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MASTER OF SCIENCE AND HONOURS

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R. J. Rodger

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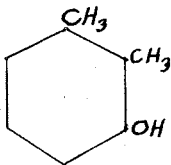
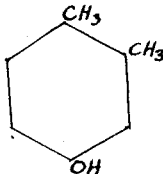
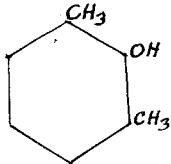
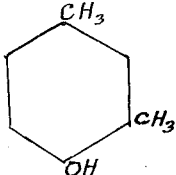
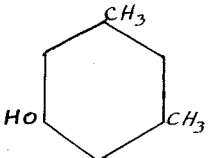
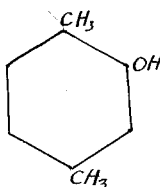
R. J. Rodger

THESIS

"THE CHLORINATION OF CERTAIN OF THE XYLENOLS
AND THE
ORIENTATION OF THE CHLORO-XYLENOLS SO OBTAINED".

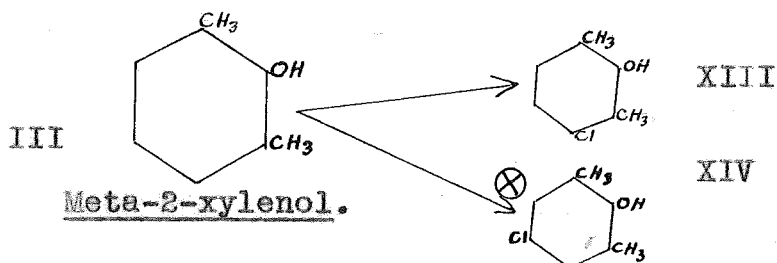
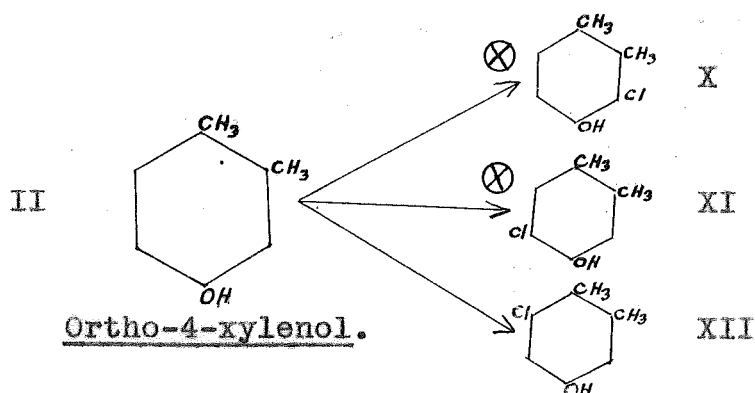
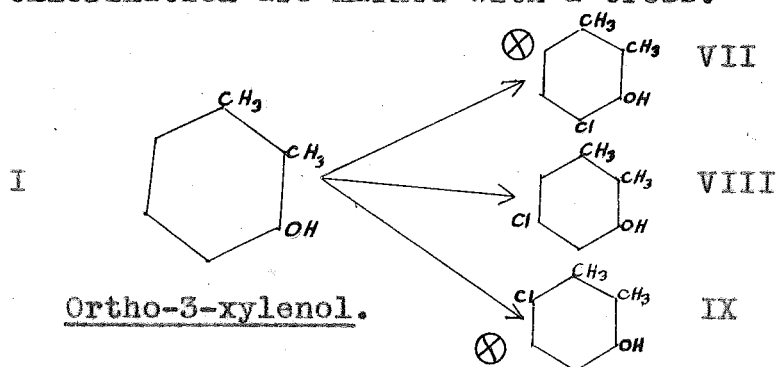
INTRODUCTION.

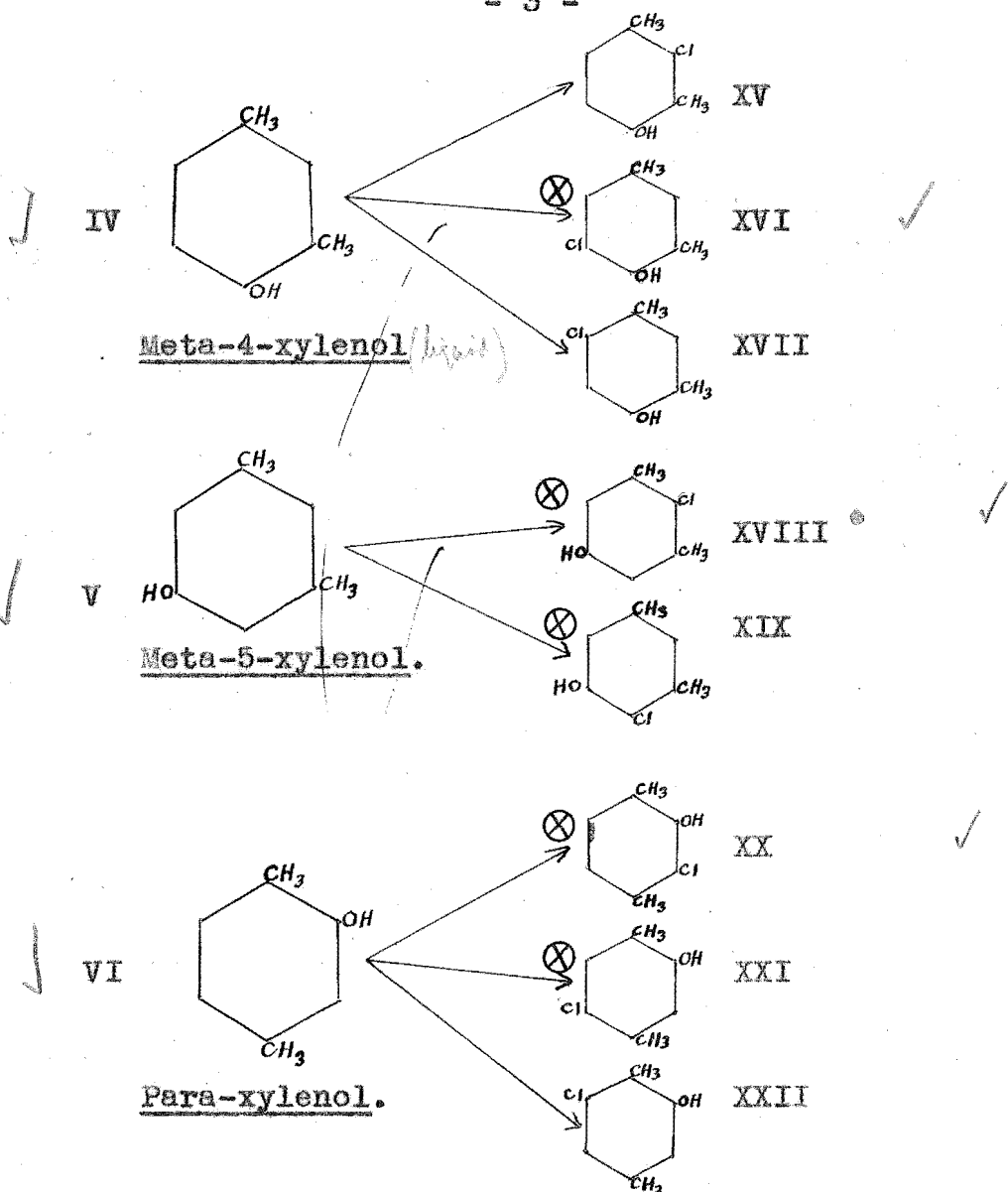
All the six possible isomeric xylenols have been described and are with one exception crystalline solids.

- I  Ortho-3-xyleneol. A crystalline solid. m.p. 75°C; b.p. 218°C.
(Nolting and Forel B. 18 2673).
- II  Ortho-4-xyleneol. A crystalline solid m.p. 61-65°C; b.p. 225°C.
(Jacobsen B. 17 161).
- III  Meta-2-xyleneol. Solid m.p. 47-48°C.
(Jacobsen B. 12 607);
b.p. 203°C. (Gattermann A. 357 327).
- IV  Meta-4-xyleneol. A refrangent colourless liquid b.p. 211°C.
(Jacobsen B. 11 24).
- V  Meta-5-xyleneol. Solid m.p. 64°C. b.p. 219°C. (Tohl B. 18 362).
- VI  Para-xyleneol. A crystalline solid m.p. 74.5°C.

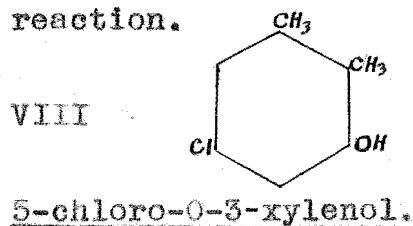
Since the phenolic (OH) group is a strong activating group and exerts a strong o-p directing influence during substitution in the benzene ring, the monochloro compounds formed by direct chlorination of the xylenols would therefore be expected to have the chlorine atoms in positions o- or p- to this phenolic group.

In the following list of possible monochloro-xylenols obtainable from the different xylenols those that are therefore most likely to be encountered by direct chlorination are marked with a cross.



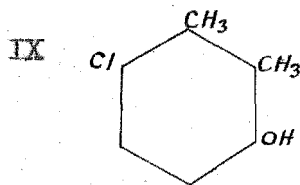


The following chloro-xyleneols have been described in the literature. (Hinkel, Collins and Ayling. J.C.S. (1923) 123, 2968 and (1924) 125, 1847). These were obtained from either the nitro-xylidines or the amino-xyleneols by diazotisation followed by the Sandmeyer reaction.



M.p. 81-82°C. Fine glistening crystals from petroleum ether.

Benzoyl Derivative. Transparent prisms from alcohol m.p. 88°C.

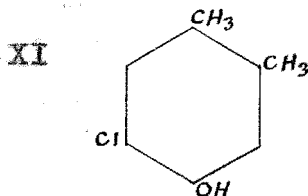


6-chloro-0-3-xyleneol.

M.p. 84-85°C. Soluble in organic solvents.

Benzoyl derivative. Transparent plates from absolute alcohol.

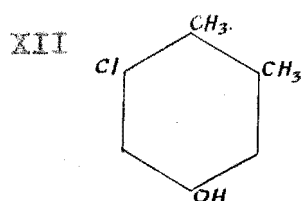
m.p. 102°C.



5-chloro-0-4-xyleneol.

M.p. 71.5-72.5°C. Colourless needles.

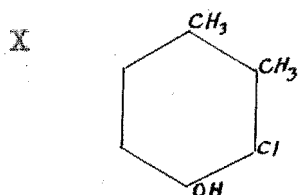
Benzoyl derivative. Transparent rhombic crystals from well cooled alcohol. m.p. 43°C.



6-chloro-0-4-xyleneol.

M.p. 98°C. Long silky needles from petrol-ether.

Benzoyl derivative. Fine needles from alcohol. m.p. 42°C.

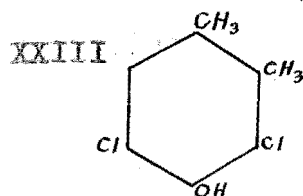


3-chloro-0-4-xyleneol.

M.p. 27°C. Transparent crystals from petrol-ether.

Benzoyl derivative. m.p. 87°C from alcohol.

The following dichloro-xyleneols are also described by the same authors.



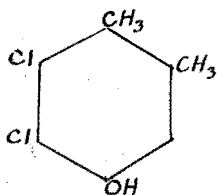
3:5-dichloro-0-4-xyleneol. m.p. 89°C.

M.p. 52°C. Feathery crystals from light petroleum.

Benzoyl derivative. White cry-

stals from light petroleum.

XXIV

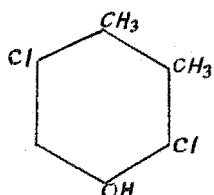


5:6-dichloro-0-4-xyleneol.

M.p. 102.5°C. Clumps of radiating crystals from light petroleum.

Benzoyl derivative from alcohol in transparent prisms m.p. 94°C.

XXV

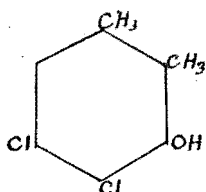


3:6-dichloro-0-4-xyleneol.

M.p. 84°C. Long flat needles from light petroleum.

Benzoyl derivative. Flat transparent needles from methyl alcohol m.p. 124°C.

XXVI



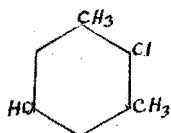
4:5-dichloro-0-3-xyleneol.

M.p. 95°C. Fine stellate masses from light petroleum.

Benzoyl derivative. Transparent crystals from light petroleum m.p. 133°C.

Rudolf Lesser and George Gad (Ber. 123. 56 B 963-978) prepared 2-chloro-m-5-xyleneol by the action of sulphuryl chloride on m-5-xyleneol dissolved in chloroform.

XVIII



2-chloro-m-5-xyleneol.

m.p. 115-116°C.

None of these compounds has been prepared by direct chlorination of the xyleneols but A.C. McClelland in work done in this laboratory in 1935 but unpublished, described

the following products obtained by the direct chlorination of ortho-, meta-, and para-xylenols obtained either commercially or from a crude xylene mixture from the local gas works. According to McClelland -

Ortho-xylene gave a monochloro-xylene. Crystalline solid m.p. 81.5°C . Benzoyl derivative m.p. 56°C .

Meta-xylene gave a monochloro-xylene. Feathery crystals m.p. 113°C . Benzoyl derivative. Fine white needles m.p. 67°C .

Para-xylene gave a monochloro-xylene. Long white crystals m.p. 70°C .

Crude xylene mixture gave (a) monochloro-xylene. Fine white crystals m.p. 114°C .

(b) Colourless refragent oil
b.p. $104-107^{\circ}\text{C}/20\text{ m.m.}$

(c) Dichloro-xylene. Crystalline m.p. 85°C .

The orientation of these compounds was not definitely determined, although he was able to assign probable structures to certain of them.

The object of this investigation was, therefore, to determine the orientation of all the chloro-xylenols which could be obtained by chlorination of all the commercially available xylenols. Also to prepare the p-nitro-benzoyl and 3:5-dinitro-benzoyl derivatives of these compounds using p-nitro-benzoyl chloride and 3:5-dinitro-benzoyl chloride as reagents.

The following were the starting materials in the present investigation.

V. Meta-5-xylene (1:3:5 xylene. L.Light & Co., London).

This was a white crystalline solid which melted at 62°C. On recrystallization from petroleum ether gave a constant melting point 64°C which agrees with that of meta-5-xylene described previously (page 1).

II. Ortho-4-xylene (1:2:4 xylene. L.Light & Co.).

A white crystalline solid which melted at 61°C. Further recrystallization from petroleum ether gave a constant melting point 64.5°C.

IV. Meta-4-xylene. (1:3:4 xylene. L.Light & Co.).

This was a colourless refragent oil which boiled at 210-212°C.

VI. Para-xylene (1:4:5 xylene. L.Light & Co.).

A white crystalline solid m.p. 71-72°C. On recrystallization from petroleum ether gave a constant m.p. 74.5°C.

Meta-xylene

As used by McClelland. This proved to be identical with the meta-5-xylene above.

Ortho-xylene (Baird and Tatlock Ltd.).

As used by McClelland. This melted at 45°C, and although recrystallized several times gave a sharp and constant melting point of 47.5°C. Evaporation of the filtrate gave a brownish crystalline solid which did not alter this melting point appreciably when the two were mixed. This substance was therefore meta-2-xylene (III)

and not a mixture of the ortho-xyleneols as he assumed.

Para-xyleneol (British Drug Houses, Ltd.).

As used by McClelland. This was a pink crystalline solid m.p. 71°C . Recrystallization finally gave a steady m.p. 74.5°C and this proved identical by a mixed melting point experiment with the para-xyleneol (VI) above. Evaporation of the filtrate gave a solid m.p. 62°C . and this proved to be identical with ortho-4-xyleneol (II) above. This "para-xyleneol" was thus a mixture of true para-xyleneol (VI) and ortho-4-xyleneol (II).

Crude Mixture of Xyleneols. (From the local gas works).

As used by McClelland. This was a pale yellow refragent oil with an objectionable smell, and darkened in colour rapidly on exposure to light. It was soluble in caustic soda and the common organic solvents. The boiling range was from $209-220^{\circ}\text{C}$ the bulk distilling in the neighbourhood of 219°C and it was assumed that a large proportion was meta-5-xyleneol. The fact that the mixture was liquid even to a temperature of -15°C showed that there was probably a fair proportion of the liquid xyleneol (meta-4-xyleneol (IV)) also present. In agreement with this fractional distillation gave a colourless refragent oil b.p. $210-210.5^{\circ}\text{C}$.; and a large quantity of crystals m.p. 64°C identical with meta-5-xyleneol (V) were ultimately obtained from the large fraction distilling at 218°C / 759 m.m.. The small fractions boiling at $216.5-217.5^{\circ}\text{C}$

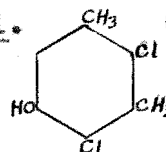
and 218-219°C gave small quantities of meta-5-xyleneol (V) crystals and on chlorination of the filtrates only the monochloro-derivative of meta-5-xyleneol could be isolated. The xyleneol mixture thus consisted of the liquid meta-4-xyleneol (IV) and meta-5-xyleneol (V), the latter being the main constituent.

The results obtained on direct chlorination of each of these xyleneols are given below.

Meta-5-xyleneol (V) on chlorination gave a white crystalline solid from petroleum ether m.p. 115°C. Benzoyl derivative white needles from petroleum ether m.p. 67°C., p-nitro-benzoyl derivative recrystallized from alcohol as white silky flakes m.p. 160.5°C. 3,5 Dinitro-benzoyl derivative white silky flakes from alcohol m.p. 177°C. None of these derivatives has been described in literature but the m.p. of the benzoyl derivative (67°C) agrees with that obtained by McClelland. The melting point 115°C of the monochloro-xyleneol obtained agrees with that of 2-chloro-m-5-xyleneol (XVIII) described earlier. In confirmation the monochloro-xyleneol on conversion to the corresponding dichloroxylylene by replacing the phenolic group with chlorine by means of phosphorus pentachloride gave a white silky crystalline solid m.p. 87°C. This has not been described in literature but the only other dichloroxylylene obtainable from a monochloro derivative of m-5-xyleneol is 4:5-dichloro-meta-xylene which has been described as an oil b.p. 231-232°C.

(Klages 1896 A1 291). Thus there can be no doubt that the product obtained from meta-5-xynol was 2-chloro-meta-5-xynol (XVIII).

Further chlorination of 2-chloro-meta-5-xynol gave a dichloro derivative which crystallized from petroleum ether in white flakes m.p. 84°C. The benzoyl derivative crystallized from petroleum ether as white needles m.p. 112°C. The p-nitro-benzoyl derivative crystallized from alcohol in white silky flakes m.p. 128°C. The 3:5-dinitro-benzoyl derivative crystallized from alcohol in white silky flakes m.p. 149.5°C. This dichloroxylenol has not been described in literature but on conversion to the corresponding trichloroxylenol it gave a white crystalline solid m.p. 96°C, which agrees with the description of 2:4:5-trichloro-m-xylene. (Carpmael 1929 P.B. 672). The product was thus 2:4-dichloro-meta-5-xynol.



Para-xynol (VI) on chlorination gave a monochloroxylenol which crystallized from petroleum ether in white needles m.p. 54°C. The benzoyl derivative crystallized from petroleum ether in white crystals m.p. 58°C. The p-nitro-benzoyl derivative crystallized from alcohol in white silky flakes m.p. 238°C. The 3:5-dinitro-benzoyl derivative crystallized from alcohol in white silky flakes m.p. 134°C.

Neither of the possible monochloro-p-xynols has been

described in literature. On conversion to the dichloro-xylene a white oil was obtained which crystallized at temperatures below -4°C and these crystals melted at -4° to -2°C . This agrees with the description of 2:3-dichloro-p-xylene (1935 A 739). The only other possible dichloroxylenes obtainable from a monochloro-derivative of para-xylenol would be 2:5-dichloro-p-xylene which has been described as a crystalline solid m.p. 71°C (Kluge 1885 A 1208). The monochloroxylenol obtained was therefore 3-chloro-para-xylenol. (XX).

Meta-4-xylenol (IV) on chlorination gave a monochloroxylenol which was a colourless refragent oil b.p. $105-106^{\circ}\text{C}/17\text{ m.m.}$. The benzoyl derivative was a white oil which crystallized at temperatures below -6°C . The p-nitro-benzoyl derivative crystallized from alcohol in white silky flakes m.p. 191.5°C . The 3:5-dinitro-benzoyl derivative crystallized from alcohol in white silky flakes m.p. 157°C .

The only monochloroxylenol to be expected from the direct chlorination of meta-4-xylenol is 5-chloro-meta-4-xylenol (XVI) and in agreement with this the dichloroxylenes produced was a colourless oil b.p. $230-232^{\circ}\text{C}$. which agrees with the description of 4:5-dichloro-m-xylene (Klages 1896 A1 291). Thus meta-4-xylenol gave 5-chloro-m-4-xylenol (XVI).

Ortho-4-xylenol (II) on chlorination gave a monochloroxylenol which crystallized from petroleum ether in white

crystals m.p. 71.5°C. Benzoyl derivative m.p. 43°C. It thus proved to be 5-chloro-ortho-4-xylene (XI) as described earlier. The p-nitro-benzoyl derivative crystallized from alcohol in white silky flakes m.p. 141°C. The 3:5-dinitro-benzoyl derivative crystallized from alcohol in white silky flakes m.p. 183°C.

Para-xylene (as used by McClelland). This as stated earlier was a mixture of para- and ortho-4-xylenes and these on chlorination gave monochloroxylenes identical with those described above. McClelland described the monochloroxylenol obtained from this paraxylene as a crystalline solid m.p. 71°C. This was probably due to his isolating the 5-chloro-ortho-4-xylene from the mixture of the two monochloroxylenes he would obtain by chlorinating the original mixture.

Meta-2-xylene (III). This was the xylene labelled "ortho" as used by McClelland and on chlorination gave a monochloroxylenol which crystallized from petroleum ether in long needles m.p. 81.5°C. Unfortunately there was insufficient material to prepare any derivatives but McClelland describes the benzoyl derivative as crystallizing from dilute alcohol in white flakes m.p. 56°C.

The only monochloroxylenol to be expected from the direct chlorination of meta-2-xylene is 5-chloro-meta-2-xylene (XIV), and on conversion to the corresponding

dichloroxylenes the monochloroxylenol gave a white silky crystalline solid m.p. 87°C identical with that obtained from 2-chloro-meta-5-xyleneol. The monochloroxylenol must therefore have been 5-chloro-meta-2-xyleneol (XIV).

The Crude "Gas Works" Xyleneol. The meta-5-xyleneol and meta-4-xyleneol obtained from this gave on chlorination 2-chloro-meta-5-xyleneol (XVIII) a small quantity of 2:4-dichloro-meta-5-xyleneol (XXVII) and 5-chloro-meta-4-xyleneol (XVI) and derivatives identical with those described earlier.

SUMMARY.

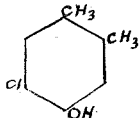
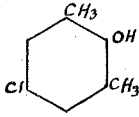
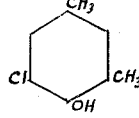
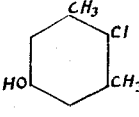
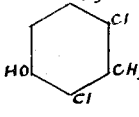
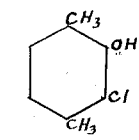
1. The chlorination of meta-5-xyleneol gave 2-chloro-meta-5-xyleneol (XVIII) m.p. 115°C. Benzoyl derivative m.p. 67°C.; p-nitro-benzoyl derivative m.p. 160.5°C.; 3:5-dinitro-benzoyl derivative m.p. 177°C.
Meta-5-xyleneol also gave 2:4-dichloro-meta-5-xyleneol (XXVII) m.p. 84°C.; benzoyl derivative m.p. 112°C.; p-nitro-benzoyl derivative m.p. 128°C.; 3:5-dinitro-benzoyl derivative m.p. 149.5°C.
2. The chlorination of ortho-4-xyleneol gave 5-chloro-ortho-4-xyleneol (XI) m.p. 71.5°C.; benzoyl derivative m.p. 43°C.; p-nitro-benzoyl derivative m.p. 141°C.; 3:5-dinitro-benzoyl derivative m.p. 183°C.
3. The chlorination of meta-4-xyleneol gave 5-chloro-meta-4-xyleneol (XVI) b.p. 105-106°C/17 m.m. Benzoyl derivative a white oil. Crystallized below -6°C.; p-nitro-benzoyl derivative m.p. 191.5°C.; 3:5-dinitro-benzoyl derivative m.p. 157°C.
4. The chlorination of meta-2-xyleneol gave 5-chloro-meta-2-xyleneol (XIV) m.p. 81.5°C. Owing to lack of material no further derivatives could be prepared.
5. The chlorination of para-xyleneol gave 3-chloro-para-xyleneol (XX) m.p. 54°C.; benzoyl derivative m.p. 58°C.; p-nitro-benzoyl derivative m.p. 238°C.; 3:5-

dinitro-benzoyl derivative m.p. 134°C.

6. The commercial (B. and T., Ltd.) ortho-xyleneol was found to be meta-2-xyleneol and the commercial (British Drug Houses Ltd.) para-xyleneol a mixture of para- and ortho-4-xyleneols.

7. The crude "gas works" xyleneol was found to consist of meta-5-xyleneol and the liquid meta-4-xyleneol.

TABLE OF CHLOROXYLENOLS AND THEIR PROPERTIES.

No.	Chloroxylenol		Benzoyl derivative	p-nitro-benzoyl derivative	3:5-dinitro-benzoyl derivative
XI	 <u>5-chloro-ortho-4-xyleneol.</u>	white crystals m.p. 71.5°C.	white crystals m.p. 43°C.	white silky flakes m.p. 141°C.	white silky flakes m.p. 183°C.
XIV	 <u>5-chloro-meta-2-xyleneol.</u>	long needles m.p. 81.5°C.	white flakes m.p. 56°C.	-	-
XVI	 <u>5-chloro-meta-4-xyleneol</u>	colourless refragent oil b.p. 105-106°C/17 m.m.	white crystals below -6°C.	white silky flakes m.p. 191.5°C	white silky flakes m.p. 157°C.
XVIII	 <u>2-chloro-meta-5-xyleneol.</u>	white crystals m.p. 115°C.	white needles m.p. 67°C.	white silky flakes m.p. 160.5°C.	white silky flakes m.p. 177°C.
XXVII	 <u>2:4-dichloro-meta-5-xyleneol.</u>	white flakes m.p. 84°C.	white needles m.p. 112°C.	white silky flakes m.p. 128°C.	white silky flakes m.p. 149.5°C.
XX	 <u>3-chloro-para-xyleneol.</u>	white needles m.p. 54°C.	white crystals m.p. 58°C.	white silky flakes m.p. 238°C.	white silky flakes m.p. 134°C.

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X.	(a) Chlorination of meta-2-xyleneol: 5-chloro-meta-2-xyleneol. (b) Conversion of 5-chloro-meta-2-xyleneol into 2:5-dichloro-m-xylene.	30 30

EXPERIMENTAL.

I. Separation of Meta-4-xyleneol and Meta-5-xyleneol from Crude Xyleneol.

The crude xyleneol as obtained from the gas works was fractionally distilled about a dozen times using a glass rod and disc fractionating column, fractions being taken at 1°C. intervals. The neck of the flask and the column were wrapped in asbestos sheets and the whole surrounded by a metal cylinder to prevent temperature fluctuations due to draughts. The products distilled over as colourless oils, the temperature range at the beginning of the fractionation being 210-219°C/759 m.m. After several fractionations two main fractions were obtained, the smaller distilling at 210-210.5°C. and the larger at 217.5-218°C. the proportions being approximately six to one.

These two fractions were immersed in a freezing mixture of ice and salt. The 210-210.5°C. fraction could not be made to crystallize, merely becoming more viscid.

The large fraction rapidly became very viscid and at a temperature of -13°C became nearly solid due to the formation of a large mass of small crystals. These were not stable above -10°C and were filtered off using a reduced pressure filtering apparatus, the funnel of which was surrounded with a freezing mixture to prevent the crystals melting during the operation. On transference to another flask the crystals melted forming a light yellow viscid oil. This was dissolved in petroleum ether (b.p. 60-80°C.) and

again immersed in the freezing mixture, white crystals forming when the temperature reached -8°C . These crystals were filtered off and the process repeated several times until white crystals were obtained which had a constant melting point of 64°C . and which a mixed melting point determination showed to be identical with meta-5-xyleneol (V). The filtrate obtained from the first filtration was again immersed in a freezing mixture and a further crop of crystals was obtained which also proved to be meta-5-xyleneol. This process was repeated until no further crystallization took place. The small portion of yellow liquid left was chlorinated, the only product obtained being 2-chloro-meta-5-xyleneol (XVIII).

The two small fractions distilling at $216.5-217.5^{\circ}\text{C}$ and $218-219^{\circ}\text{C}$ were also immersed in a freezing mixture. They became very viscid, and on seeding with crystals of meta-5-xyleneol, crystals slowly formed. These were worked up as above and also found to be meta-5-xyleneol. The filtrates were chlorinated and gave small quantities of 2-chloro-meta-5-xyleneol.

II. General Method of Chlorination and Separation of Chloro-derivatives.

The chlorine was generated by the action of sulphuric acid on a mixture of manganese dioxide and sodium chloride and then passed through a wash bottle containing conc.

sulphuric acid, two U tubes filled with pumice soaked with conc. sulphuric acid and a further wash bottle containing conc. sulphuric acid to ensure the gas being perfectly dry. The gas was led through a trap and then into the reaction vessel which contained the xylenol dissolved in glacial acetic acid and a little iron gauze as catalyst. The outlet from the vessel consisted of a glass tube drawn fine so that there would be a steady stream of hydrochloric acid gas escaping and thus preventing the entrance of any water vapour. When the calculated weight of chlorine had been added the solution was poured into ice cold water, ether added, and the acetic acid neutralised with sodium carbonate solution. The whole was then transferred to a large separating funnel, shaken, and the aqueous layer run off. The ether layer was dried over anhydrous sodium carbonate, filtered, and the residue washed with small quantities of warm ether. The ether was then evaporated off the filtrate and the material left purified by recrystallization from petroleum ether (60° - 80°C).

III. Methods for the Preparation of the Derivatives of the Chloroxylenols.

(a) Benzoyl derivatives.

Schotten-Baumann Method. The chloroxylenol was dissolved in excess of 10% NaOH solution and the calculated amount of benzoyl chloride added in small quantities, the solution being shaken vigorously after each addition until the smell of the chloride had disappeared and kept cool by

immersion in running water. The products were then poured into ice cold water and a white solid separated out. This was filtered off, washed with distilled water, dried on a porous plate, and recrystallized from petroleum ether (b.p. 60° - 80° C).

(b) p-Nitro-benzoyl Derivatives.

The chloroxylenol and the calculated amount of p-nitro-benzoyl chloride were heated together for several minutes in a test tube immersed in water maintained at a temperature of 75° - 80° C. The product obtained was then purified by recrystallization from alcohol.

(c) 3:5-dinitro-benzoyl Derivatives.

The chloroxylenol was first dissolved in a minimum quantity of 10% NaOH solution and the calculated amount of 3:5-dinitro-benzoyl chloride added. The solution was then treated as for the p-nitro-benzoyl derivatives.

IV. Analysis for Chlorine.

The percentage of chlorine in the chloroxylenols was found by ter Meulen's Method (Organic Chemical Analysis. Thorpe and Whiteley).

The hydrogen was generated in a Kipp's apparatus from zinc and dilute sulphuric acid. It was then purified by passing through two wash bottles containing alkaline and acid permanganate respectively and then bubbled through a

wash bottle containing a concentrated ammonia solution. The mixed gases passed through a long silica tube closed at the far end with a small asbestos plug and heated in the centre by a Fletcher furnace. A small known weight of the chloroxylenol to be analysed was introduced into the near end of the tube in a porcelain boat and when the air in the tube had been completely replaced by the mixed gases and the centre of the tube was red hot, the tube near the boat was very cautiously heated by a small bunsen flame. Great care was necessary in heating as some of the chloroxylenols were found to be very volatile in the mixed gases. The ammonium chloride formed collected in the cold section of the tube and was washed into a flask with distilled water and estimated by Volhard's method.

V. (a) Chlorination of Meta-5-xyleneol: 2-chloro-meta-5-xyleneol.

The meta-5-xyleneol (150 gms.) was dissolved in glacial acetic acid and on chlorination the solution became hot and light yellow in colour. When the requisite weight (17.5 gms.) of chlorine had been added and the acid neutralized the ether layer was a light yellow changing to a light brown on drying. On evaporation of the ether a dark brown solid was left. After repeated recrystallization^s, fine white needles obtained with a constant melting point of 115°C. Yield 35 gms. On analysis it gave Chlorine

22.51%. 22.63% Mean 22.57%. Calculated percentage
for $C_8H_9(OH)Cl$. 22.68%.

Evaporation of the mother liquor gave a reddish
brown crystalline mass which on recrystallization several
times with small quantities of petroleum ether gave light
pink needle crystals m.p. $84^{\circ}C$. On analysis it gave
chlorine 37.08%; 36.94%. Mean 37.01%. Calculated
percentage for $C_8H_7(OH)Cl_2$. 37.14%.

Benzoyl derivative of 2-chloro-meta-5-xyleneol. 1 gm.
of the chloroxylenol was dissolved in 10 ccs. of 10% NaOH
solution, and 1.2 gms. of benzoyl chloride added. After
pouring the products of the reaction into ice cold water,
a white powder separated out. On drying and recrystal-
lizing white needles were obtained m.p. $76^{\circ}C$.

p-Nitro-benzoyl derivative of 2-chloro-meta-5-xyleneol.
1 gm. of the chloroxylenol was mixed with 1.2 gms. of
p-nitro-benzoyl chloride and on heating the mixture melted
and turned dark red in colour. On pouring into a little
cold alcohol a bright yellow crystalline mass was obtained.
The crystals dissolved with difficulty in hot alcohol and
on cooling white silky flakes were obtained which on
further purification gave a constant m.p. $160.5^{\circ}C$.

3:5-dinitro-benzoyl derivative of 2-chloro-meta-5-
xyleneol. 2 gms. of the xyleneol was dissolved in the
minimum quantity of 10% NaOH solution and 3 gms. of
3:5-dinitro-benzoyl chloride added. The mixture on

heating gave a light orange solution which changed to light yellow on solidifying in cold alcohol. The first recrystallization gave hard white crystals. Further purification gave white silky flakes m.p. 177°C. which were not very soluble in hot alcohol.

(b) Conversion of 2-chloro-meta-5-xyleneol into 2:5-dichloro-m-xylene.

1 gm. of the chloroxylenol was dissolved in 10 ccs. of dry benzene and 1.3 gms. of phosphorus pentachloride added. On heating a vigorous reaction occurred, fumes of phosphorus oxychloride and hydrochloric acid gas being given off and a white solid was precipitated. The solid was filtered off and purified by recrystallization from acetic acid giving white crystals m.p. 87 °C.

VI. (a) Chlorination of 2-chloro-meta-5-xyleneol: 2:4-dichloro-meta-5-xyleneol.

As described above the chlorination of meta-5-xyleneol gave a small quantity of 2:4-dichloro-meta-5-xyleneol. This was also obtained by dissolving 20 gms. of 2-chloro-m-5-xyleneol in glacial acetic acid and chlorinating this solution. The solution became hot and turned a light red in colour. The solution in ether was a light orange and the solid left on evaporation of this ether was dark red. On repeated recrystallization light pink

crystals were obtained with m.p. 84°C . A mixed melting point experiment showed these to be identical with the product obtained from the direct chlorination of the meta-5-xyleneol. Approximately 6 gms. were produced.

Benzoyl derivative 1 gm. was dissolved in 10 ccs. of 10% NaOH solution and 1.2 gms. of benzoyl chloride added.

The white oil produced by the reaction gave a white solid on pouring into ice cold water. On filtering, drying, and recrystallizing white radiating crystals were obtained melting point 112°C .

p-Nitro-benzoyl derivative 1 gm. of the dichloroxylenol was mixed with 1.2 gms. of p-nitro-benzoyl chloride and on heating the solution became light red colour changing to a light yellow on cooling. The crystals dissolved with difficulty in hot alcohol and after several recrystallizations gave white silky flakes m.p. 128°C .

3:5-dinitro-benzoyl derivative 1 gm. of the dichloroxylenol was dissolved in the minimum quantity of 10% NaOH solution and 1.5 gms. of 3:5-dinitro-benzoyl chloride added. The hot solution was a light red in colour changing to a dark yellow on solidifying in cold alcohol. Purification gave white silky flakes m.p. 149.5°C .

(b) Conversion of 2:4-dichloro-meta-5-xyleneol into 2:4:5-trichloro-m-xylene. 1 gm. of the dichloroxylenol was dissolved in 10 ccs. of dry benzene and 1.3 gms. of phosphorus pentachloride added. On heating white crystals were pre-

cipitated and fumes of phosphorus oxychloride and hydrochloric acid given off. The crystals were filtered off, dried and recrystallized several times from acetic acid giving white crystals m.p. 96°C.

VII. Chlorination of ortho-4-xyleneol: -5-chloro-ortho-4-xyleneol.

50 gms. of the xyleneol were dissolved in acetic acid and on chlorination the solution became hot and bright orange in colour. The dry solution was dark yellow and the evaporation of this ether gave a dark yellow mass which solidified slowly in a freezing mixture. On recrystallization the colour gradually became lighter, the final product being fine white needles m.p. 71.5°C. Yield 10 gms. On analysis it gave chlorine 22.63%. 22.56%
Mean 22.595%.

Benzoyl derivative 1 gm. of the chloroxylenol was dissolved in 10 ccs. of 10% NaOH solution and 1.2 gms. of benzoyl chloride added. The white oil produced during the reaction gave a white solid on pouring into ice cold water and on purification gave white crystals m.p. 43°C.

p-Nitro-benzoyl derivative 1 gm. of the chloroxylenol was mixed with 1.2 gms. of p-nitro-benzoyl chloride. The hot mixture was a bright red colour changing to a bright yellow on solidifying in cold alcohol. Purification gave white silky flakes m.p. 141°C.

3:5-dinitro-benzoyl derivative 1 gm. of the chloroxylenol was dissolved in the minimum quantity of 10% NaOH solution

and 1.5 gms. of 3:5-dinitro-benzoyl chloride added. The hot solution was red in colour and the crystalline mass obtained on cooling was a light yellow. Purification gave white silky flakes m.p. 183°C .

VIII.(a) Chlorination of para-xyleneol:-6-chloro-para-xyleneol.

50 gms. of the para-xyleneol were dissolved in glacial acetic acid and on chlorination this solution became hot and a light yellow in colour. The dried ether solution was orange and a dark red crystalline mass was left on evaporation of this ether. The colour of the crystals gradually lightened on recrystallization and ultimately white needle crystals were obtained m.p. 54°C . On analysis it gave chlorine 22.45%; 22.59%. Mean 22.52%. Yield 12 gms.

Benzoyl derivative 1 gm. of the chloroxylenol was dissolved in 10 ccs. of 10% NaOH solution and 1.2 gms. of benzoyl chloride added. After the reaction, the white oil produced gave a white solid precipitate on pouring into ice cold water which on washing, drying, and recrystallizing gave white flakes m.p. 58°C .

p-Nitro-benzoyl derivative 1 gm. of the chloroxylenol was mixed with 1.2 gms. of p-nitro-benzoyl chloride and on heating a bright red solution was obtained which gave a bright yellow crystalline mass on cooling in cold alcohol. White silky flakes were obtained on recrystallization m.p. 238°C .

3:5-dinitro-benzoyl derivative 1 gm. of the chloroxylenol was dissolved in the minimum quantity of 10% NaOH solution and 1.5 gms. of 3:5-dinitro-benzoyl chloride added. When heated this solution turned a bright orange, changing to a bright yellow crystalline mass on cooling. Several recrystallizations gave white silky flakes m.p. 134°C .

(b) Conversion of 3-chloro-para-xylene into 2:3-dichloro-p-xylene. 1 gm. of the chloroxylenol was dissolved in 10 ccs. of dry benzene and 1.3 gms. of phosphorus pentachloride added. On heating a vigorous reaction took place phosphorus oxychloride and hydrochloric acid gas being given off and a colourless oil separating out. The benzene was evaporated off and the white oil left immersed in a freezing mixture. The oil crystallized below -5°C the crystals melting at -4° to -2°C .

IX. (a) Chlorination of Meta-4-xylene:-5-chloro-meta-4-xylene. 40 gms. of the xylene were dissolved in glacial acetic acid and on chlorination gave a bright red solution with the evolution of considerable heat. The colour changed to a bright yellow in ether and a light red oily liquid was left after evaporation of this ether. The oil was immersed in a freezing mixture but gave no sign of crystallizing at temperatures down to -14°C . It was distilled under reduced pressure and a colourless oil b.p. $105-106^{\circ}\text{C}/17$ m.m. was obtained which changed to a light yellow colour on keeping.

Yield 8 gms. Analysis gave chlorine, 22.46%; 22.52%.
Mean 22.49%.

Benzoyl derivative, 1 gm. of the chloroxylenol was dissolved in 10 ccs. of 10% NaOH solution and 1.2 gms. of benzoyl chloride added. The product of the reaction was a white oil which would not solidify on pouring some into ice cold water. The oil was extracted with ether, dried, and the ether evaporated off. The oil then gave white flakes at temperatures below -6°C .

p-Nitro-benzoyl derivative, 1 gm. of the chloroxylenol was mixed with 1.2 gms. of p-nitro-benzoyl chloride and on heating the mixture gave a light red solution the colour changing to a bright orange on solidifying in cold alcohol. Several recrystallizations gave white silky flakes m.p. 191.5°C .

3:5-dinitro-benzoyl derivative, 1 gm. of the chloroxylenol was dissolved in the minimum quantity of 10% NaOH solution and 1.5 gms. of 3:5-dinitro-benzoyl chloride added. This solution gave a red oily substance on heating which solidified slowly on cooling to a yellow crystalline mass. Purification gave white silky needles m.p. 157°C .

(b) Conversion of 5-chloro-meta-4-xylene into 4:5-dichloro-m-xylene, 1 gm. of the chloroxylenol was dissolved in 10 ccs. of dry benzene and 1.3 gms. of phosphorus pentachloride added. On heating fumes of phosphorus oxychloride and hydrochloric acid gas were given off and

a light yellow oil separated out. The benzene was evaporated off and the oil gave a b.p. 230-232°C.

X. (a) Chlorination of meta-2-xyleneol: 5-chloro-meta-2-xyleneol, 7 gms. of the xyleneol were dissolved in glacial acetic acid giving on chlorination a hot yellow solution. After evaporation of the ether a red solid was left which on purification gave white needle crystals m.p. 81.5°C. Yield 1.2 gms. On analysis it gave chlorine 22.58%; 22.52%. Mean 22.55%.

(b) Conversion of 5-chloro-meta-2-xyleneol into 2:5-dichloro-m-xylene, 1 gm. of the chloroxylenol was dissolved in 10 ccs. of dry benzene and 1.3 gms. of phosphorus pentachloride added. The product obtained proved to be identical with the crystalline solid obtained from the conversion of 2-chloro-meta-5-xyleneol into 2:5-dichloro-m-xylene.

There was insufficient material for the preparation of the derivatives.