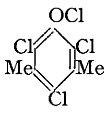
89. *Halogenation of* m-5- *and* m-2-*Xylenols. Preparation and Structure of Certain Polyhalogeno*-m-5- *and* -m-2-*xylenols.*

By C. H. R. Elston, A. T. Peters, and (the late) F. M. Rowe.

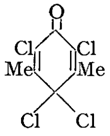
Chemical and absorption-spectra data are examined in an attempt to clarify the constitution of certain polyhalogeno-phenols and -xylenols, and the respective merits of the quinonoid and hypohalite configurations are discussed. 1 Mol. of chlorine and 1 mol. of 2 : 4 : 6-tribromo-*m*-5-xylenol afford 2-*chloro*-2 : 4 : 6-*tribromo*-1 : 3-*dimethyl*cyclo*hexa*-3 : 6-*diene*-5-*one* (VI), but 2·5 mols. of chlorine cause replacement of bromine to give the 2 : 2 : 4-*trichloro*-6-*bromo*-analogue of (VI). 2 : 4 : 6-*Trichloro*-m-5-*xylenol bromide* (VIII) and 4 : 5 : 6-*tribromo*-m-2-*xylenol chloride* and *bromide* are characterised. Chlorination of 4 : 6-dichloro-2-bromo-*m*-2-xylenol yields, with replacement of bromine, 2 : 2 : 4 : 6-tetrachloro-1 : 3-dimethyl*cyclo*hexa-3 : 6-diene-5-one.

In view of the work of Lauer (*J. Amer. Chem. Soc.*, 1926, **48**, 442) and of Ssuknewitsch and Budnitzky (*J. pr. Chem.*, 1933, **138**, 22), it is possible that 2 : 2 : 4 : 6-tetrachloro-1 : 3-dimethyl*cyclo*hexa-3 : 6-diene-5-one may possess a hypohalite (I) rather than a hemiquinonoid structure (II).

The above workers showed that different isomerides, $C_6H_2OClBr_3$, were obtained from the action of chlorine water on 2 : 4 : 6-tribromophenol, and of bromine water on 4-chloro-2 : 6-dibromophenol, whereas the quinonoid configuration would require them to be identical (V). The same workers favour the respective hypohalite structures (III) and (IV), but Lauer (*loc. cit.*) postulates a partial rearrangement of phenol chlorides with a *p*-bromine atom into *p*-chlorophenol bromides. We found that chlorination of 2 : 4 : 6-tribromophenol gives 2 : 4 : 6-tribromophenol chloride, which is readily decomposed by passing sulphur dioxide through its alcohol solution, to give a mixture of trihalogenophenols, *i.e.*, there is loss of bromine *and* chlorine. On the other hand, 4-chloro-2 : 6-dibromophenol and bromine give 4-chloro-2 : 6-dibromophenol bromide, which decomposes with loss of bromine only, to yield 4-chloro-2 : 6-dibromophenol.



(I.)



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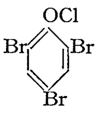
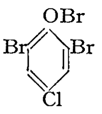


(III.)



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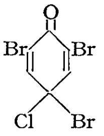


(V.)

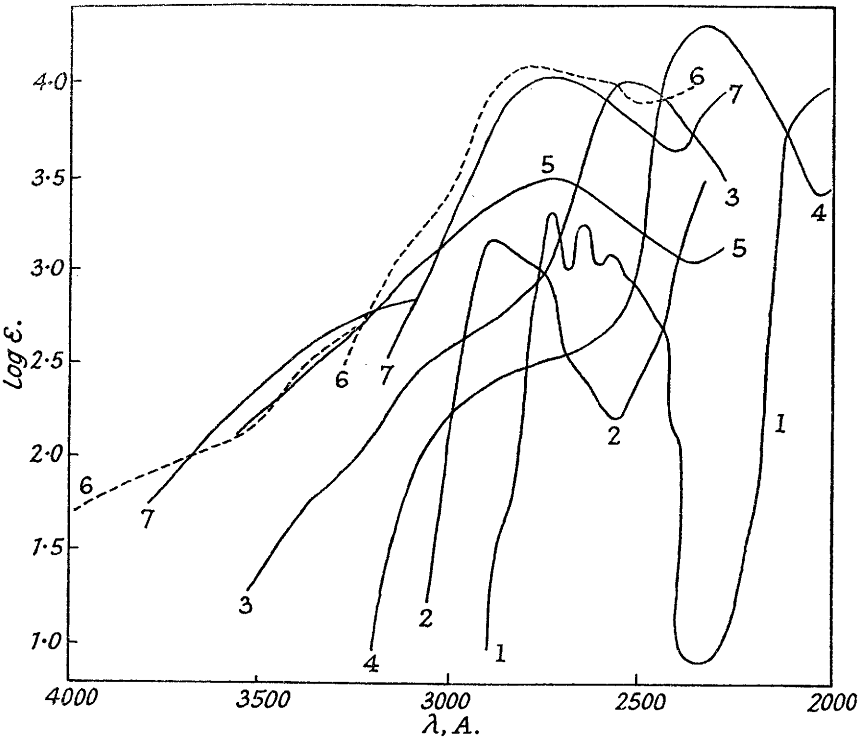
We suggest that a possible explanation of the above results is that chlorine reacts with 2 : 4 : 6-tribromophenol to give (III), which then tautomerises to some extent to (V), and thence to some (IV); bromine and 4-chloro-2 : 6-dibromophenol, however, give (IV), which tautomerises to (V) to a very small extent only. (III) would probably lose chlorine on degradation, whereas (IV) and (V) would probably lose bromine.

A mixed m. p. curve of 2 : 4 : 6-tribromophenol and 4-chloro-2 : 6-dibromophenol, or of their respective methyl ethers, showed little depression in m. p. of mixtures, and this method of identification is unreliable, a factor noted in other cases of related trihalogeno-*m*-xylenols. It was considered that a study of absorption spectra might clarify the position. Accordingly, freshly-prepared specimens of 2 : 4 : 6-tribromophenol chloride, 2 : 2 : 4 : 6-tetrachloro-1 : 3-dimethyl*cyclo*hexa-3 : 6-diene-5-one, and 2 : 4 : 6-trichloro-*m*-5-xylenol were sent to Dr. C. B. Allsopp and Miss D. M. Simpson, of Cambridge University, to whom our warm appreciation and thanks are due. These workers plotted absorption curves in *cyclo*hexane and compared them with those obtained from phenol and benzoquinone, respectively.

There is close similarity between the curves for 2 : 4 : 6-trichloro-*m*-5-xylenol and phenol, as expected, and the effect of the chlorine is to displace the band to slightly longer wave-lengths and to reduce the intensity. The curve for the tetrachloro-compound is similar to that for benzoquinone. 2 : 4 : 6-Tribromophenol chloride gave a similar curve to that for the quinone, although there seemed to be a breakdown in Beer's law at a certain concentration, and it is possible that some change in structure occurs. The results can be given only in support, but not proof, of the quinonoid structure for the polyhalogeno-compounds, as no comparison was possible with a curve obtained from a compound of definite hypohalite structure. We do, however, consider that the properties of the tetrachloro-compound are best explained on the quinonoid basis (II).

Work was then begun to compare the identity or otherwise of the products of:

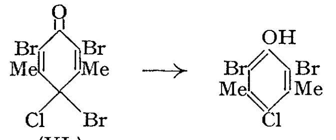
(i) chlorination of 2 : 4 : 6-tribromo-*m*-5-xylenol and bromination of 2-chloro-4 : 6-dibromo-*m*-5-xylenol, and (ii) bromination of 2 : 4 : 6-trichloro-*m*-5-xylenol, and chlorination of 4 : 6-dichloro-2-bromo-*m*-5-xylenol. Chlorine (1 mol.) and 2 : 4 : 6-tribromo-*m*-5-xylenol in acetic acid at below 30° gave, probably, *2-chloro-2 : 4 : 6-tribromo-1 : 3-dimethyl*cyclo*hexa-3 : 6-diene-5-one* (VI), decomposed by boiling alcohol, or sulphur dioxide in aqueous alcohol, to give a trihalogeno-compound which appeared to be 2-chloro-4 : 6-dibromo-*m*-5-xylenol. The mixed m. p. method being unreliable, it is important that full analyses and general properties be examined.



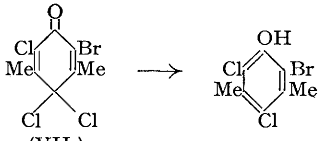
Absorption curves.

1. *Phenol.*
2. 2 : 4 : 6-*Trichloro*-m-5-*xylenol.*
3. *Tetrachloro*-m-5-*xylenol.*
4. *Benzoquinone.*
5. *Tetrabromo*-m-2-*xylenol.*
6, 7. 2 : 4 : 6-*Tribromophenol chloride* (*two specimens*).

The action of chlorine (2·5 mols.) on 2 : 4 : 6-tribromo-*m*-5-xylenol at 10°, gave a trichlorobromo-derivative, probably 2 : 2 : *4-trichloro-6-bromo-1 : 3-dimethyl*cyclo*hexa-3 : 6-diene-5-one* (VII), which on removal of labile halogen yielded a compound whose analysis and properties agreed with those of 2 : 6-dichloro-4-bromo-*m*-5-xylenol.

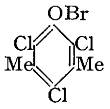


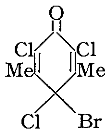
(VI.)

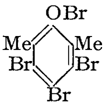


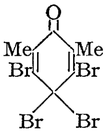
(VII.)

Bromine did not react with 2-chloro-4 : 6-dibromo-*m*-5-xylenol to give a polyhalogeno-derivative, although a variety of conditions was examined : it did, however, react with 2 : 4 : 6-trichloro-*m*-5-xylenol in acetic acid to give a very unstable trichlorobromo-compound, probably 2 : 4 : *6-trichloro-m-5-xylenol bromide* (VIII), with some tautomeric form (IX) ; the product lost bromine readily on boiling with alcohol, to give 2 : 4 : 6-trichloro-*m*-5-xylenol. Chlorination of 4 : 6-dichloro-2-bromo-*m*-5-xylenol provided interesting results. The main product was 2 : 2 : 4 : 6-tetrachloro-1 : 3-dimethyl*cyclo*hex-3 : 6-diene-5-one, identical with that prepared by chlorination of *m*-5-xylenol. It was separated by careful fractional crystallisation of the reaction product from light petroleum, followed by separation of the crystals by mechanical means. This affords a further instance of the ease of elimination of bromine by chlorine in this series. A second product was not identified.


(VIII.)


(IX.)


(X.)


(XI.)

Addition of 4 : 5 : 6-tribromo-*m*-2-xylenol to aqueous bromine gave a tetrabromo-compound, probably mainly 4 : 5 : 6-*tribromo*-m-2-*xylenol bromide* (X), with a little of the quinonoid form (XI). Removal of labile bromine with sulphur dioxide in alcohol gave 4 : 5 : 6-tribromo-*m*-2-xylenol, whereas zinc dust and water afford the same tribromo-compound with some 4 : 5-dibromo-*m*-2-xylenol.

The absorption curve of compound (X) conforms to the quinonoid type, although there was possibly some change in *cyclo*hexane solution.

Tetrabromo-*m*-2-xylenol and aqueous potassium iodide gave a red *adduct* of 2 mols. of 4 : 5 : 6-tribromo-*m*-2-xylenol and 1 mol. of 4 : 6-dibromo-*m*-xyloquinone, the constitution of which was confirmed by synthesis.

Chlorine and 4 : 5 : 6-tribromo-*m*-2-xylenol in acetic acid yielded 4 : 5 : 6-*tribromo*-m-2-*xylenol chloride*, which loses its chlorine in boiling alcohol, or with zinc dust and water affords a mixture of 4 : 5-dibromo- and 4 : 5 : 6-tribromo-*m*-2-xylenol. The only products isolated from the interaction of bromine and 5-chloro-4 : 6-dibromo-*m*-2-xylenol were 4 : 6-dibromo-*m*-xyloquinone and an adduct, m. p. 138—140°, identical with that synthesised from 1 mol. of the above quinone and 2 mols. of 5-chloro-4 : 6-dibromo-*m*-2-xylenol.

EXPERIMENTAL.

2 : 4 : 6-*Tribromophenol Chloride.*—Saturated chlorine water (2000 c.c.; chlorine, 16 g., 4·4 mols.) was added to a paste of 2 : 4 : 6-tribromophenol (16 g.; 1 mol.) in water (20 c.c.) at room temperature. The yellow precipitate was filtered off, dissolved in ether, the solution dried, and solvent removed under reduced pressure until yellow needles began to separate. The *product* crystallised from ether in fine, yellow needles, m. p. 125—130° (decomp.) (Found : 0·1188 g. gave 0·2233 g. of AgCl + AgBr. Calc. for $C_6H_2OClBr_3$: AgCl + AgBr, 0·2328 g.). A trace of chloranil was recovered from the ether mother-liquors. On passing sulphur dioxide through an alcoholic solution of the yellow needles until decolorised, and diluting with water, almost colourless needles separated, m. p. 79—82°, with previous softening (Found in crude product : C, 23·3, 24·7; H, 1·3, 1·4; 2 mg. gave 3·48 mg. of AgCl + AgBr. Calc. for $C_6H_3OBr_3$: C, 21·7; H, 1·0%; AgCl + AgBr, 3·408 mg. $C_6H_3OClBr_2$ requires C, 25·1; H, 1·05%; AgCl + AgBr, 3·63 mg.), probably a mixture of 2 : 4 : 6-tribromo- and 4-chloro-2 : 6-dibromophenol. Crystallisation from light petroleum yielded colourless needles, m. p. 86—87° (Found : C, 22·9, 22·85; H, 1·0, 1·3%; 2 mg. gave 3·48 mg. AgCl + AgBr) of a mixed trihalogeno-compound.

4-*Chloro*-2 : 6-*dibromophenol Bromide.*—Bromine (8·8 g.; 1·1 mols.) in acetic acid (30 c.c.) and water (460 c.c.) was added to a suspension of 4-chloro-2 : 6-dibromophenol (14·3 g.; 1 mol.) in the minimum amount of water. After 3 hours' stirring at room temperature, the product was filtered off; it crystallised from ether in pale yellow needles, m. p. 99—100°, decomp. at 120° (Found : 0·0989 g. gave 0·1910 of AgCl + AgBr. Calc. for $C_6H_2OClBr_3$: AgCl + AgBr, 0·1916 g.).

Degradation with sulphur dioxide in alcohol solution gave colourless needles, m. p. 91—92° (Found : C, 25·7; H, 1·4; 2 mg. gave 3·61 mg., 3·68 mg. AgCl + AgBr. Calc. for $C_6H_3OClBr_2$: C, 25·1; H, 1·05%; AgCl + AgBr, 3·63 mg.), of 4-chloro-2 : 6-dibromophenol.

2-*Chloro*-2 : 4 : 6-*tribromo*-1 : 3-*dimethyl*cyclo*hexa*-3 : 6-*diene*-5-*one* (VI).—Chlorine (8 g.; 1 mol.) was introduced into a solution of 2 : 4 : 6-tribromo-*m*-5-xylenol (40 g.; 1 mol.) in acetic acid (800 c.c.) during 2 hours, at below 30°. On adding the mixture to water, a pale yellow precipitate separated, but this decomposed quickly when collected and dried; crystallisation then yielded a trihalogeno-*m*-5-xylenol in almost colourless needles, m. p. 164°. The crude wet *product* was dissolved immediately in light petroleum at 30—40°, the aqueous layer separated, and the solvent dried. Air was passed over the surface to remove the solvent, and the residue was crystallised quickly from dry light petroleum from which it separated in colourless plates, m. p. 120—122° (Found : C, 25·7; H, 1·7; total halogen, 69·15. $C_8H_6OClBr_3$ requires C, 24·4; H, 1·5; total halogen, 70·0%). Removal of halogen by sulphur dioxide–alcohol gave colourless needles, m. p. 164° (Found : C, 28·7; H, 2·0; total halogen, 63·9; 10·66 mg. gave 16·90 mg. of AgCl + AgBr. Calc. for $C_8H_7OClBr_2$: C, 30·5; H, 2·2; total halogen, 62·2%; AgCl + AgBr, 17·61 mg.), mainly of 2-chloro-4 : 6-dibromo-*m*-5-xylenol.

2 : 2 : 4-*Trichloro*-6-*bromo*-1 : 3-*dimethyl*cyclo*hexa*-3 : 6-*diene*-5-*one* (VII).—Chlorine (2·5 g.; 2·5 mols.) was introduced rapidly into a solution of 2 : 4 : 6-tribromo-*m*-5-xylenol (5 g.) in acetic acid (200 c.c.) at 10°. Next day the mixture was poured on ice–water and the precipitate treated as described in the previous experiment. Large, very pale yellow rectangular prisms, m. p. 105°, separated (Found : C, 31·2; H, 2·05; total halogen, 62·1; 10·997 mg. gave 21·95 mg. of AgCl + AgBr. $C_8H_6OCl_3Br$ requires

C, 31·5; H, 2·0; total halogen, 61·25%; AgCl + AgBr, 22·31 mg.), which are moderately stable when pure, although the crude *product* decomposes readily. Removal of labile halogen gave colourless needles, m. p. 165—166° (Found: C, 35·1; H, 2·6; total halogen, 55·5; 12·21 mg. gave 21·26 mg. of AgCl + AgBr. Calc. for $C_8H_7OCl_2Br$: C, 35·55; H, 2·6; total halogen, 55·9%; AgCl + AgBr, 21·48 mg.), not depressed on admixture with 2 : 4 : 6-tribromo- (m. p. 165—166°), 2-chloro-4 : 6-dibromo- (m. p. 164°), or 2 : 6-dichloro-4-bromo-*m*-5-xylenol (m. p. 165—166°); analyses, however, supported the last-named constitution.

2 : 4 : 6-*Trichloro*-m-5-*xylenol Bromide* (VIII).—Bromine (8 g.; 1·4 mols.) in acetic acid (20 c.c.) was added to 2 : 4 : 6-trichloro-*m*-5-xylenol (8 g.) in the same solvent (300 c.c.) at 60°. The mixture was heated to 110° for 2 minutes, and then kept at room temperature overnight. After addition of water, the pale yellow precipitate was filtered off and dissolved immediately in light petroleum and the aqueous layer separated. Removal of part of the solvent by air, followed by cooling at 0°, gave long, yellow plates of the *bromide*, m. p. 112°, unchanged on crystallisation from dry light petroleum. In air it decomposed rapidly with evolution of bromine, and it was analysed immediately (Found: 0·1418 g. gave 0·2865 g. of AgCl + AgBr. $C_8H_6OCl_3Br$ requires AgCl + AgBr, 0·2880 g.). On boiling it with alcohol, 2 : 4 : 6-trichloro-*m*-5-xylenol separated.

Chlorination of 4 : 6-*Dichloro*-2-*bromo*-m-5-*xylenol. Preparation of* 2 : 2 : 4 : 6-*Tetrachloro*-1 : 3-*dimethyl*cyclo*hexa*-3 : 6-*diene*-5-*one*.—Chlorine (3·2 g.; 1·2 mols.) was introduced into a solution of 4 : 6-dichloro-2-bromo-*m*-5-xylenol (10 g.) in acetic acid (250 c.c.) at 40—50°. Next day, after addition to water, the resulting precipitate was crystallised from light petroleum to give crystals, m. p. 70—90°. On allowing a solution in light petroleum to evaporate slowly during three weeks, a mixture of large, almost colourless, hexagonal prisms, m. p. 107—108° (approximately 4 parts) and a smaller amount of long, colourless, rectangular prisms, m. p. 106—107° (1 part) was separated by hand. A mixture of the two compounds melted at 70—90°. The former compound, m. p. 107—108°, was 2 : 2 : 4 : 6-tetrachloro-1 : 3-dimethyl*cyclo*hexa-3 : 6-diene-5-one (Found: C, 36·6; H, 2·3; total halogen, 54·1; 15·15 mg. gave 33·13 mg. AgCl + AgBr. Calc. for $C_8H_6OCl_4$: C, 36·9; H, 2·3; total halogen, 54·6%; AgCl + AgBr, 33·45 mg.), but the constitution of the substance, m. p. 106—107° (Found: C, 24·9; H, 1·65; total halogen, 68·6%; 12·12 mg. gave 28·58 mg. of AgCl + AgBr), was not established. It was stable to sulphur dioxide in aqueous alcohol.

4 : 5 : 6-*Tribromo*-m-2-*xylenol Bromide* (X).—4 : 5 : 6-Tribromo-*m*-2-xylenol (7·2 g.; 1 mol.) was added to a mixture of bromine (6·7 g.; 2·1 mols.) and water (150 c.c.); partial solution in the bromine layer was accompanied by reaction to give a solid mass. Crystallisation from dry ether gave very pale yellow prisms of the *compound*, m. p. 139—140° (yield, 7·5 g.; 85·3%) [Analysis (immediately): Found: Br, 73·3. $C_8H_6OBr_4$ requires Br, 73·05%]. Decomposition by boiling alcohol, and more readily by sulphur dioxide in alcohol, yielded 4 : 5 : 6-tribromo-*m*-2-xylenol; heating with zinc dust and water gave the same compound with some 4 : 5-dibromo-derivative. Compound (X) and boiling aqueous potassium iodide gave scarlet needles, m. p. 156—158° (from light petroleum), of the adduct of 4 : 6-dibromo-*m*-xyloquinone (1 mol.) and 4 : 5 : 6-tribromo-*m*-2-xylenol (2 mols.); the adduct was identical with a synthetic specimen, obtained by melting the two constituents and crystallising the product from chloroform.

4 : 5 : 6-*Tribromo*-m-2-*xylenol Chloride*.—4 : 5 : 6-Tribromo-*m*-2-xylenol (12 g.; 1 mol.) in acetic acid (75 c.c.) was mixed with chlorine (5 g.; 2·1 mols.) in the same solvent (75 c.c.), and a crystal of iodine added. After being warmed at 60° for 2 minutes, the mixture was kept at room temperature for 2 hours and poured on ice, and 15% aqueous sodium hydroxide (200 c.c.) was added; the resulting solid *product* crystallised from light petroleum in yellow prisms, m. p. 60—61° (Found: 0·0744 g. gave 0·137 g. of AgCl + AgBr. $C_8H_6OClBr_3$ requires 0·1338 g. AgCl + AgBr), decomposed to 4 : 5 : 6-tribromo-*m*-2-xylenol on prolonged boiling with alcohol, or to the same tribomo-compound with some 4 : 5-dibromo-*m*-2-xylenol, with zinc dust and water.

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