Electrophilic Substitution with Rearrangement. Part 10.[1] Some Products of Bromination of 2,4-Dimethylphenol and of 4-t-Butyl-2- methylphenol

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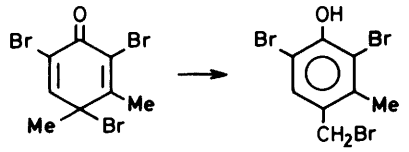
The reaction of 2,4-dimethylphenol with bromine gives first 6-bromo-2,4-dimethylphenol, which according to the conditions of further bromination can give 4,6-dibromo-2,4-dimethylcyclohexa-2,5-dienone; a mixture of 5,6- with some 3,6-dibromo-2,4-dimethylphenol; 6-bromo-4-bromomethyl-2-methylphenol with none of the 2-bromomethyl-4-methyl isomer; or a mixture from which 6-bromo-2,4-bis(bromomethyl)phenol can be isolated. The corresponding dienone from 6-bromo-4-t-butyl-2-methylphenol reacts by more complex pathways, and the products include those of de-t-butylation. The probable mechanisms involved in these reactions are discussed.

In previous papers,[1,2] some of the competing rearrangements of cyclohexadienones derived from methyl-substituted phenols have been discussed. The 3,4-dimethyl dienone (1) rearranges in the solid state or in aprotic solvents to give exclusively the bromomethylphenol (2), (the so-called 'quinobromide' rearrangement). Its 2,4-dimethyl analogue (3) is reported to rearrange with similar regiospecificity to give (4).[3]



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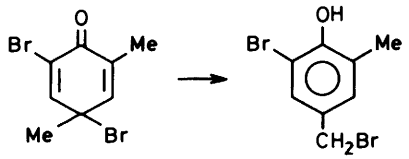


(3) (4)

Previous studies of the bromination of 2,4-dimethylphenol have established only in part the courses which can be taken. Jacobsen [4] prepared and characterised 6-bromo-2,4-dimethylphenol, an *x*,*x*-dibromo-2,4-dimethylphenol, and 3,5,6-tribromo-2,4-dimethylphenol by bromination of the phenol. 4,6-Dibromo-2,4-dimethylcyclohexa-2,5-dienone (3) could be presumed to be an intermediate in reactions involving more than one molecular proportion of bromine, since it has been obtained [3,5] by the action of bromine on 6-bromo-2,4-dimethylphenol in acetic acid containing fused sodium acetate. 3,5,6-Tribromo-4-bromomethyl-2-methylphenol and 3,5,6-tribromo-2,4-bis(bromomethyl)phenol have also been characterized.[6] The former was prepared by direct bromination of 2,4-dimethylphenol in acetic acid with excess of bromine, but the extent to which these reactions are regiospecific has not been established, and no evidence is available as to the mechanism of bromination of a methyl group *ortho* to a hydroxy-group.

We have therefore re-examined some of these reactions, characterizing the products and the pathways leading to them more fully. Long-range (^2J, ^3J) coupling constants in the ^{13}C n.m.r. spectra of some of the products of bromination have been helpful in establishing or confirming their structures. The corresponding reactions of 4-t-butyl-2-methylphenol have been examined in rather less detail.

EXPERIMENTAL

Many of the materials and methods have been described in earlier papers.[1,2] 2,4-Dimethylphenol was a commercial product used without further purification. 4-t-Butyl-2-methylphenol has previously been prepared by t-butylation of 2-methylphenol with t-butyl alcohol and phosphoric acid.[7] We tried to use polyphosphoric acid and 85% phosphoric acid, but obtained only complex mixtures of products, so the following method was used. To a solution of 2-methylphenol (5.4 g) in t-butyl chloride (5.1 g) was added $AlCl_3$ (*ca.* 3 g) in small portions. Evolution of HCl began after *ca.* 5 min, and the mixture was stirred for *ca.* 30 min. The product was poured onto ice and extracted with diethyl ether. The ether extract was washed (aqueous $NaHCO_3$, then H_2O) and dried ($MgSO_4$). Removal of the ether left a yellow oil which from its ^1H n.m.r. spectrum still contained much 2-methylphenol. A portion (1 g) of the oil was chromatographed on silica gel, elution being with $CHCl_3$. Middle fractions (0.2 g) were the required 4-t-butyl-2-methylphenol; its ^1H n.m.r. spectrum had signals at δ 1.3 (9H, s, CMe_3), 2.15 (3 H, s, Me), 5.50 (1 H, s, OH), 6.6—6.95 (3 H, m, ArH; $J_{5,6}$ 10, other couplings ≯ 2Hz).

Monobromination of 2,4-Dimethylphenol.—6-Bromo-2,4-dimethylphenol was prepared from 2,4-dimethylphenol and one molecular equivalent of bromine in 90% acetic acid [a mixture of acetic acid (90 cm^3) and water (10 cm^3)] as an oil, m.p. 4 °C (lit.,[4] 4—5 °C). Its ^1H n.m.r. spectrum had signals at δ 2.20 [6 H, s, Me(C-2) and Me(C-4)], 5.25 (1 H, s, OH), 6.18 [1 H, s, ArH(C-3)], and 7.20 [1 H, s, ArH(C-5)]. Details of its ^{13}C spectrum are given in the Supplementary Publication No. SUP 23323 (39 pp.).†

Bromine (6.6 g, 1 mol. equiv.) in CCl_4 (60 cm^3) was added to a stirred solution of 2,4-dimethylphenol (5.0 g) in CCl_4 (60 cm^3), the mixture in a Pyrex flask being cooled by a

† For details of Supplementary Publications see Notice to Authors No. 7. in *J. Chem. Soc., Perkin Trans. 2*, 1981, Index issue.

current of air and illuminated by a 1 kW lamp located *ca.* 30 cm from the flask. The reaction was complete in *ca.* 30 min, and after removal of the solvent, was shown (^{1}H n.m.r.) to be largely 6-bromo-2,4-dimethylphenol. A similar reaction carried out in the dark and then illuminated for 30 min when reaction was nearly complete gave the same product, which could be purified by chromatography on silica gel with CCl_4 as eluant.

Dibromination of 2,4-Dimethylphenol.—A solution of 2,4-dimethylphenol (1 g) in acetic acid (75 cm^3) and water (7.5 cm^3) was cooled to −2 °C, and bromine (0.9 cm^3) was added. The mixture immediately became orange in colour; water and ice (*ca.* 150 cm^3) were then added immediately. The mixture was stirred (5 min), and the precipitate was filtered off and washed with ice-cold water. The crude product, 4,6-dibromo-2,4-dimethylcyclohexa-2,5-dienone, was a yellow solid (1.95 g) which was unstable and decomposed on attempted recrystallization from light petroleum (b.p. 40—60 °C). In our hands it had m.p. 51—53 °C (lit.,[3,5] 63 °C). Its u.v. spectrum in ethanol had $\lambda_{max.}$ 260 nm ($\varepsilon_{max.}$ 6 645); i.r., maxima at 1 655 (conjugated C=O) and 1 598 cm^{-1} (C=C). Its ^{1}H n.m.r. spectrum ($CDCl_3$) had signals at δ 1.95 [3 H, s, Me(C-2)], 2.9 [3 H, s, Me(C-4)], 6.95 [1 H, m, ArH(C-3)], and 7.57 [1 H, d, ArH-(C-5)]. Its ^{13}C n.m.r. spectrum is given in SUP 23323; in this spectrum, no signals other than those attributable to the compound were detected, though most proton spectra had a subsidiary signal of low intensity adjacent to the signal for the methyl group.

When the above dienone (3) was left as a solid overnight at room temperature in the dark, it underwent spontaneous rearrangement. The product was entirely 6-bromo-4-bromomethyl-2-methylphenol, m.p. 103—104 °C (lit.,[3] 104 °C). Its ^{1}H n.m.r. spectrum (CCl_4) had signals at δ 2.25 [3 H, s, Me(C-2)], 4.40 [2 H, s, CH_2Br(C-4)], 5.60 [1 H, s, OH(C-6)], 7.71 [1 H, s, ArH(C-5)], and 7.34 [1 H, m, ArH(C-3)]. Details of its ^{13}C n.m.r. spectrum are given in SUP 23323.

The dienone (3) could be rearranged also by treating it with sulphuric acid. Cooled concentrated H_2SO_4 (2 cm^3) was added to the dienone (*ca.* 0.8 g). After 2 min, ice-cold water (10 cm^3) was added to the reaction mixture. The crude product was examined by ^{1}H n.m.r. spectroscopy, and was a mixture of which the major component (75%) was 5,6-dibromo-2,4-dimethylphenol. This was prepared in a separate experiment by adding bromine (2 mol. equiv.) over *ca.* 20 min. The resulting solid was recrystallized three times from aqueous methanol to give needles, m.p. 68—69 °C (Found: C, 34.3; H, 3.0; Br, 56.7. Calc. for $C_8H_8Br_2O$: C, 34.3; H, 3.9; Br, 57.1%). Its ^{1}H n.m.r. spectrum had signals at δ 2.20 [3 H, s, Me (C-4)], 5.41 [1 H, s, OH (C-1)], and 6.92 [1 H, s, ArH(C-3)]. Its structure is established from its ^{13}C n.m.r. spectra, given in SUP 23323 and discussed below. It is almost certainly the substance reported by Jacobsen [4] as *x*,*x*-dibromo-2,4-dimethylphenol, needles, m.p. 73 °C, and is probably the same as the product, m.p. 66—70 °C, obtained by Wessely *et al.*[5] by treating 2-acetoxy-6-bromo-2,4-dimethylcyclohexa-3,5-dienone with hydrogen bromide in dry chloroform.

The ^{1}H n.m.r. spectrum of the product of rearrangement of 4,6-dibromo-2,4-dimethylcyclohexa-2,5-dienone contained an additional signal (δ 7.2) attributable to the aromatic hydrogen atom of 3,6-dibromo-2,4-dimethylphenol, and other signals which overlapped those of its 5,6-dibromo-isomer. The residue remaining after crystallization of the 5,6-dibromo-compound from the mixture obtained by dibromination of 2,4-dimethylphenol was similar. In its fully decoupled ^{13}C n.m.r. spectrum, the signals for the eight carbon atoms of 5,6-dibromo-3,4-dimethylphenol were accompanied by those attributable to all the eight carbon atoms of its isomer; only traces of impurities were present. We did not succeed in separating the two isomers completely, but the identity of the minor component is confirmed by the signals of the methyl group in the single-resonance spectrum of the mixture. The ratio of isomers in the crude product of rearrangement, estimated from the integration of the signals for the aromatic hydrogen atoms in the ^{1}H n.m.r. spectrum, was 5,6- : 3,6- = 3 : 1.

Dibromination of 2,4-dimethylphenol in carbon tetrachloride took a course different from that taken in acetic acid, or without solvent. The procedure was as for monobromination, 2 mol. equiv. of bromine being used. After 2 h, the colour of bromine had almost gone, and the solvent was removed under reduced pressure. The ^{1}H n.m.r. spectrum of the crude product was complex; the signals for 6-bromo-4-bromomethyl-2-methylphenol were present, accompanied by *ca.* 30% of a second component having signals which evidently represented a methyl and a bromomethyl group. We presume, therefore, that this reaction is not regiospecific, but gives *ca.* 70% of 6-bromo-4-bromomethyl-2-methylphenol and *ca.* 30% of 6-bromo-2-bromomethyl-4-methylphenol, first prepared by Adler *et al.*[8] The same products were obtained by monobromination of 6-bromo-2-bromomethylphenol in carbon tetrachloride; signals attributable to the presence of traces of compounds containing a $CHBr_2$ group were present in the ^{1}H n.m.r. spectrum of the crude product.

Tribromination of 2,4-Dimethylphenol.—Bromination of 2,4-dimethylphenol with three molecular equivalents of bromine gave 3,5,6-tribromo-2,4-dimethylphenol which after being recrystallized from aqueous methanol had m.p. 178—179.5 °C (lit.,[4] 179 °C), δ 2.34 [3 H, s, Me(C-2)], 2.61 [3 H, s, Me(C-4)], and 5.62 [1 H, s, OH(C-6)]. Its ^{13}C n.m.r. spectrum is included in SUP 23323 and discussed below.

The corresponding bromination in carbon tetrachloride as solvent under strong illumination gave a mixture from which 6-bromo-2,4-bis(bromomethyl)phenol, m.p. 117—118 °C, was obtained by recrystallization from n-hexane (Found: C, 27.0; H, 2.3; Br, 66.4. Calc. for $C_8H_7Br_3O$: C, 26.8; H, 2.0; Br, 66.8%), δ 4.36 [2 H, s, CH_2Br (C-4)], 4.50 [2 H, s, CH_2Br(C-2)], 5.80br [1 H, s, OH(C-1)], 7.30 [1 H, d, ArH(C-3)], and 7.44 [1 H, d, ArH(C-5), $J_{3,5}$ 2 Hz]. The main additional components of the reaction mixture are considered to be 6-bromo-2(and 4)-dibromethyl-4(and 2)-methylphenols, since the major additional signals were at δ 2.2—2.4 ($ArCH_3$) and 6.5—6.6 ($ArCHBr_2$), integrating in approximately the ratio of 3 : 1, and [by comparison with the signals for 6-bromo-2,4-bis(bromomethyl)phenol] comprising *ca.* 40% of the total product. Similar mixtures of products were obtained by dibromination of 6-bromo-2,4-dimethylphenol and by monobromination of 6-bromo-4-bromomethyl-2-methylphenol in CCl_4 under strong illumination.

Treatment of 6-bromo-4-bromomethyl-2-methylphenol (1 g) at 0 °C in acetic acid (75 cm^3) containing water (7.5 cm^3) and sodium acetate (0.5 g) with bromine (1 mol. equiv.) gave an unstable mixture of products which was extracted into diethyl ether. The ethereal solution was washed (aqueous $NaHCO_3$) and dried ($MgSO_4$). Removal of ether under reduced pressure left a yellow oil, the ^{1}H n.m.r.

spectrum of which included signals not affected by D_2O at δ 2.1, 4.45, 6.84, and 7.40, consistent with the presence of 4,6-dibromo-4-bromomethyl-2-methylcyclohexa-2,5-dienone. After being left overnight, these signals had disappeared, and a complex mixture of products had been formed.

Bromination of 4-t-Butyl-2-methylphenol.—The reaction of bromine with one molecular equivalent of 4-t-butyl-2-methylphenol in aqueous acetic acid gave a product which had a ^1H n.m.r. spectrum consistent with that expected for 6-bromo-4-t-butyl-2-methylphenol [signals at δ 1.25 (9 H, s, Bu^t), 2.25 (3 H, s, Me), 5.25br (1 H, s, OH), and 7.0—7.2 (2 H, dd, $J_{3,5}$ 2 Hz, ArH)]. This material (*ca.* 1 g) was dissolved in acetic acid (30 cm^3) containing water (3 cm^3) and to it was added a further molecular equivalent of bromine in acetic acid (7.5 cm^3). The resulting orange solution was stirred for 30 min, and then ice (50 g) was added. The precipitated yellow solid was filtered off and carefully dried in air (yield 1.6 g). A portion was recrystallized (light petroleum, b.p. 60—80 °C) to give large yellow needles of *4,6-dibromo-4-t-butyl-2-methylcyclohexa-2,5-dienone*, m.p. 93—95 °C (decomp.), δ 1.15 (9 H, s, CMe_3), 2.0 (3 H, s, Me), 6.9 (1 H, m, *J* 3 and 1.5 Hz, H-3), and 7.5 (1 H, d, *J* 3 Hz, H-5). Its u.v. spectrum in acetic acid comprised a single broad absorption, $\lambda_{max.}$ 262 nm, $\varepsilon_{max.}$ 9 100, with no sign of a maximum above 300 nm. Its i.r. spectrum ($CHCl_3$) confirmed the presence of conjugated C=O (max. at 1 680 cm^{-1}) and C=C (1 610 cm^{-1}).

Reactions of 4,6-Dibromo-4-t-butyl-2-methylcyclohexa-2,5-dienone.—This dienone (0.3 g) was stirred with concentrated H_2SO_4 (10 cm^3) for 10 min. The product was poured onto ice, and the precipitate was washed and dried. From its ^1H n.m.r. spectrum it was 4,6-dibromo-2-methylphenol with very little impurity; after recrystallization from light petroleum (b.p. 40—60 °C) it had m.p. 56 °C (lit.,[9] 58 °C).

When the dienone (0.1 g) was treated with CF_3SO_3H (3 cm^3) for 2 min and then the mixture was poured onto ice and the organic product was recovered in the usual way, its ^1H n.m.r. spectrum showed that the starting material was absent, and that 4,6-dibromo-2-methylphenol had been formed, together with *ca.* 40% of phenolic product retaining the t-butyl group. We think, therefore, that, under these conditions, 1,2-shift of bromine accompanies loss of the t-butyl group.

When the dienone was exposed to the atmosphere for 2 days it became a yellow syrup the ^1H n.m.r. spectrum of which indicated that a substantial proportion of 6-bromo-4-t-butyl-2-methylphenol had been formed by loss of 'Br^+' and rearrangement. On being exposed to laboratory daylight in hexane or in CCl_4 for a day, the solution developed an orange colour (probably of bromine) after *ca.* 1 h, and this gradually disappeared. Fumes of HBr were apparent, and the products contained signals in the region expected for a bromomethyl group.

DISCUSSION

Structures of the Bromo-derivatives.—Details of the ^1H and ^{13}C n.m.r. spectra of most of the bromodienones and bromophenols encountered in this work are given in SUP 23323. Complete assignment of the signals was possible from the chemical shifts and decoupling experiments. Here we discuss the most important features relevant to the structures of the compounds which we have encountered. 6-Bromo-2,4-dimethylphenol is a well known compound, the ^{13}C spectrum of which is consistent with its structure. The dibromo-2,4-dimethylphenol, m.p. 68—69 °C, can be seen to be the 5,6-dibromo-isomer, since in the single-resonance spectrum each component of the quartets representing the two methyl carbon atoms are doublets as the result of coupling with the aromatic hydrogen atom, which must therefore lie between these methyl groups ($^3J_{3\text{-H, C(Me)}}$ 4.9, 4.9 Hz). The mixture of isomers obtained by dibromination of 2,4-dimethylphenol, on the other hand, included a component in which the signals comprising one of the quartets were singlets. Since a mixture having the same two components can be prepared also by rearrangement of 4,6-dibromo-2,4-dimethylcyclohexa-2,5-dienone, the second component must be 3,6-dibromo-2,4-dimethylphenol.

A similar method was used to establish unambiguously the structure of 6-bromo-4-bromomethyl-2-methylphenol. The signals for the methyl group comprise a quartet each split into a doublet ($^3J_{3\text{-H, C(Me)}}$ 4.9 Hz). The methyl group must therefore be adjacent to a single hydrogen, and must therefore be in the 2-position. The signals for the CH_2Br group, centred as expected downfield of those for the CH_3 group, comprise a triplet each branch of which is split into a triplet ($^3J_{3\text{-H, CH}_2\text{Br}} \sim {}^3J_{5\text{-H, CH}_2\text{Br}} = 5.2$ Hz), and must therefore lie in the 4-position, between two aromatic protons.

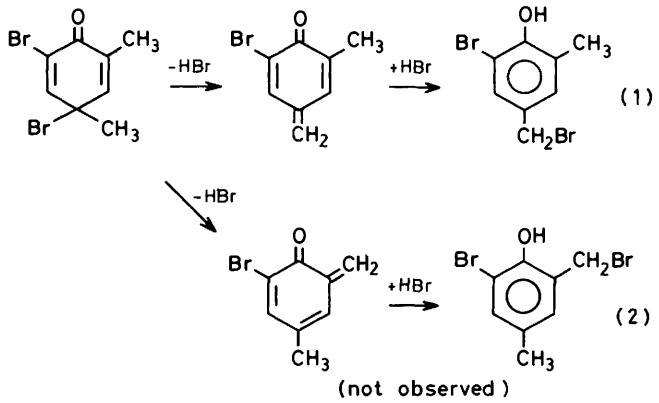
Our dibromo-2,4-dimethylcyclohexa-2,5-dienone must also have the 4,6-dibromo-structure, for several reasons apparent in the ^{13}C n.m.r. spectrum. First, the signal for the carbonyl carbon atom appears at δ 177.97, in the range expected for 2,5- as distinct from 3,5-dienones.[1,10] Secondly, the signals for the upfield methyl carbon appear as a quartet of doublets, the long-range coupling constant being 6 Hz. Only one hydrogen atom is therefore adjacent to the vinylic methyl carbon, which must therefore be in the 2-position. Thirdly, the signals for the downfield methyl carbon appear as a quartet of triplets, long-range coupling *ca.* 2 Hz. This methyl carbon, much less strongly coupled than the other methyl group to adjacent hydrogen atoms, and hence confirmed to be at a tetrahedral rather than at a vinylic position, is coupled with a low coupling constant to two protons rather than to one, and hence must be at the 4- rather than the 2-position.

The structure of this dienone was established also through its u.v. spectrum; we used this criterion, together with the ^1H n.m.r. spectrum, to establish that the dienone from 4-t-butyl-2-methylphenol was 4,6-dibromo-4-t-butyl-2-methylcyclohexa-2,5-dienone. It was characteristic of both these dienones that $^3J_{3\text{-H, 5-H}}$ (2.9 Hz) was significantly larger than the corresponding *meta*-coupling (≯2 Hz) in the related phenols.

It was evident from its ^1H n.m.r. spectrum that the compound, m.p. 117—118 °C, isolated from the mixture obtained by the tribromination of 2,4-dimethylphenol in CCl_4 was 6-bromo-2,4-bis(bromomethyl)phenol, since the signals for two bromomethyl groups were apparent near δ 4.5. Possible isomers having a dibromomethyl group would have signals (singlets) near δ 6.5, as has been

found for example in 2,6-dibromo-4-dibromomethylphenol (unpublished work).

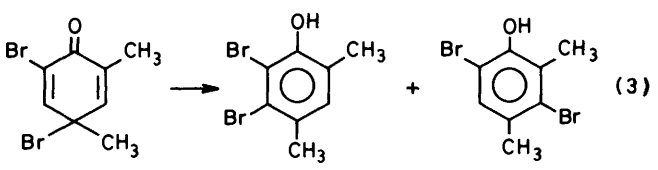
Mechanisms available for Bromination.—The results obtained in the present work are consistent with the views set out earlier.[1] The first stage of bromination of 2,4-dimethylphenol gives 6-bromo-2,4-dimethylphenol, probably through a dienone which then rearranges prototropically though details of this stage have not been



established. The second stage normally gives 4,6-dibromo-2,4-dimethylcyclohexa-2,5-dienone, and this can rearrange in two ways. One gives 6-bromo-4-bromomethyl-2-methylphenol with none, or very little, of its 2-bromomethyl isomer. The reaction proceeds spontaneously in the solid and in solutions in aprotic solvents; it does not involve free bromine atoms, since brominations under similar conditions with bromine and light are much less regioselective. An addition–elimination sequence involving a quinone methide is the most likely pathway [equation (1)], and the vinylogous process involving an *ortho*-quinone methide [equation (2)] does not compete effectively with the pathway of equation (1).

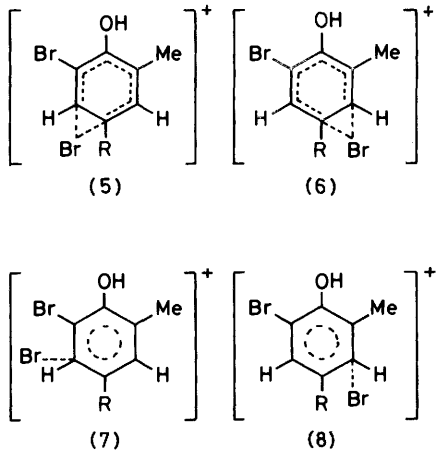
The second mode of rearrangement occurs under catalysis by strong acids, and is regioselective [equation (3)] as in related cases discussed earlier.[1]

The ratio of isomers formed in this rearrangement was 3 : 1 in favour of the isomer having bromine *para* rather than *ortho* to the 2-methyl group. This orientation was maintained in the bromination of 2,4-dimethylphenol



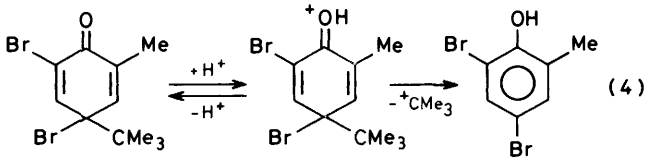
with bromine in the absence of solvent other than the reactants. Qualitatively, this orientation is in the same direction as that observed for 4,4,6-tribromo-2-methylcyclohexa-2,5-dienone (4,5,6- : 3,4,6- = 7.5 : 1), though the isomeric ratios are not identical. The transition states (5) and (6) which would generally be presumed to be concerned in the competitive 1,2-shifts leading to rearrangement [1,11] are isomeric with those, (7) and (8), concerned in the analogous aromatic substitutions by reagents which supply ' positive bromine '.

Orientation is in each comparison determined by the competition between the electronic and steric influences of the 2-Me and 6-Br substituents. If the principle of additivity could be applied to the results of Olah *et al.*[12] for the bromination of toluene and bromobenzene catalysed by $FeCl_3$ in nitromethane, one would predict a strong preference for bromination of 3-bromotoluene *ortho* to



methyl, rather than to bromine. In qualitative agreement with this, the mononitration of 3-bromotoluene gives 54% of 3-bromo-6-nitrotoluene and 33% of 3-bromo-4-nitrotoluene.[13] The reason why our 1,2-migrations favour shifts *ortho* to the bromine substituent is therefore not explained by analogies with aromatic substitution, and the results suggest that one or other of the pairs of transition states, (5) and (6), (7) and (8), is not exactly as represented in the formulae.

The first two stages of heterolytic bromination of 4-t-butyl-2-methylphenol were evidently analogous to those of 2,4-dimethylphenol, but the acid-catalysed rearrangement of the resulting dienone revealed a further anomaly. It might not have been unexpected that treatment with sulphuric acid should result in de-t-butylation to the not quite complete exclusion of 1,2-shift of bromine [equation (4)]. This is a ' conventional ' S_E2' electro-

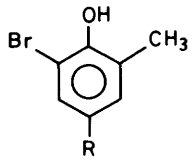


philic displacement with rearrangement. Less expected, however, was the fact that the course of the reaction in trifluoromethanesulphonic acid was quite markedly different, the S_E2' process being accompanied by reaction (probably a 1,2-shift) in which the t-butyl group was not displaced. It is possible that the relatively nucleophilic hydrogensulphate ion is concerned in the protiode-t-butylation.

The behaviour of this dienone in the solid phase at

room temperature, or in carbon tetrachloride, was indicative of the mode of bromination available for substitution in a methyl group '*ortho*' rather than '*para*' to the carbonyl carbon. Without solvent, bromine was lost and 6-bromo-2-methyl-4-t-butylphenol was formed. When CCl_4 was used as solvent, however, a mixture of products was formed in which substitution had proceeded in part into the 2-methyl group; apparently before that, free bromine had been formed in the solution. We think, therefore, that, as with the dienone from 2-methylphenol,[1] transfer of bromine from the 4-position of a 2,5-dienone to a 2-methyl group normally involves a complex course in which a proton is found from some catalytic source, then HBr is generated along with free bromine, which can then brominate the 2-methyl group by a homolytic substitution.

Homolytic side-chain brominations presumably involve bromine atoms which can be derived either from bromine or from bromodienones. They are clearly much less selective than the 'quinobromide' rearrangement, and there is little preference for attack as between a 2-methyl group, a 4-methyl group, or a CH_2Br group; dibromination of 6-bromo-2,4-dimethylphenol, or mono-



(9)

bromination of 6-bromo-4-bromomethyl-2-methylphenol, gave mixtures containing isolable quantities of 6-bromo-2,4-bis(bromomethyl)phenol.

In this and in an earlier paper,[1] we have encountered 2,5-dienones derived from three phenols of the type (9; R = Me, Bu^t, Br). Although analogous 3,5-dienones have been obtained by some workers by using low temperatures and dipolar aprotic solvents,[14] such dienones have not been encountered in the course of the present work. If they are formed, they rearrange to the isomeric 2,5-dienones more rapidly than they undergo other types of rearrangement. It is not yet known, we believe, whether a 'quinobenzylic' rearrangement of the type exemplified in equation (2) can be realized.

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