Electrophilic Substitution with Rearrangement. Part 8.[1] Some Products of Bromination of 3,4-Dimethylphenol; a Route to Substitution *meta*- to a Hydroxy-group

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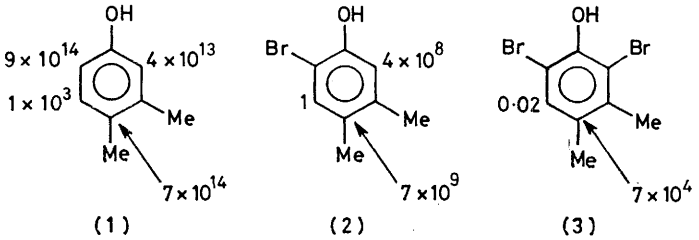
The brominations of 3,4-dimethylphenol, 2- or 6-bromo-3,4-dimethylphenol, and 2,6-dibromo-3,4-dimethylphenol can lead under defined conditions either to 2,5,6-tribromo-3,4-dimethylphenol or to 2,4,6-tribromo-3,4-dimethylcyclohexa-2,5-dienone. The latter compound rearranges to give the former when it is dissolved in concentrated sulphuric acid; and to give 2,6-dibromo-4-bromomethyl-3-methylphenol when it is set aside in the light at room temperature. When 2,5,6-tribromo-3,4-dimethylphenol is heated with concentrated aqueous hydrogen iodide, 5-bromo-3,4-dimethylphenol is obtained; this with bromine gives a mixture of 2,5- and 5,6-dibromo-3,4-dimethylphenol. The mechanisms of these reactions are outlined.

It is commonly held, following the work of Francis,[2] that in the bromination of amines and phenols, substitution occurs in such a way as successively to occupy all the available positions *ortho*- and *para*- to the OH or NH_2 group. Certain other groups (*e.g.* SO_3H and CO_2H) which can be replaced readily as potentially positively charged species are displaced also;[2-4] there are few studies which define the relative rates of these processes. Dienones can be intermediates in these brominations,[5] and in suitable cases can be isolated, either as apparently the stable end-product of bromination with excess of bromine [6] or as an intermediate on the pathway to replacement of hydrogen [7] or of some other substituent.[3,8]



Calculated partial rate factors for molecular bromination in acetic acid at 25 °C

The entry of a bromine substituent into a position *meta*- to a hydroxy-group would be expected, generally, not to be very easy, especially when some of the remaining positions are already occupied by deactivating bromine substituents. Thus we can use standard tabulations [9] of values of σ^+ for *m*- and *p*-methyl, bromine, and hydroxy-substituents and of ρ^+ for molecular bromination in acetic acid, taking $\sigma^+_{m\text{-OMe}} \simeq \sigma^+_{m\text{-OH}}$. Corresponding estimates for *o*-substitution can then be estimated from known isomer ratios in bromination.[10] Partial rate factors for the stages of bromination of 3,4-dimethylphenol to give successively 6-bromo-3,4-dimethylphenol, 2,6-dibromo-3,4-dimethylphenol, and 2,5,6-tribromo-3,4-dimethylphenol in acetic acid at 25 °C can then be calculated to take the values shown in structures (1)—(3). These values are to be regarded as illustrative only; they represent what would be expected if the theory of additivity of substituent effects, together with a linear free-energy relationship between σ^+ and $\log_{10}f$ for bromination, held exactly. On this basis, 5-substitution in 2,6-dibromo-3,4-dimethylphenol would be expected to be negligibly slow in acetic acid at room temperature; benzene itself does not undergo bromination under these conditions.

Despite this expectation, bromination *m*- to a phenolic hydroxy-group has been reported for a number of well authenticated examples,[11-14] including that of 3,4-dimethylphenol.[11] These processes do not seem to have attracted mechanistic investigation; we became interested in them because of their possible relation to the unusual pathways concerned in bromination of aryl acetates [15] and in the chlorination of phenols and their derivatives.[16] Consequently, we have re-examined the bromination of 3,4-dimethylphenol, from which earlier workers have obtained the successive products of substitution, namely: (*a*) with one molecular proportion of bromine a mixture of 6-bromo- and 2-bromo-3,4-dimethylphenol;[17] (*b*) with two molecular proportions, 2,6-dibromo-3,4-dimethylphenol;[18] and (*c*), with an excess of bromine, 2,5,6-tribromo-3,4-dimethylphenol.[11] It has been recorded also that the bromination of 3,4-dimethylphenol in aqueous sulphuric acid gives 2,5-dibromo-3,4-dimethylphenol,[19] and it had been presumed that 3,4-dimethyl-6-sulphophenol is formed first, and the sulphonic acid group protects the 6-position from bromination.[4] This reaction was investigated also; we have been unable to substantiate this claim. A preliminary account (herein corrected by revision of some details) of some of the present work has been given elsewhere.[20]

EXPERIMENTAL

Materials and Methods.—Some of the materials and methods have been described in earlier papers in this series.[1]

Proton or carbon-13 nuclear magnetic resonance spectra were determined by using a Varian T60 or a JEOL FX60 spectrometer, with $SiMe_4$ as the internal reference, and are described conventionally.[1] Details of the spectra, on which assignment of structure has in some cases depended, are given in Supplementary Publication No. 22491 (28 pp.) * submitted to accompany this paper. I.r. spectra were measured by using a Shimadzu IR-27G, and u.v. spectra by using a Unicam SP 800A instrument. Silica gel (Kieselgel S 31614) was used for column chromatography, and Kieselguhr PF 254 or PF 366 for t.l.c. Mass spectra were determined by using a Varian CH7 mass spectrometer. 3,4-Dimethylphenol and the other common reagents were of B.D.H. Laboratory Reagent grade or similar, and for the preparative work of this paper were used without further purification. 2,5,6-Tribromo-3,4-dimethylphenol was prepared by Auwers and Rapp's method;[11] after recrystallisation from methanol it had m.p. 169—171 °C (lit.,[11] 171 °C).

The Monobromo-3,4-dimethylphenols.—The product of treatment of 3,4-dimethylphenol (5 g) with one molecular proportion of bromine in 10% aqueous acetic acid (250 cm^3) contained the 6- and 2-monobromo-derivatives in the ratio *ca.* 85 : 15. It was recovered and chromatographed on silica gel with n-hexane–benzene–diethyl ether (2 : 1 : 1) as eluant. 6-Bromo-3,4-dimethylphenol, m.p. 79 °C (lit.,[17] 80°) after recrystallisation from methanol–water, and 2-bromo-3,4-dimethylphenol (an oil [21]) were thus separated and characterised further by their ^1H n.m.r. spectra. (See Supplementary Publication No. 22491). To prepare 5-bromo-3,4-dimethylphenol (8) [see Scheme for this and structures (4)—(10)], 2,5,6-tribromo-3,4-dimethylphenol (25 g) was suspended in aqueous (55%) hydrogen iodide (200 cm^3) and the mixture was heated under reflux for 150 min. After being cooled, the product (which solidified as a lump), was washed with aq. $Na_2S_2O_3$ and then with much water, and crystallised from n-hexane to give fine white crystals m.p. 101 °C (lit.,[22] 103 °C) (Found: C, 47.8; H, 4.4; Br, 39.4. Calc. for C_8H_9BrO: C, 47.8; H, 4.5; Br, 39.8%).

The Dibromo-3,4-dimethylphenols.—2,6-Dibromo-3,4-dimethylphenol (3) was prepared in quantitative yield by the bromination of 3,4-dimethylphenol (5 g) with two molecular equivalents of bromine in 10% aqueous acetic acid (250 cm^3). After recrystallisation from methanol–water it had m.p. 38.5—39.5 °C (lit.,[18] 39—40 °C). Its isomers were prepared by treating 5-bromo-3,4-dimethylphenol (5 g) with bromine (4 g, added dropwise) in CCl_4 (40 cm^3). When reaction was complete, the solvent and HBr were removed under reduced pressure. The resulting white solid was chromatographed on silica gel, n-hexane–benzene–diethyl ether (3 : 2 : 1) being used as eluant.

From early fractions, 2,5-*dibromo*-3,4-*dimethylphenol* (9) was obtained as white crystals, m.p. 74 °C (Found: C, 34.8; H, 2.8; Br, 56.9. $C_8H_8Br_2O$ requires C, 34.3; H, 2.9; Br, 57.1%).†

Later fractions gave 5,6-*dibromo*-3,4-*dimethylphenol* (10), m.p. 75 °C (Found: C, 34.3; H, 2.7; Br, 56.5%).

The above bromination gave (9) and (10) in the ratio *ca.* 2 : 3; their structures are established by the details of their ^1H n.m.r. spectra (see Supplementary Publication No. 22491, and Discussion).

Tribromination of 3,4-Dimethylphenol.—It has already been noted that treatment of 3,4-dimethylphenol with an excess of bromine without solvent [11] gives 2,5,6-tribromo-3,4-dimethylphenol (6). Under other conditions, however, the reaction takes a different course. To a rapidly stirred solution of 3,4-dimethylphenol (5 g) in 10% aqueous acetic acid (250 cm^3), bromine (19.5 g) was added dropwise. A yellow flocculent solid separated and was filtered off. Water (200 cm^3) was added to the filtrate to give a second crop of the product. The combined solid product was washed with water and crystallised from methanol–water to give pale yellow platelets of 2,4,6-*tribromo*-3,4-*dimethylcyclohexa*-2,5-*dienone* (4), m.p. 98—101 °C (decomp.) (Found: C, 27.0; H, 2.0; Br, 65.7. $C_8H_7Br_3O$ requires C, 26.7; H, 1.9; Br, 66.9%). Its i.r. spectrum had signals at $\nu_{max.}$ 1 670 (C=O) and 1 585 (C=C) cm^{-1}. Its mass spectrum had peaks at M^+ 356, 358, 360, and 362 (intensity 1 : 3 : 3 : 1) and major fragmentation peaks at $M - 14$, $M - 28$, $M - HBr$, and $M - Br_2$. Its u.v. spectrum had $\lambda_{max.}$ 269 nm ($\varepsilon_{max.}$ 10 700; solvent, HOAc).

This compound was also prepared by bromination in aqueous sulphuric acid, following Datta and Bhoumik's procedure [19] (which they thought gave 2,5-dibromo-3,4-dimethylphenol), and by various modifications of this. Thus bromine (4.8 g) was added dropwise to a solution of 3,4-dimethylphenol (1.2 g) in a mixture of conc. H_2SO_4 (10 cm^3) and water (100 cm^3). The heavy pale yellow precipitate was filtered off and recrystallised from aqueous methanol to give the dienone, m.p. 98—101 °C (decomp.).

Reactions of the Dienone (4).—2,4,6-Tribromo-3,4-dimethylcyclohexa-2,5-dienone underwent rearrangement when it was set aside in the ordinary light of the laboratory at room temperature for some time. In early experiments, reaction occurred within <12 days; repeated purification of the dienone, however, gave samples which were stable for longer periods (30 days or more). Recrystallisation of the product of rearrangement from n-hexane gave white crystals of 2,6-*dibromo*-4-*bromomethyl*-3-*methylphenol* [(5) see Scheme], m.p. 102—104 °C (Found: C, 27.3; H, 2.1; Br, 65.5%). Its structure is established by the details of its ^{13}C n.m.r. spectrum (see Supplementary Publication No. 22491, and Discussion). The crude product contained also a small proportion (*ca.* 5%) of 2,6-dibromo-3,4-dimethylphenol. The rearrangement proceeded also in CCl_4 as solvent, rather slowly but without the formation of any significant amounts of other side-chain substituted product as judged by monitoring the course of the rearrangement by ^1H n.m.r. spectroscopy.

A different isomeric rearrangement of the dienone (4) could be effected by dissolving it in conc. H_2SO_4, when 2,5,6-tribromo-3,4-dimethylphenol (6) was obtained rapidly and nearly quantitatively. The product was recovered by adding the mixture to water, filtering off the product, and crystallising it from n-hexane.

The dienone (4) (2 g) when dissolved in a 45% solution of HBr in acetic acid (2 cm^3) gave an equilibrium in which bromine was liberated (mainly as HBr_3) and 2,6-dibromo-3,4-dimethylphenol was formed. The ratio of dienone : phenol was *ca.* 2 : 1 as judged by ^1H n.m.r. spectroscopy; no significant signals attributable to other products were detected. Attempts to bring 2,5,6-tribromo-3,4-dimethylphenol into equilibrium similarly in HOAc–HBr or in $CHCl_3$–HBr in our hands failed.

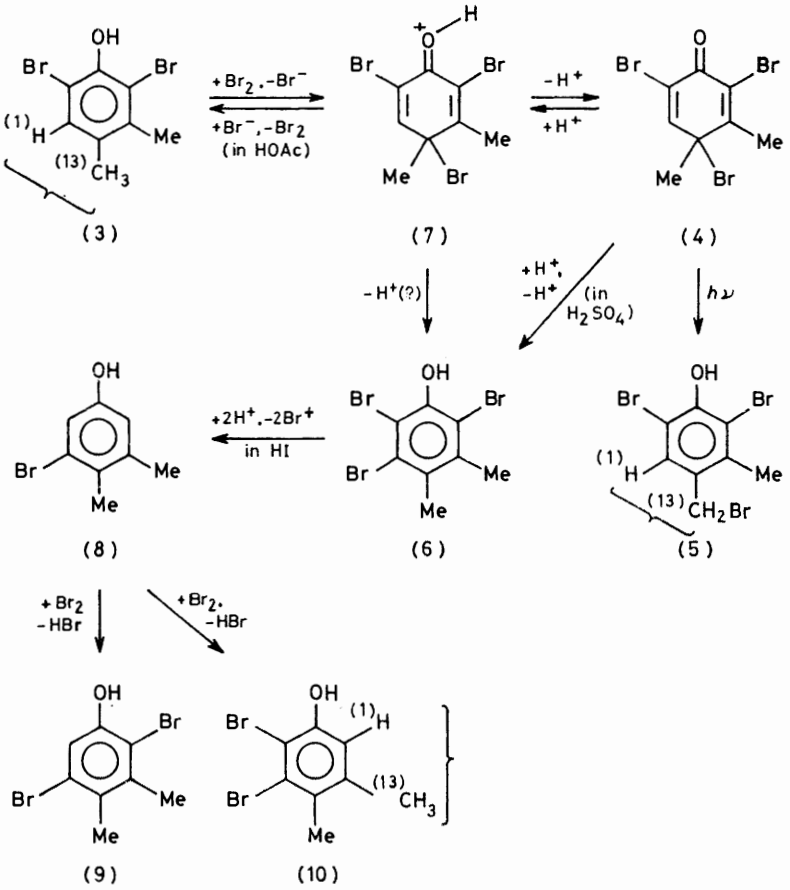
Brominations under Other Conditions.—The bromination of 6-bromo-3,4-dimethylphenol and of 2,6-dibromo-3,4-dimethylphenol followed the courses expected from the

* For details of the Supplementary publication scheme see Notices to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.

† The description of this compound in the literature [19] is evidently incorrect.

above experiments. No evidence was obtained for the intervention of dienone intermediates in the first two stages of bromination of 3,4-dimethylphenol.

A number of other preparative brominations were carried out, in which the aromatic substrate (1 g) was dissolved in the appropriate solvent (10 cm³) and then treated with the appropriate quantity of liquid bromine added dropwise at room temperature. The results are summarised in the Supplementary Publication No. 22491. Yields were nearly quantitative in all cases, as far as could be judged by ^{1}H n.m.r. spectroscopy, and the results were mainly as expected from the above descriptions.



SCHEME Formation and reactions of 2,4,6-tribromo-3,4-dimethylcyclohexa-2,5-dienone (4)

DISCUSSION

The Monobromo-3,4-dimethylphenols.—All of these have been prepared before. 6-Bromo-3,4-dimethylphenol is easily obtained as the major product of monobromination of 3,4-dimethylphenol in acetic acid or in chloroform, and its 2-bromo-isomer can be separated from the crude mixture by chromatography. The relative proportions (87 : 13) from the ^{1}H n.m.r. spectrum of the crude mixture are reasonably in accordance with prediction from the additivity principle (80 : 20), and differ in the direction expected if there were slight steric hindrance to attack at the more congested 2-position.

5-Bromo-3,4-dimethylphenol has been obtained previously only by an indirect method;[22] our procedure, involving tribromination followed by protodebromination with hydrogen iodide, enables its preparation rapidly and in good yield. The method can be regarded as analogous to a procedure investigated by O'Bara *et al.*[23] They showed that the bromo-derivatives of *m*-cresol (and of some other alkylphenols) can be brought into equilibrium by treatment with chloroform saturated with hydrogen bromide at 25 °C. In our experience 2,5,6-tribromo-3,4-dimethylphenol was not affected by chloroform saturated with hydrogen bromide or with 45% hydrogen bromide in acetic acid at room temperature for several days. When heated under reflux with an excess of 55% aqueous hydrogen iodide, however, bromine was removed from the two positions activated by the hydroxy-group, and 5-bromo-3,4-dimethylphenol was obtained nearly quantitatively (see Scheme). We presume that the function of hydrogen iodide is two-fold: to provide the electrophile for displacement of Br^+, and to provide a nucleophile to assist its removal.[24,25]

The Dibromo-3,4-dimethylphenols.—2,6-Dibromo-3,4-dimethylphenol is a well known compound easily prepared by dibromination of 3,4-dimethylphenol in any one of a number of solvents. Neither of its isomers has previously been described correctly, as far as we are aware. We obtained them as a mixture (2,5- : 5,6- = *ca.* 2 : 3) by monobromination of 5-bromo-3,4-dimethylphenol in carbon tetrachloride. From the

isomeric proportions recorded in the literature [10] for monobromination of toluene and bromobenzene, a ratio of 76 : 24 would have been expected; but, since these results were obtained in different solvents, a real breakdown in the additivity principle cannot be claimed with confidence. The ^{1}H n.m.r. spectra of these compounds provided evidence towards assignment of their structures. In the 5,6-isomer (as in the 2,6-isomer), benzylic coupling between the single aromatic hydrogen atom and one of the methyl groups was apparent through broadening of one of the methyl signals; only in 2,5-dibromo-3,4-dimethylphenol were the two methyl signals of approximately equal height. Their ^{13}C spectra provided unambiguous confirmatory evidence from the long-range [$^3J(^1H-^{13}C)$] couplings between the aromatic proton and the carbon of a methyl group, and between the protons of a methyl group and the proton-bearing aromatic carbon atom, clearly evident in the undecoupled spectra of 2,6- and 5,6- but not of 2,5-dibromo-3,4-dimethylphenol.

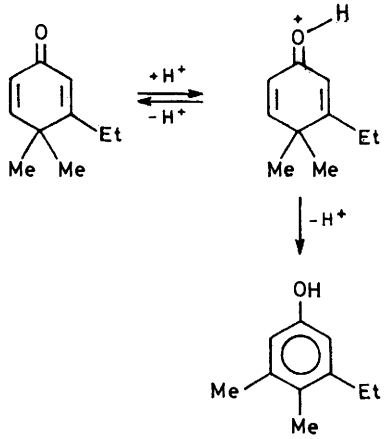
Tribromination of 3,4-*Dimethylphenol; Formation of* 2,4,6-*Tribromo*-3,4-*dimethylcyclohexa*-2,5-*dienone* (4).— Although attack on the 5-position in 2,6-dibromo-3,4-dimethylphenol would be expected to be very slow [see structure (3)], attack on the 4-position, *ipso*- to a methyl group at a position activated by a hydroxy-substituent, would be expected to be quite reasonably fast; the partial rate factor of *ca.* 7×10^4 indicated in Structure (3) has been calculated by using Baciocchi and Illuminati's values for the rates of dienone-formation in the bromination of 4-substituted 2,6-di-t-butylphenols [26] to give the effect of a methyl group on the rate of attack on the position to which it is attached. The only unexpected feature of the formation of the dienone (4) by reaction of 3,4-dimethylphenol or its normal mono- and dibromo-derivatives with enough bromine, therefore, is that no-one seems to have reported it before. It seems probable from the results of our experiments that this, or its product of homolytic rearrangement, was the compound described by Datta and Bhoumik [19] as 2,5-dibromo-3,4-dimethylphenol.

The bromination to form the dienone is reversible and the equilibrium is established rapidly in the presence of concentrated aqueous hydrogen bromide, excess of which forces the equilibrium towards the phenol through the subsidiary equilibrium ($Br_2 + HBr \rightleftharpoons HBr_3$) which lies well on the side of HBr_3.

Rearrangements of the Cyclohexa-2,5-*dienone* (4).— Two different modes of rearrangement of the dienone have been established. In the first, reaction proceeded spontaneously when the solid was set aside in the laboratory for some weeks. The product (5) was formed nearly quantitatively as judged by ^{1}H n.m.r. spectroscopy. In our preliminary communication,[20] we reported that in this rearrangement the bromine had migrated to the 3-, rather than to the 4-methyl group, because we believed that the observed broadening and partial splitting of the methyl signal had resulted from long-range coupling between the protons of the methyl group and the single aromatic proton. Such couplings have been reported [27] to be *ca.* 0.5—1 Hz. Examination of the ^{13}C spectrum, however, showed that this conclusion was incorrect. Details are shown in the Supplementary Publication No. 22491. It should first be noted that, of the dibromo-3,4-dimethylphenols (3), (9), and (10), only (9) shows at the resolution of our instrument no significant long-range coupling between the carbon atom of a methyl group and the single aromatic proton; whereas (3) and (10) show a ^3J(H–C) coupling of *ca.* 4.9 Hz through the fact that one (and only one) of the quartets attributable to a methyl group has each signal split into a doublet [^1J(H–C) = 127 Hz; ^3J(H–C) = 4.9 Hz]. This, together with the fact that (3) is of known structure, not only establishes the structures of the remaining isomers but also establishes that the coupling observed is a $^3J(^1H-^{13}C)$ rather than a $^4J(^1H-^{13}C)$, which in any case would be expected to be the smaller of the two types of coupling. From the undecoupled spectrum of (5) now being examined, it is clear that the quartet attributable to the methyl group is not subject to further fine coupling, but that each peak of the triplet attributable to the CH_2Br groups has become a doublet (^1J = 154 Hz; ^3J = 5.9 Hz). Structure (5) is clearly established by these findings; the only alternatives consistent with the spectral details mentioned would require profound and quite unexpected rearrangements.

We presume that the rearrangement (4) to (6) is homolytic, since it proceeds slowly and autocatalytically in carbon tetrachloride, being accelerated by laboratory illumination. It is of the ' quinobenzylic ' type,[28] and clearly is quite regioselective, none of the 3-CH_2Br isomer being detectable by ^{1}H n.m.r. spectroscopy.

The second mode of rearrangement is undergone by the dienone when it is dissolved in concentrated sulphuric acid. It involves a 1,2-shift of bromine to the adjacent position (4)→(6), formally analogous to the 1,2-alkyl shift which occurs in the dienone–phenol rearrangement. The latter reaction is known to be catalysed by acids, and is normally considered to involve a pre-equilibrium protonation of the dienone,[29] thus for example proceeding by the following sequence:



In our example, the exact nature of the rearrangement process is not known in detail; it is clear, however, that it is acid-catalysed, and so might be presumed to involve the protonated dienone (7). This, however, also should be an intermediate in the formation of the dienone (4) by bromination. The contrast between the smooth debromination of the dienone (4) under the influence of hydrogen bromide in acetic acid and its smooth rearrangement to give the tribromophenol (6) in sulphuric acid leads us to doubt whether the same intermediate is concerned in both cases. Ion-pairing, known [25] to be significant for the bromide-catalysed reactions of protonated dienones such as (7), might alter the rates of formation of reaction products but should not prevent the ultimate formation of the fully aromatic product (6).

In our preliminary communication,[20] we claimed that 2,5-dibromo-3,4-dimethylphenol could under some circumstances be a product of bromination of 3,4-dimethylphenol in aqueous sulphuric acid. We have been unable to reproduce this finding; but it should be noted that the products described in the present work are formed in good yield only under closely defined conditions. In aqueous sulphuric acid, other products including other side-chain-substituted compounds and products of demethylation can be formed. Waring and his coworkers [30] have noted that side-reactions of demethylation can accompany more conventional dienone–phenol rearrangements.

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