

ABNORMAL REACTION PATHWAYS IN THE BROMINATION OF 3,4-DIMETHYLPHENOL

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Electrophilic bromination of phenols usually leads easily to the expected products of substitution ortho- or para to the hydroxyl group. Dienone intermediates may be involved, but (except with hindered phenols¹) usually re-aromatise rapidly.²

When the activated ring-positions are all occupied, further bromination often gives relatively stable dienones.^{3,4} There have been reports, however, of phenols which can be brominated further to give products of substitution meta- to the hydroxyl group;^{5,6} and protection of one or more of the normally activated positions by sulphonation has been thought^{7,8} to provide routes to such abnormally substituted products.

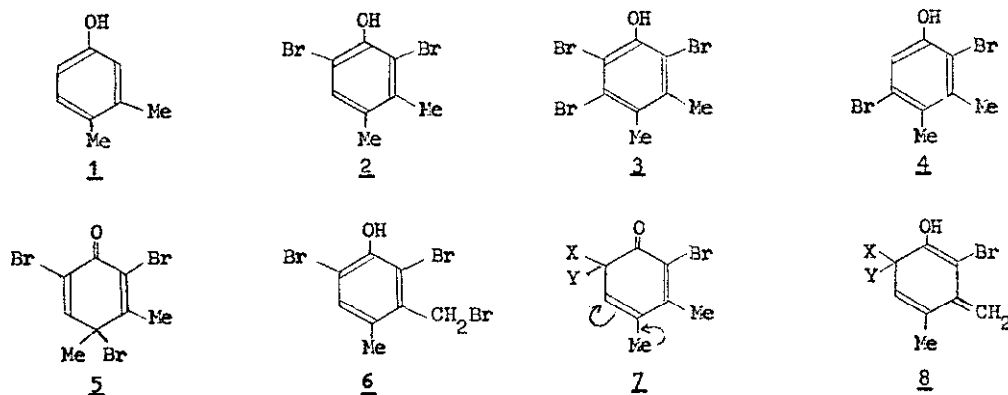
An example is provided by 3,4-dimethylphenol (1), which gives first the normal products (2- and 6-bromo- and thence 2,6-dibromo-3,4-dimethylphenol, 2).^{9,10} Further bromination is then reported to give 2,5,6-tribromo-3,4-dimethylphenol (3);^{11,12} bromination after first sulphonating 3,4-dimethylphenol, on the other hand, has been claimed⁷ to provide a route to 2,5-dibromo-3,4-dimethylphenol (4).

We have now shown that bromination of 3,4-dimethylphenol (1) or of 2,6-dibromo-3,4-dimethylphenol (2) (ca. 0.5M, in acetic acid at 20°, the appropriate amount of bromine being used) gives instead nearly quantitatively the tribromodienone 5, as pale yellow platelets m.p. 98-101° (decomp.), of correct analysis and having the expected ¹H n.m.r. and i.r. spectrum. The same compound is the major product obtained by following Datta and Bhoumik's procedure,⁷ namely by first sulphonating 3,4-dimethylphenol by dissolving it in sulphuric acid and then adding the product to water and treating it with bromine. The dienone is stable for some days at room temperature; in due course, however, it rearranges autocatalytically and presumably homolytically in the solid phase, giving 3-bromomethyl-2,6-dibromo-4-methylphenol (6) (white crystals, m.p. 105°), identified from its ¹H n.m.r. spectrum.

Side-chain substituted products can be recognised also in the mixture of products obtained by bromination of 3,4-dimethylphenol if this is dissolved in sulphuric acid, then diluted with

water and brominated while the solution is still warm. 5-Substituted products, including 2,5-dibromo-3,4-dimethylphenol (**4**), are also major components of these reaction mixtures. To obtain 2,5,6-tribromo-3,4-dimethylphenol in good yield, however, it is necessary to brominate 3,4-dimethylphenol without solvent, or by first dissolving it in only a little acetic acid.

It seems unlikely that 5-substituted derivatives (e.g. **3** and **4**) are obtained by normal substitutions of the deactivated bromophenols or bromophenolsulphonic acids. Instead, dienones are probably involved. ortho-Dienones such as **7** ($X = H, Br, SO_3H; Y = Br$), formed reversibly where necessary from their para-isomers, would allow activation of the 5-position by the 4-methyl group. Furthermore, **7** by acid-catalysed tautomeric shift could give **8**, and thence provide a heterolytic pathway to side-chain-substituted products. Addition-elimination pathways, involving such intermediates as were considered by Auwers et al.,^{5,9,12,13} also need consideration; further details, and other alkylphenols, are under investigation.



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