3-dimethylbenzonitrile, 2,3-dimethyl-4-nitrobenzonitrile, and from some experiments small quantities of 6-acetoxy-2,3-dimethylbenzonitrile and 2,3-dimethyl-5-nitrobenzonitrile (Table 9). From shorter experiments the yields of the acetate were much larger (Table 10). When 4-fluorophenol, a good nitronium trap, was included in the reaction solution, and the reactions were allowed to run for 10 half-lives of the nitration of the phenol, 4-fluoro-2-nitrophenol was formed in yields which were within experimental error equal to those of 2,3-dimethylbenzonitrile (Table 9, Figure 2), themselves unchanged by the addition of the phenol. The presence of sulphanilic acid in all the solvolysis solutions excludes the involvement of nitrous acid in generating the nitrophenol, and strengthens the view that it is formed by conventional nitration. The ratio of the yield of 2,3-dimethylbenzonitrile to that of 2,3-dimethyl-4-nitrobenzonitrile did not change substantially over the range

Table 6. Rate coefficients for the hydrolyses of 6-acetoxy-2,3-dimethylbenzonitrile [a] in aqueous sulphuric acids at 25.0 ± 0.1 °C

H_2SO_4 (%)	$10^4k_2/s^{-1}$	H_2SO_4 (%)	$10^4k_2/s^{-1}$
15.2	0.99	55.1	12.9
21.0	1.50	56.7	15.2
28.8	2.3	58.6	15.3
33.2	3.0	59.6	17.8
36.2	4.0	61.8	20.5
41.0	5.3	63.2	22
45.3	6.9	64.8	27
47.8	7.95	69.3	41
50.2	9.2	70.4	47.5
52.8	10.9	72.3	67

[a] In >50% H_2SO_4, [Ar] 1.08×10^{-4}M. In <50% H_2SO_4, [Ar] 5.4×10^{-5}M. The increasing absorbance at 310 nm was measured. Above 74% H_2SO_4 an unidentified reaction interfered with the simple hydrolysis.

Table 7. Recovery of 6-acetoxy-2,3-dimethylbenzonitrile [a] by extraction with dichloromethane after reaction for 5 min in aqueous sulphuric acids at 25.0 ± 0.1 °C

H_2SO_4 (%)	Recovery of acetate (%)	Calculated recovery (%) [b]
61.8	59.7	54.9
65.5	47.6	45.4
70.4	24.9	23.8

[a] [Ar] 3.96×10^{-5}M. [b] Based on $[Ar]_t = [Ar]_0 \exp(-k_1 t)$. See Table 6.

Table 8. Rate coefficients for the solvolyses of 2-cyano-3,4-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate in aqueous sulphuric acid [a]

H_2SO_4 (%)	10^2 [Sulphanilic acid]/M	$10^3k_1/s^{-1}$
61.8	1.17	2.7
63.2	1.40	3.3
64.8	1.12	6.3
66.3	1.22	7.8
69.3	1.20	15.5
69.3	2.75	1.22
70.4	2.79	1.83
72.2	2.96	3.5
74.3	3.10	7.1
75.3	*ca.* 2	12.8
76.8	3.16	23
77.4	*ca.* 2	37
78.4	4.19	59
79.5	*ca.* 2	113

[a] The first five results relate to 25.0 ± 0.1 °C and all others to 5.0 ± 0.1 °C. All measurements were made at λ 300 nm. [Ar] 6.65×10^{-5}M to 1.04×10^{-4}M.

of acidities used, averaging *ca.* 14 over all the results in Table 9.

Discussion

We shall consider first our results for the solvolysis of the diene (2) in terms of the mechanisms which we believe to be operating, and which are shown in the Scheme. As in related solvolyses [4,5] there are two competing primary reactions; an elimination of nitrous acid which we represent as an $E1$ reaction, proceeding *via* the carbocation (4) [row (A) of the Scheme] though this description may need modification or refinement, and an $A_{AL}1$ reaction producing the W_t^{Me} (3). The latter rearranges intramolecularly by 1,2-migration of the nitro-group and intermolecularly by loss of nitronium ion, and is also captured by water [rows (B)—(D), respectively]. The products of the first two of these processes we have isolated or captured and have determined their yields, but the capture products [row (D)] were not isolated. Because 2,3-dimethylbenzonitrile is nitrated at a rate far below the encounter rate, extramolecular rearrangement of (3) is not important. Further, the reversion of (3) to 2,3-dimethylbenzonitrile and nitronium ion does not, even in the solvolyses run for comparatively long times, generate significant quantities of the products of intermolecular rearrangement (*i.e.* of the products of nitration of the nitrile, which would be 2,3-dimethyl-4-, -5-, and -6-nitrobenzonitrile, of which the 5-isomer would be the most important) because of the low reactivity of 2,3-dimethylbenzonitrile and the low concentrations of it and of nitronium ions in the solvolysis solutions.

When a reactive nitronium trap, 4-fluorophenol, was added in good concentrations to the solvolysis solutions it captured the nitronium ions and 4-fluoro-2-nitrophenol was formed [row (C)]. What is more, it was formed in the same yields as those of 2,3-dimethylbenzonitrile (Table 9, Figure 2; the points on the upper curve of Figure 2 are not *strictly* comparable because they do not all relate to the same temperature, but this factor is insignificant) as required by the mechanism. The yields of 2,3-dimethyl-4-nitrobenzonitrile (7) and 2,3-dimethylbenzonitrile (8) isolated from the solvolyses measure the relative importance of the intra- [row (B)] and intermolecular rearrangements [row (C)] of (3). The two reactions would not be expected to be much influenced in this respect by changes in acidity, and, as noted (see Results section), the ratio of (7) to (8) did not change much over the acidity range studied. The inter- was always more important (*ca.* 14 times) than the intra-molecular rearrangement.

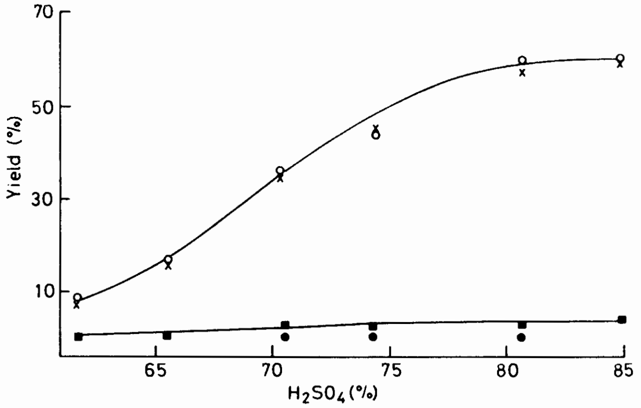


Figure 2. Yields of products from the solvolysis of 2-cyano-3,4-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate in sulphuric acid in the presence of 4-fluorophenol: ×, 2,3-dimethylbenzonitrile; ○, 4-fluoro-2-nitrophenol; ■, 2,3-dimethyl-4-nitrobenzonitrile; ●, 6-acetoxy-2,3-dimethylbenzonitrile

In contrast, the balance between rearrangement [rows (B) and (C)] and nucleophilic capture should move in favour of the former as the acidity of the solvolysis medium is increased. Furthermore, the partitioning of (2) between the $A_{AL}1$ and E reactions should likewise move in favour of the former with increasing acidity. Knowledge of the overall rate coefficient (k_1) for the solvolysis of (2), of the rate coefficient (k_2) for the hydrolysis (5) ⟶ (6), and of the yields of (5) produced by the solvolyses permits analysis of these circumstances. Treating

Table 9. The products of acid solvolyses of 2-cyano-3,4-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate in aqueous sulphuric acids carried out at each acidity for not less than 10 half-lives of nitration of 4-fluorophenol [a] at that acidity

H_2SO_4 [b] (%)	4-Fluoro-2-nitrophenol (%)	6-Acetoxy-2,3-dimethylbenzonitrile (%) [c]	2,3-Dimethylbenzonitrile (%)	2,3-Dimethylnitrobenzonitriles (%) [f] 4-nitro	5-nitro
61.8 [d]			7.5	0.6	
	9.4		7.3	0.6	
65.5 [d]			17.1	1.4	
	16.8		16.8	1.2	
70.4 [d]		1.2	36.4	2.8	<0.1
	36.2	1.2	35.3	2.9	
74.3 [e]		1.3	45.5	3.1	
	44.8	0.6	45.0	2.8	
80.6 [e]			58.9	4.0	0.6
	60.8	0.7	57.8	3.2	
84.3 [e]		<0.1	44.2	4.9	1.4
	60.1		59.1	4.2	

[a] [4-Fluorophenol] 5.00 × 10^{-3}M. [b] [Sulphanilic acid] 2.0 × 10^{-2}M. [c] Under the conditions used much of the acetate formed would be hydrolysed. Observed yields of acetate are consistent with those predicted from measured hydrolysis rate coefficients (Table 6). The derived phenol could not be measured because of its very low response factor in g.c. [d] [Diene] 3.93 × 10^{-5}M. Solvolyses at 25.0 ± 0.1 °C. [e] [Diene] 1.96 × 10^{-4}M. Solvolyses at 5.0 ± 0.1 °C. [f] Because of the long g.c. retention time of the 6-nitro-compound (causing peak broadening) it was not possible to detect <*ca.* 4%.

Table 10. The products of acid solvolyses of 2-cyano-3,4-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate [a] in aqueous sulphuric acids at 25.0 ± 0.1 °C, for not more than eight half-lives of the solvolyses

H_2SO_4 (%)	$10^3 k_1/s^{-1}$	$10^3 k_2/s^{-1}$	Reaction time (s) (no. of half-lives)	4-Fluoro-2-nitrophenol (%) [d]	2,3-Dimethylbenzonitrile (%)	2,3-Dimethyl-4-nitrobenzonitrile (%)	6-Acetoxy-2,3-dimethylbenzonitrile (%) [e]
61.8	2.7 [b]	2.0 [c]	720 (2.82)		10.5	0.4	13.5
65.5	6.5 [b]	2.6 [c]	300 (2.81)		18.6	0.9	19.6
70.4	21 [b]	4.8 [c]	280 (8.48)	25.4	35.6	2.5	9.1

[a] [Diene] 3.93 × 10^{-5}M. [Sulphanilic acid] 1.0 × 10^{-2}M. [b] Interpolated from experimental values (Table 8). [c] Interpolated from experimental values (Table 6). [d] [4-Fluorophenol] 1.00 × 10^{-3}M. The first two experiments did not run long enough for 4-fluoro-2-nitrophenol to be formed. [e] From the first two reactions (2.8 half-lives) some unchanged diene was presumably extracted by the dichloromethane used in work-up. On g.c. it would be expected to give 2,3-dimethyl-5-nitrobenzonitrile and 2,3-dimethylbenzonitrile; the amounts were too small to be detected. A trace of 6-acetoxy-2,3-dimethylbenzonitrile would also be formed (see Experimental section) but would not be significant in the measured yield.

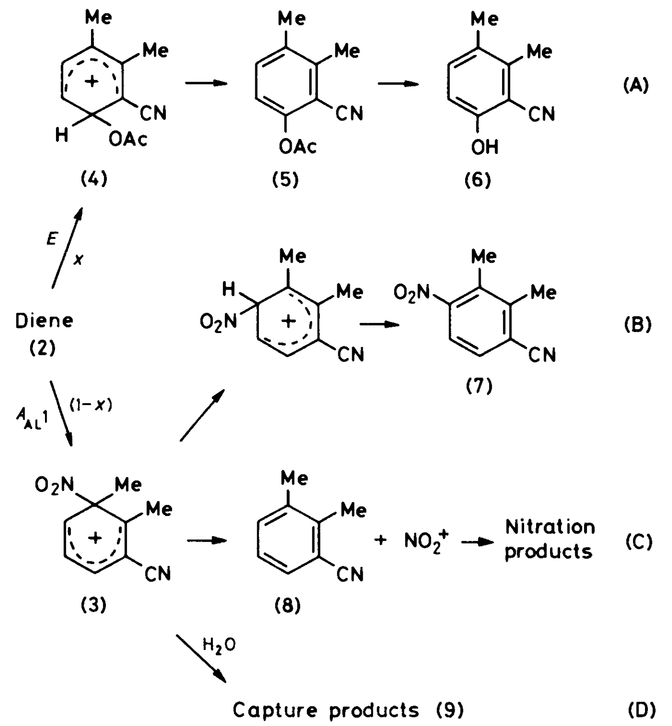
Table 11. The reactions of (3)

Acidity	Intramolecular 1,2-migration (%)	Intermolecular rearrangement (%)	Nucleophilic capture (%)
61.8	0.6	16.8	82.6
65.5	1.4	29.8	68.9
70.4	3.4	48.8	47.3

the reactions (2) ⟶ (5) ⟶ (6) as an A ⟶ B ⟶ C set, and writing x for the fraction of the solvolysis of (2) which follows the E mechanism we have $[(5)] = xY[(2)]_{t=0}$, where $Y = [k_1/(k_2 - k_1)]\,[\exp(-k_1t) - \exp(-k_2t)]$.

The values calculated for x and $(1 - x)$ are in the caption to the Scheme, and they do show the outcome of solvolysis moving in favour of the $A_{AL}1$ reaction as the acidity increases. Since $(1 - x) = [(7) + (8) + (9)]\%/100$ it is possible to calculate the values of (9)%, the percentages of (2) which end as nucleophilic capture products of (3) at different acidities. These results are also in the caption to the Scheme, and are readily transformed into the percentages, given in Table 11, of the W_t^{Me} (3) which at a particular acidity suffer intramolecular 1,2-migration, intermolecular rearrangement, and nucleophilic capture. The most striking fact which emerges is that intramolecular 1,2-migration of the nitro-group is of minor importance amongst the reactions of (3). The analogue of (3) lacking a cyano-group reacts by intramolecular 1,2-migration to the extent of *ca.* 18 and 79%, respectively, at the lowest and highest acidities shown in Table 11 above.[5] The electron-withdrawing cyano-group at the *p*-position with respect to the terminus of migration in (3) powerfully discourages this reaction and encourages intermolecular rearrangement, relative to capture.

One further point relating to the solvolysis of the diene (2) remains to be made. That such solvolyses proceed by the $A_{AL}1$ mechanism has hitherto been an assumption, since in examples studied previously[4,5] it was not possible to make kinetic measurements. In the present case the measurement of the rate coefficient (k_1) for the overall solvolysis at various acidities, combined with knowledge of the partitioning of (2) between the E and supposed $A_{AL}1$ reaction, permits the partitioning of k_1 itself, to give $k = k_1[(1 - x)\%]/100$, the rate coefficient at various acidities for the latter component of the total solvolysis. Consequently it is possible to evaluate $d(\log k)/d(\%\ H_2SO_4)$ for this reaction and to compare it with this quantity for other acetate solvolyses occurring by the $A_{AL}1$ mechanism (Table 12). Results for a single acidity range are not available, and that for benzyl acetate is probably depressed because in the lower part of its acidity range there is an overlap of two mechanisms. Nevertheless, the high acidity dependence to be expected for an $A_{AL}1$ reaction is clearly seen in the case of (2); the gradients for all the $A_{AL}1$ reactions are markedly greater than that for the solvolysis of phenyl



Scheme. The proportions (%) of 2-cyano-3,4-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate (2) reacting, *via* E (x%) and $A_{AL}1$ [$(1-x)$%] mechanisms in acid solvolyses, and the proportions of (2) ending as the products of intramolecular 1,2-rearrangement [(7)%], intermolecular rearrangement [(8)%], and nucleophilic capture [(9)%] of (3)

H_2SO_4 (%)	$[(5)]_t$ (%)[a]	100Y[b]	x (%)[c]	$(1-x)$ (%)	(7) (%)[a]	(8) (%)[a]	(9) (%)[b]
61.8	13.5	36.1	37.4	62.6	0.4	10.5	51.7
65.5	19.6	52.5	37.3	62.7	0.9	18.6	43.2
70.4	9.1	33.6	27.1	72.9	2.5	35.6	34.5

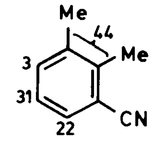
[a] Table 10. [b] For definition see Discussion. Values of k_1 and k_2 used in calculating Y in Table 10. [c] [(5)] %/100Y.

Table 12. Values of d(log k)/d(% H_2SO_4) for acid-catalysed solvolyses of acetates proceeding by the $A_{AL}1$ mechanism

Acetate	Benzyl[a]	*s*-Butyl[a]	Isopropyl[a]	(2)
H_2SO_4 (%)	67—70	80—87	80—88	62—70
10^2 d(log k)/d(% H_2SO_4)	4.7	11.7	11.0	8.7

[a] Ref. 8.

acetate [10^2 d(log k)/d(% H_2SO_4) = 1.3 in the range 60—74% H_2SO_4], an $A_{Ac}1$ reaction.[8] As regards the elimination reaction our results reveal it to be acid-catalysed {10^2d[log(k_1 − k)]/d(% H_2SO_4) = 7.7}, suggesting that its description as a simple $E1$ reaction [4,5] over the whole acidity range may be inadequate.



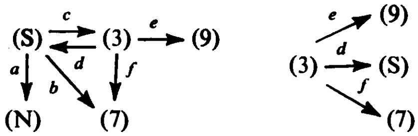
(10)

In considering the relationship between the information about the reactions of W_t^{Me} (3), provided by the results for the solvolysis of (2), and that about the nitration of 2,3-dimethylbenzonitrile in sulphuric acid, we assume as already indicated (see Results section) that the loss in aggregate yield of nitration products with falling acidity (Table 5, Figure 1) is due to increasing nucleophilic capture of (3). For nitration in 70.4% H_2SO_4 the loss is 26%. Although we know that at this acidity 47.3% of any W_t^{Me} formed would suffer nucleophilic capture, we cannot *simply* transform the observed loss of yield into the degree of direct *ipso*-attack in nitration because the degree of loss observed, like the yields of 2,3-dimethyl-4-, -5-, and -6-nitrobenzonitrile, is affected by the process of re-nitration consequent upon the intermolecular rearrangement of W_t^{Me}. It is possible to allow for this effect (see Appendix), and when this is done the percentage proportions of *primary positional nitration* in 70.4% H_2SO_4 prove to be as shown in (10). These proportions would not be expected to be wholly independent of acidity [5,9] but it is clear that *ipso*-attack is the major reaction. This is confirmed, and the dependence of positional reactivity upon the medium possibly supported (the uncertainty arising from inaccuracy of measurement) by the fact that, as indicated by the ^1H n.m.r. spectrum of the reaction solution, the diene (2) is formed in *ca.* 51% yield in the nitration of 2,3-dimethylbenzonitrile in acetic anhydride. The major proportion of the *ipso*-attack must occur at C-3, as indeed is shown by the lack of any positional isomer of (2) amongst the products of the nitration in acetic anhydride.

The work described above demonstrates conclusively that the W_t^{Me} (3) reacts by intramolecular 1,2-migration and by intermolecular migration of the nitro-group, and by nucleophilic capture. It does not undergo intramolecular 1,3-rearrangement. Thus, intramolecular 1,3-migration of the nitro-group does not occur in the solvolytic reactions of the diene (2). It is clear however that 1,3-migration of the nitro-group in (2) does occur thermally, as shown by Fischer and Greig[3] and confirmed by us (see Experimental section); this is probably a reaction of molecular diene (2).

Appendix

The processes below represent the nitration of 2,3-dimethylbenzonitrile (S), [proceeding *via* the W_i^{Me} (3) to capture products (9), 2,3-dimethyl-4-nitrobenzonitrile (7), and 2,3-dimethyl-(5 + 6)-nitrobenzonitrile (N)], and the reactions of the W_i^{Me} (3) generated by diene solvolysis, as already discussed. The fractions of ***primary nitration*** occurring at the (5 + 6)- (g), *ipso*- (h), and 4-position ($1 - g - h$) are $g = a/(a + b + c)$, $h = c/(a + b + c)$, and $(1 - g - h) = b/(a + b + c)$. The results for diene solvolysis provide the fraction of (3) giving S [$y = d/(d + e + f)$], the fraction giving capture products [$z = e/(d + e + f)$], and the fraction giving the 4-nitro-compound by 1,2-rearrangement [$(1 - y - z) = f/(d + e + f)$]. From the nitration scheme, by treating (3) as a steady-state intermediate we have $\mathrm{d(9)}/\mathrm{d}t = cz\mathrm{S}$, $\mathrm{dN}/\mathrm{d}t = a\mathrm{S}$, and $\mathrm{d(7)}/\mathrm{d}t = [b + c(1 - y - z)]\mathrm{S}$. Then, in nitration the fraction of S lost is $\{L = \mathrm{d(9)}/[\mathrm{d(9)} + \mathrm{dN} + \mathrm{d(7)}]\}$, the fraction giving (5 + 6)-nitro-compounds is $\{J = \mathrm{dN}/[\mathrm{d(9)} + \mathrm{dN} + \mathrm{d(7)}]\}$, and the fraction giving the 4-nitro-compound is $(1 - L - J)$, where $L = cz/(a + b + c - cy)$ and $J = a/(a + b + c - cy)$. Rearrangement and combination of the expressions for L, J, g, and h gives $g = Jz/(z + Ly)$ and $h = L/(z + Ly)$, so that the desired primary quantities, g, h, and $(1 - g - h)$ can be evaluated from the experimental results.



a—f are rate coefficients

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