The Kinetics and Mechanisms of Aromatic Halogen Substitution. Part XXXIII.[1] Kinetics and Products of Chlorination of Some Aryl Acetates

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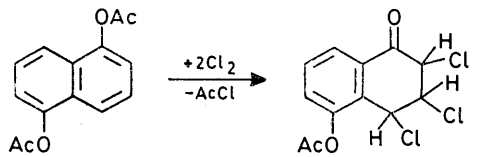
The rates and products of reaction of 4-methylphenyl acetate, 3,4- and 2,6-dimethylphenyl acetate, and 2,3,5,6-tetramethylphenyl acetate with molecular chlorine in acetic acid have been studied. 'Abnormal' reaction paths play a large part in the determination of the products of the chlorination of the first two of these compounds, probably through electrophilic attack on an activated '*ipso*'-position. The observed rates of reaction are compared with those calculated on the basis of additivity of substituent effects; they allow an estimate to be made of the effect of steric inhibition of resonance on the directing power of the acetoxy-group. The products of chlorination of the corresponding phenols are recorded also.

MOLECULAR chlorination and bromination of aromatic compounds often give products of substitution expected in terms of the well known theories which describe the effects of substituents in these reactions. Unexpected products are, however, sometimes to be recognized, and there is much current interest in the variety of so-called 'non-conventional' pathways available not only in halogenations[2,3] but also in aromatic substitutions generally.[4]

Detailed identification of 'abnormal' reaction pathways is often not easy, because the products formed initially are unstable, undergoing further reaction before they can be characterized with certainty. Thus the chlorination of naphthalene gives substitution accompanied by addition to give, *inter alia*, stable tetrachloride adducts;[5] corresponding evidence relating to the bromination of naphthalene[6] suggests some involvement of pathways involving adducts, but the extent of 'abnormal' reaction is not known. Similarly it has been speculated for many years[7] that phenols may undergo substitutions by a route involving two replacements with rearrangement; direct proof of the existence of this pathway has been obtained only in a limited number of cases.[8] The intermediates involved in side-chain halogenation of polyalkylbenzenes[9] and related compounds are also difficult to identify with certainty.

Displacement of groups other than hydrogen can also occur by way of abnormal paths. In an earlier paper,[10] the chlorination of 1,5-diacetoxynaphthalene with addition and displacement of the acetyl cation was described [equation (1)].



(1)

Among the problems still outstanding in relation to such reactions, however, are included the question of whether addition to the unsaturated system is essential to halogenodeacylation; and whether the presence of potentially nucleophilic halogen on the carbon atom adjacent to the acyloxy-group is helpful.[11] Molecular chlorination is kinetically simpler than bromination; and is more rapid, so that the less reactive acetates can be more conveniently studied. The intermediates likely to be formed are also more stable and so more easily identified. We have therefore undertaken studies of some of these reactions, with the hope of establishing more fully what types of substrate, and what types of reaction path, lead to abnormal products. A preliminary account has been given elsewhere.[12]

[1] Part XXXII, P. B. D. de la Mare, N. S. Isaacs, and M. J. McGlone, *J.C.S. Perkin II*, 1976, 784.
[2] P. B. D. de la Mare, in 'Rodd's Chemistry of Carbon Compounds,' ed. S. Coffey, Elsevier, Amsterdam, 1971, 2nd edn., vol. IIIA, pp. 7 *et seq.*
[3] P. B. D. de la Mare, *Accounts Chem. Res.*, 1974, **7**, 361.
[4] S. R. Hartshorn, *Chem. Soc. Rev.*, 1974, **3**, 167.
[5] P. B. D. de la Mare, M. D. Johnson, J. S. Lomas, and V. Sanchez del Olmo, *J. Chem. Soc.* (*B*), 1966, 827.
[6] F. R. Mayo and W. B. Hardy, *J. Amer. Chem. Soc.*, 1952, **74**, 911.
[7] A. Lapworth, *J. Chem. Soc.*, 1901, **79**, 1265.
[8] A. A. Volod'kin and V. V. Ershov, *Bull. Acad. Sci., U.S.S.R.*, 1962, 1039.
[9] E. Baciocchi and G. Illuminati, *Progr. Phys. Org. Chem.*, 1967, **5**, 1.
[10] P. B. D. de la Mare, S. de la Mare, and H. Suzuki, *J. Chem. Soc.* (*B*), 1969, 429.
[11] P. B. D. de la Mare and B. N. B. Hannan, *J.C.S. Perkin II*, 1973, 1086.
[12] P. B. D. de la Mare and B. N. B. Hannan, *Chem. Comm.*, 1971, 1324.

EXPERIMENTAL

Most of the materials and methods have been described in earlier Parts.[1] 4-Methylphenyl acetate, prepared from *p*-cresol, had b.p. 108° at 15 mmHg (lit.,[13] 108—110° at 23 mmHg). 2,6-Dimethylphenyl acetate, prepared from 2,6-dimethylphenol of m.p. 46° (lit.,[14] 45—46°), had b.p. 218—220° at 760 mmHg (lit.,[14] 219—220° at 755 mmHg). 2,3,5,6-Tetramethylphenyl acetate, prepared from 2,3,5,6-tetramethylphenol of m.p. 116—117° (lit.,[15] 116—117°), had m.p. 79—80° (lit.,[16] 78—79°). 3,4-Dimethylphenol was a commercial sample, purified by recrystallisation from light petroleum (b.p. 40—60°), m.p. 64—65° (lit.,[17] 62.5°). Its acetate, b.p. 56° at 1.5 mmHg, was prepared as usual, and had the expected ^{1}H n.m.r. spectrum. The rates of chlorination of these acetates in acetic acid at 25°, determined in the usual way, gave second-order rate coefficients substantially constant over at least 50% reaction, the values being: for 4-methylphenyl acetate 0.003 3; 3,4-dimethylphenyl acetate 0.40; 2,6-dimethylphenyl acetate 0.047; 2,3,5,6-tetramethylphenyl acetate 37 l mol^{-1} min^{-1}.

Products of Chlorination of 4-Methylphenyl Acetate.—Although the chlorination of *p*-cresol is known [18] to give 2-chloro-4-methylphenol, the corresponding reaction of its acetate does not seem to have been investigated. When 4-methylphenyl acetate (0.1M) was allowed to react with chlorine (0.1M) for 24 h, when most of the chlorine had undergone reaction, the ^{1}H n.m.r. spectrum of the product included a complex set of signals in the alicyclic region (τ 4—7); the ratio of the integral of these signals to that of the aromatic signals was 0.22. If only substitution products and tetrachlorides had been produced, this would imply that *ca.* 17% adduct had been formed and survived decomposition, but it will be seen that this does not adequately describe the situation.

The progress of chlorination of 4-methylphenyl acetate (0.1M) with chlorine (0.17M) in acetic acid at 25° was followed by g.l.c., and representative reaction mixtures were examined also by preparative g.l.c. and by g.l.c. in association with a Varian CH7 mass spectrometer; we thank The University of Reading for use of this facility for certain of the measurements. The g.l.c. traces showed that these reaction mixtures contained the expected 2- and 3-chloro-4-methylphenyl acetates, which built up progressively as the reaction proceeded; the ratio of the two isomers, from integration of the g.l.c. traces, was [2-chloro] : [3-chloro] = 4 : 1 after 4 h (*ca.* 10% reaction) and 3 : 1 after 30 h (*ca.* 50% reaction). The structure of the isomer formed in preponderance was confirmed by showing that it is identical in behaviour on g.l.c. with the main product of monochlorination of *p*-cresol after this had been acetylated.

The g.l.c. traces showed also, however, that the reaction mixtures contained numerous other components occurring in varying minor amounts. Of these, we were able to identify in successive order of elution the following fractions: (i) a chloro-4-methylphenol, eluted before the monochloro-derivatives of 4-methylphenyl acetate, in a proportion which increased towards the end of the reaction, identified from its molecular weight (*m/e* 142); (ii) several unstable compounds which were destroyed when the reaction mixture was heated; (iii) a dichloro-4-methylphenyl acetate, also formed in a proportion which increased with the progress of reaction, identified from its molecular weight (*m/e* 218); (iv) a trichloro-compound of molecular weight 210 (from m.s.), and hence a trichlorodienone or phenol, $C_7H_5OCl_3$, formed in a proportion which decreased slightly with the progress of the reaction; (v) a trichloroacetate of molecular weight 254 (from m.s.), and hence probably an acetoxychlorodichloride, $C_9H_9O_2Cl_3$; (vi) a pentachloroenone, formed in proportion increasing with progress of the reaction, and recoverable by preparative g.l.c. as needles, m.p. 66—69°, τ (CCl_4) at τ 2.8 (1 H, s), 5.0 (1 H, s), and 7.8 (3 H, s); hence probably the pentachloroenone, $C_7H_5OCl_5$ (1); *m/e* 280—290 (intensities found, 64 : 100 : 66 : 25 : 5 : 0; Cl_5 requires 61 : 100 : 65 : 21 : 4 : 0.2) and at 245—253 (loss of Cl; intensities found, 79 : 100 : 49 : 12 : 2; Cl_4 requires 77 : 100 : 49 : 11 : 1).

Control experiments showed that neither the starting material nor the monochloroacetates decompose to give phenols or other materials under the conditions used for g.l.c. analysis.

Products of Chlorination of 3,4-Dimethylphenol and of 3,4-Dimethylphenyl Acetate.—The following chlorophenols were prepared for reference by preparative chromatography of the products obtained by chlorination of 3,4-dimethylphenol in acetic acid; n-hexane–benzene (3 : 1) was used for development, and the isolated fractions were recrystallised from light petroleum (b.p. 40—60°). 2-Chloro-3,4-dimethylphenol had m.p. 25° (lit.,[19] 27°). 6-Chloro-3,4-dimethylphenol had m.p. 71° (lit.,[20] 70.7°). 2,6-Dichloro-3,4-dimethylphenol had m.p. 49—51° (lit.,[19] 52°). The corresponding acetates were prepared from these samples in the usual way, and used as reference materials for g.l.c. analyses.

Several unstable intermediates were identified spectroscopically in the isolated reaction mixtures from these chlorinations. 4-Chloro-3,4-dimethylcyclohexa-2,5-dienone (2) was isolated in admixture with other more saturated adducts by chromatography on alumina [Spence, type H, deactivated by being mixed with 5% of acetic acid–water (9 : 1 v/v)] of the crude product of chlorination of 3,4-dimethylphenol in acetic acid. Light petroleum (b.p. 40—60°) was used for elution, with a loading ratio of 1 : 40. Details of the spectra have already been published; [12] the possible isomeric structure (3), having a vinylic AB quartet, would not show the observed allylic coupling between the signals for an aromatic proton and a methyl group.

The product mixture obtained by chlorination of 3,4-dimethylphenyl acetate in acetic acid was separated similarly by column chromatography. Elution with light petroleum containing 5% diethyl ether gave 2,4-dichloro-4,5-dimethylcyclohexa-2,5-dienone (4) as an unstable pale green oil (for spectroscopic details, see ref. 12). Of possible isomeric structures, only those having two vinylic protons need be considered; of these, (5) and (8) would have signals of an AB quartet; in (7), both the methyl groups would be coupled allylically with a vinylic proton; and (6) can be excluded not only because the signals for both the vinylic protons would be upfield, in the region τ 3.7—4, but also because the isolated dichlorodienone, on being allowed to decompose in acetic acid or as the isolated liquid, gives a

[13] J. Meisenheimer and L.-H. Chou, *Annalen*, 1939, **539**, 78, 86.
[14] R. J. Highet and P. F. Highet, *J. Org. Chem.*, 1965, **30**, 902.
[15] J. S. Fitzgerald, *J. Appl. Chem.*, 1955, **5**, 289.
[16] J. C. Roberts, *J. Chem. Soc.*, 1955, 2989.
[17] O. Jacobsen, *Ber.*, 1884, **17**, 161.
[18] T. Zinke, *Annalen*, 1903, **328**, 277.
[19] L. E. Hinkel, E. E. Ayling, and L. C. Bevan, *J. Chem. Soc.*, 1928, 2529.
[20] B. M. Ashall, H. F. Bondy, and V. Kelsey, B.P. 1,037,548 (*Chem. Abs.*, 1966, **65**, 16,900).

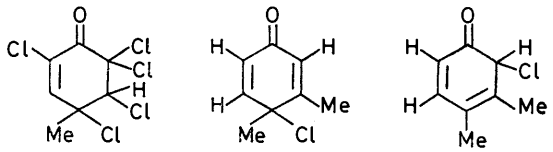
mixture of 2-chloro-4,5- and 2,6-dichloro-3,4-dimethylphenol.

The product mixtures from chlorination of 3,4-dimethylphenol and of 3,4-dimethylphenyl acetate in acetic acid showed also, in their ^{1}H n.m.r. spectra,[12] signals attributable to 3,4-dimethyl-4,5,6-trichlorocyclohex-2-enone (9). On being allowed to stand in acetic acid, this compound lost hydrogen chloride to give the dichlorodienone (4). Small amounts of other partly saturated adducts were present also in these reaction mixtures. In Table 1, the analytical results obtained on products of chlorination of the phenol and of the acetate are summarised.

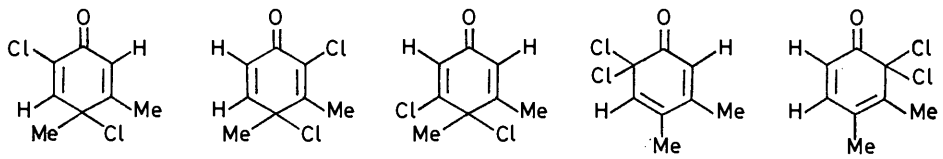
Products of Chlorination of 2,6-*Dimethylphenol and of* 2,6-*Dimethylphenyl Acetate.*—4-Chloro-2,6-dimethylphenol was the main product of chlorination of 2,6-dimethylphenol in acetic acid. After recrystallisation from light petroleum (b.p. 40—60°) it had m.p. 81° (lit.,[21] 81—82°). Its acetate was obtained in the usual way; the ^{1}H n.m.r. spectra were characteristic of the symmetrical substitution pattern.

3-*Chloro*-2,6-*dimethylphenyl acetate*, on the other hand, was obtained from the product of chlorination of 2,6-dimethylphenyl acetate by preparative t.l.c. as an oil (Found: C, 60.7; H, 5.7; Cl, 17.5. $C_{10}H_{11}ClO_2$ requires C, 60.5; H, 5.6; Cl, 17.8%). It had the expected spectral properties; adjacent 4- and 5-aromatic protons appeared as the expected doublet of doublets, $J_{4,5}$ 8 Hz. Hydrolysis by heating this acetate under reflux with sodium methoxide in methanol for 30 min gave after acidification 3-chloro-2,6-dimethylphenol, m.p. 57—58.5° (lit.,[22] 58—60°).

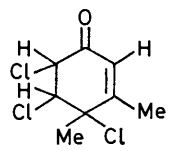
Chlorination of 2,6-dimethylphenyl acetate at various concentrations in the range 0.1—0.5M in acetic acid, in acetic acid containing lithium chloride (0.2M) and in nitromethane gave products in which a small proportion of adduct could be detected, but the sole product of substitution was 3-chloro-2,6-dimethylphenyl acetate, g.l.c. analysis being used, and conditions chosen under which the 3- and 4-chloro-derivatives were separated clearly.



(1) (2) (3)



(4) (5) (6) (7) (8)



(9)

TABLE 1

Products of chlorination of 3,4-dimethylphenol and of 3,4-dimethylphenyl acetate in acetic acid at 25°

Aromatic compound	3,4-Dimethylphenol							3,4-Dimethylphenyl acetate		
[ArH]/M	0.1	0.1	0.15	0.5	0.5	0.25	0.25	0.25	0.25	0.25
[Cl_2]/M	0.2	0.2	0.15	0.5	0.5	0.11	0.11	0.25	0.11	0.11
Reaction time/min	5	5 000	2	2	10 000	4 000	10 000	15	4 000	10 000
% Trichloroenone (9) [a]	34	Trace	Trace	3	Trace			21	Trace	
% Dichlorodienone (4) [a]	29	60	Trace	6	6	1		1	17	2
% Chlorodienone (2) [a]	3	Trace	28	24	4	13	9	Trace		
% 3,4-Dimethylphenol [b]	1		38	38	29	44	44		Trace	1
% 2-Chloro-3,4-dimethylphenol	2	5	17	15	11	17	17	Trace	Trace	Trace
% 6-Chloro-3,4-dimethylphenol [b]	43	51	43	35	46	38	38	10	10	10
% 2,6-Dichloro-3,4-dimethylphenol	54	44	2	12	14	1	1	Trace	2	1
% 3,4-Dimethylphenyl acetate [b]								55	58	59
% 6-Chloro-3,4-dimethylphenyl acetate [b]								35	30	29

[a] Analyses are of the isolated reaction mixture, ^{1}H n.m.r. spectroscopy being used. Each of the known intermediates (9), (4), and (2) showed separate distinct signals for a methyl group attached to a carbon bearing a chlorine atom. The integrals for these signals were proportioned against the integral for the total methyl resonance, and hence the proportion of each adduct was estimated. [b] Analyses are by g.l.c., under which conditions the adducts decompose variously. The dichlorodienone (4) gives some 3,4-dimethylphenol, and the chlorodienone (2) gives some 3,4-dimethylphenol, but their contribution is not known quantitatively.

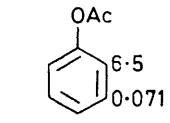
[21] A. S. Kende and P. MacGregor, *J. Amer. Chem. Soc.*, 1961, **83**, 4197.

[22] A. Siegel and H. Clodi, *Monatsh.*, 1961, **92**, 914.

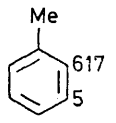
Chlorination of 2,3,5,6-Tetramethylphenol and of 2,3,5,6-Tetramethylphenyl Acetate.—The chlorination of 2,3,5,6-tetramethylphenol in acetic acid gave 4-chloro-2,3,5,6-tetramethylphenol which after recrystallisation from light petroleum (b.p. 40—60°) had m.p. 113—114° (lit.,[15] 114—115°), and this on acetylation gave the corresponding acetate, identical (^{1}H n.m.r. and g.l.c.) with the sole product detected from the chlorination of 2,3,5,6-tetramethylphenyl acetate in acetic acid under conditions similar to those used for 2,6-dimethylphenyl acetate.

DISCUSSION

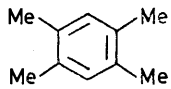
(a) *Rates of Chlorination.*—The rates of chlorination of these acetates are in reasonable agreement with expectation, effects of secondary steric hindrance (steric inhibition of resonance) being allowed for. In an earlier paper,[1] partial rate factors for the chlorination of acetoxybenzene were given, as shown in diagram (10). By using



87
Cl_2, HOAc, 25°
(10)



820
Cl_2, HOAc, 25°
(11)



$4·9 \times 10^6$
Cl_2, HOAc, 25°
(12)

the corresponding values for toluene [23] [diagram (11)] and the polymethylbenzenes [24] [*e.g.*, durene, diagram (12)], the rates of chlorination of the acetates studied in the present work can be calculated by assuming that the effects of substituents are independent and additive, and then can be compared with experiment, as is shown in Table 2.

TABLE 2

Found and calculated rates of chlorination of some aryl acetates in acetic acid at 25°

Rate (k_2/l mol^{-1} min^{-1})	Found	Calculated
4-Methylphenyl acetate	0.003 3	0.002 3
3,4-Dimethylphenyl acetate	0.40	0.64
2,6-Dimethylphenyl acetate	0.047	0.90
2,3,5,6-Tetramethylphenyl acetate	37	6 607

These four compounds fall into two groups. For the first two, steric hindrance, whether primary or secondary, would not be expected to be significantly greater than in the reference compounds, and the extent of agreement between found and calculated rates of reaction is reasonable in view of the approximations involved in the 'additivity' treatment.

For the last two compounds, the acetoxy-group is flanked on both sides by a methyl group, and so its conjugative power would be expected to be reduced. Diagram (10) shows that a *p*-acetoxy-group, despite its electron-withdrawing inductive effect, activates the aromatic ring for molecular chlorination by the modest factor of 87. In 2,3,5,6-tetramethylphenyl acetate, the rate of chlorination has been reduced by a factor of 178 below the expected value; so that this compound (k_2 37 l mol^{-1} min^{-1}) is in fact less reactive than durene [24] (k_2 150 l mol^{-1} min^{-1}), even if allowance is made for the unfavourable statistical factor.

In 2,6-dimethylphenyl acetate, the calculated rate of substitution is almost entirely that of reaction at the 3-position, *meta* to the acetoxy-group. If this position were affected only by the inductive effect, no major influence on the rate would be expected from steric inhibition of resonance. In Part XXXII [1] it was argued, however, that the discrepancy between values of σ_m^+ calculated from rates of chlorination and σ_m calculated from the strengths of benzoic acids suggested that some leakage of conjugation from the OAc substituent to the *meta*-position could occur. The present results confirm this view; the 3-position in 2,6-dimethylphenyl acetate is less reactive than expected by a factor of *ca.* 19. If a ρ value of −10 for molecular chlorination [1,23] is applicable to this activated aromatic system, a deactivation by this factor accords almost exactly with that expected if steric inhibition of resonance had reduced $\sigma_{m\text{-OAc}}^+$ from its value (0.26) derived from the rate of chlorination of *p*-acetoxyacetanilide to that derived by equating it with σ_m (0.39). These results are in quite good accord, therefore, with expectations in terms of the approximations of additivity of substituent effects modified by steric inhibition of resonance. It must be accepted as a possibility, of course, that the directing power of a *meta*-acetoxy-group may depend on its orientation with respect to the attacked aromatic ring in the same direction as, but through a cause other than that of, modification of its power of conjugation with the ring.

Products of Chlorination; the Phenols.—The products of monochlorination of the three phenols having free positions *para* to the hydroxy-group were those expected. No search was made for quinonoid intermediates, since it was expected that these, if formed, would rearrange relatively rapidly to give the substituted phenol.

The chlorination of 3,4-dimethylphenol, however, took in part the unexpected course shown in Scheme 1, as is apparent from the results given in Table 1. A large proportion of the reaction proceeds by attack at the 4-methyl group to give the chlorodienone (2) by substitution with double-bond rearrangement (the S_E2' reaction). This compound is unstable, and can revert to starting material acting as a source of positive chlorine, or rearrange to the monochlorophenol under appropriate conditions. With excess of chlorine, it is chlorinated further to give the trichloroenone (9), which itself can lose hydrogen chloride to give the dienone (4), and this also can rearrange or act as a chlorinating agent; the amount of (9) and (4) detected after reaction with two molecular proportions of chlorine indicates that at least 60% of the original phenol is attacked at the 4-methyl group. The fact that reaction is partitioned between 6- and 4-attack (a minor proportion of 2-substitution being found also) indicates that an *ipso*-methyl ring position, if appropriately activated, is about as readily attacked as a

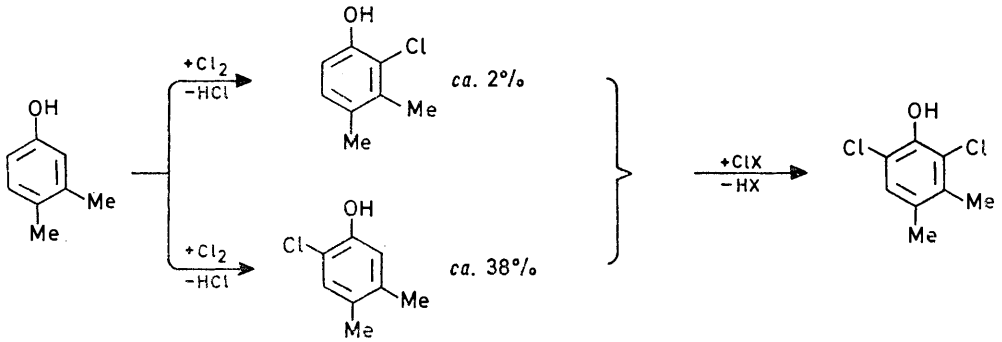
[23] H. C. Brown and L. M. Stock, *J. Amer. Chem. Soc.*, 1957, **79**, 5175.

[24] E. Baciocchi and G. Illuminati, *Gazzetta*, 1962, **92**, 89.

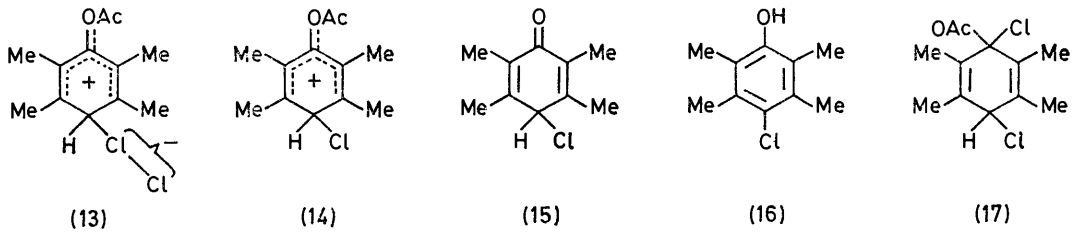
correspondingly activated position bearing a hydrogen atom.

Products of Chlorination; 2,6-Dimethylphenyl Acetate and 2,3,5,6-Tetramethylphenyl Acetate.—Calculations of the reactivities expected at the free positions of 2,6-dimethylphenyl acetate indicates that attack should occur almost exclusively at the 3-position. Accordingly, the major product of chlorination is the 3-chloro-derivative, and abnormal products derived by addition or by other unusual pathways comprise only a very minor part of the total. In this respect, chlorination differs significantly from bromination.[25] Chlorination of 2,3,5,6-tetramethylphenyl acetate also gives the expected product, being attacked as expected at the 4-position to give the corresponding chloro-substituted acetate. This result is significant in relation to the fate of the carbocationic intermediates (13) and (14), presumed to be formed in the course of chlorination. It seems clear that the preferred reactions of these involve loss of the hydrogen atom from the position attacked by electrophilic chlorine, rather than the displacement of an acetyl cation with rearrangement to give (15) and hence the phenol (16), or capture of chloride ion to give (17), which itself should easily lose acetyl chloride to give (15) and hence (16).

Products of Chlorination; 4-Methylphenyl Acetate.—In contrast with the chlorinations of the acetates discussed in the previous section, the products from 4-methylphenyl acetate show a number of unusual features. Although the abnormal products, and the intermediates concerned in their formation, have not all been identified fully, their general nature can be inferred and interpreted as shown in Scheme 2. First, the major product of substitution (21) involves displacement of the 2-hydrogen atom; whereas calculations based on additivity suggest that 3-attack to give (22) should predominate by a small factor. The proportion of 2-substitution as determined by g.l.c. decreases significantly with progress of the reaction.

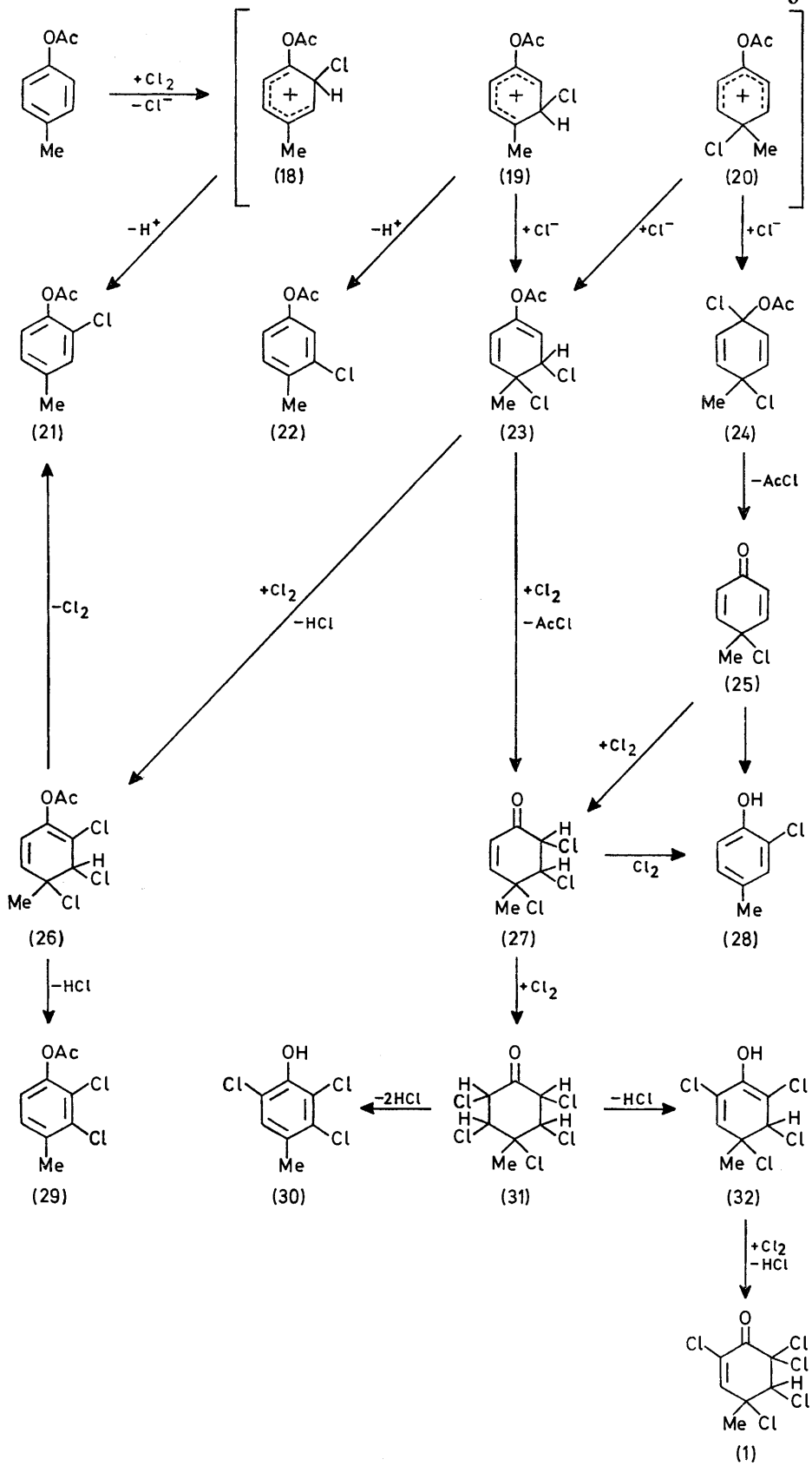


SCHEME 1 Course taken in the chlorination of 3,4-dimethylphenol in acetic acid



Secondly, the reaction products contain adducts, some of which are unstable and decompose or undergo further chlorination. Mass spectral analysis shows that some of these compounds have undergone deacylation. The main source of these abnormal products is suggested to be the dichloride (23), which can be formed either by 3- or by *ipso*-electrophilic attack from (19) or (20). This by further chlorination and subsequent loss of HCl and Cl_2 can be responsible for the formation of the unexpectedly large proportion of 2-chloro-4-methylphenyl acetate (21). It can lead also to a chlorophenol (28), to a trichlorophenol (30), to an acetoxychlorodichloride (26), and to a

[25] P. B. D. de la Mare and B. N. B. Hannan, *Chem. Comm.*, 1970, 156.

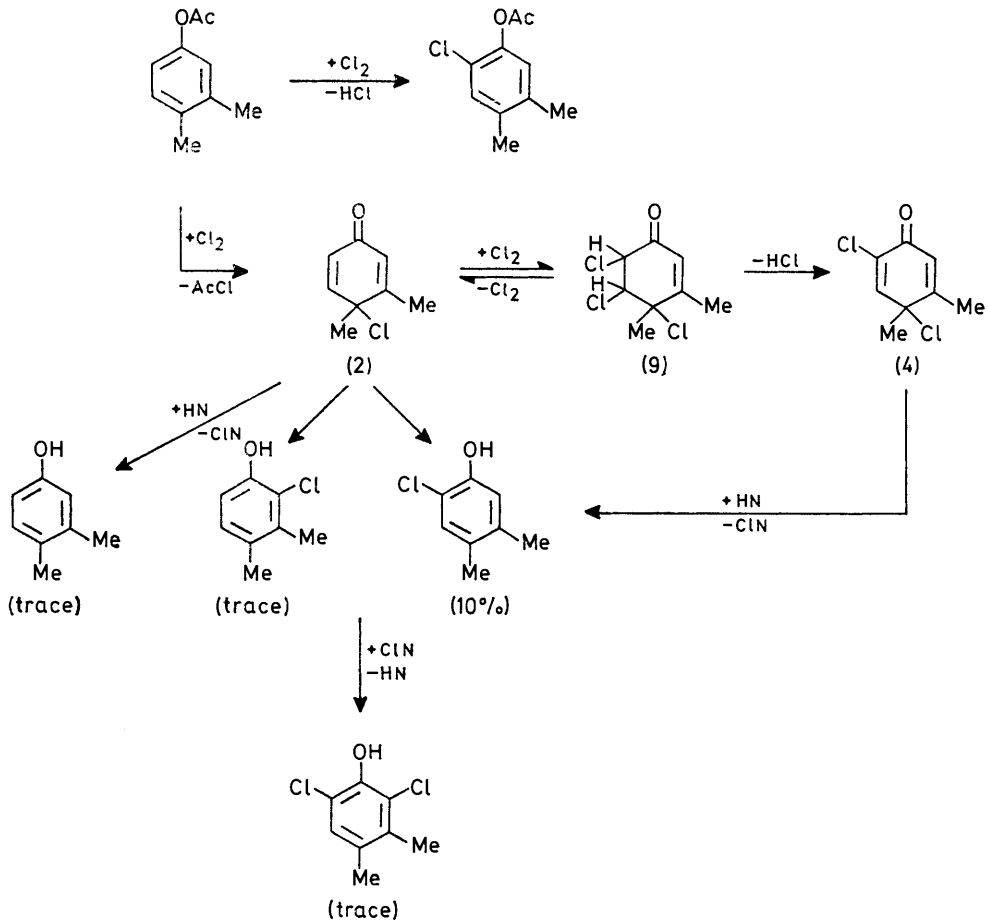


SCHEME 2 Possible reaction pathways in the chlorination of 4-methylphenyl acetate. Compounds (1), (21), (22), (26), and (28)—(30) (or, in the case of the last four, isomers thereof) have been characterised by g.l.c.–m.s. (see text) as components of the reaction mixture. Compounds (23)—(25), (27), (31), and (32) are intermediates which can plausibly be considered as concerned in the formation of abnormal products (see text)

pentachloroenone (1) (see Experimental section). These compounds, or isomers, together with other more unstable materials, were detected in the reaction mixture by mass spectrometric examination of g.l.c. fractions.

All the pathways indicated in Scheme 2 are chemically acceptable as contributors to the reaction sequence; and the selection of (23) as the main intermediate leading to abnormal products allows interpretation of the formation of ' abnormally ' substituted acetates (21), (26), and (29) instead of ketones or phenols. Alternative routes *via* the 1,4-dichloride (24) or the chlorodienone (25) are possible; but it is characteristic of routes *via* such intermediates, characteristically formed in many nitrations in acetic anhydride studied by Vaughan, Wright, Fischer, and their co-workers,[26-28] that the 1,4-adducts either can be identified themselves as intermediates or readily undergo deacylation. If (24) is formed, therefore, we think that it is more likely to be the source of the deacylated products than of those still bearing the acetoxy-group.

Products of Chlorination; 3,4-*Dimethylphenyl Acetate.* —This compound also is chlorinated to give first a succession of intermediates which can be detected in the reaction mixtures, identified spectroscopically, and in part separated. Their modes of decomposition can also be identified in part. The results described in the Experimental section and in Table 1 enable us to propose the set of pathways shown in Scheme 3. It is clear that the reaction partitions between formation of the ' normal ' substitution product, 6-chloro-3,4-dimethylphenyl acetate (*ca.* 75% of the aromatic compound used up, accompanied by very little of its 2-isomer), and of the product of chlorodeacylation with rearrangement, followed by reaction with further chlorine (*ca.* 25% of the aromatic compound used up). The latter decomposes on g.l.c. to give a mixture of products, of which the major component is 6-chloro-3,4-dimethylphenol. The highly chlorinated intermediates (9) and (4), themselves obtained because (2) reacts with chlorine more rapidly than the starting material, give much 6-chloro-3,4-dimethylphenol also when allowed to decompose in acetic acid.



SCHEME 3 Possible intermediates and pathways in the chlorination of 3,4-dimethylphenyl acetate

[26] D. J. Blackstock, M. P. Hartshorn, A. J. Lewis, K. E. Richards, J. Vaughan, and G. J. Wright, *J. Chem. Soc.* (*B*), 1971, 1212.

[27] D. J. Blackstock, A. Fischer, K. E. Richards, and G. J. Wright, *Austral. J. Chem.*, 1973, **26**, 775.

[28] A. Fischer and D. R. A. Leonard, *J.C.S. Chem. Comm.*, 1973, 300; A. Fischer and A. L. Wilkinson, *Canad. J. Chem.*, 1972, **50**, 3988.

Whereas for 4-methylphenyl acetate we were able to identify abnormal products in which the acetyl group had been retained in the product, for 3,4-dimethylphenyl acetate it was easier to identify the formation of deacylated compounds. Probably, however, both types of route are available for both compounds, since in each case the reaction mixtures contained other unidentified unstable adducts. For both these compounds, abnormal pathways involving electrophilic attack at a methyl-bearing position (*ipso*-attack) lead to the formation of a significant and easily recognisable proportion of the final product. The contribution of abnormal paths is, however, less than for the nitration of 3,4-dimethylphenyl acetate in acetic anhydride,[26] under which conditions 3,4-dimethyl-6-nitrophenyl acetate makes up only 25% of the product, the remainder being the nitrodienone corresponding in structure to its chloro-analogue (2) (see also Scheme 3).

The formation of abnormal products by molecular chlorination is not nearly so marked for 2,6-dimethylphenyl acetate, where attack occurs *meta* to an acetoxy-group, nor for 2,3,5,6-tetramethylphenyl acetate, where attack directed by the acetoxy-group can be followed by proton loss from the attacked carbon. We hope to present information derived from a wider range of aryl acetates to enable fuller assessment of the structural situations which lead to the dominance of *ipso*-attack.

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