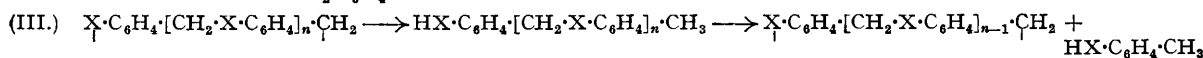


108. A Method of Nuclear Methylation of Phenolic Substances.

By (Miss) M. G. BARCLAY, A. BURAWOY, and G. H. THOMSON.

A method of nuclear methylation of phenolic substances is described. *o*- or *p*-Hydroxyaryl alcohols and -hydroxyarylamines form, when heated above 250°, anhydrohydroxyaryl alcohols (I, X = O) or (II, X = O), which, analogously to the anhydro-4-aminoaryl alcohols (X = NR), spontaneously undergo two reactions: (i) Disproportionation with formation of methylated phenols and unidentified oxidised resins serving as a source of hydrogen. (ii) Condensation to substances containing two or more phenolic groups connected by methylene linkages, such as the crystalline dihydroxydiarylmethanes or the complicated high-molecular phenol-formaldehyde resins, which subsequently decompose with the formation mainly of the original phenols. The second reaction is prevented to a varying degree when the heating is carried out in the presence of suitable alkalis. The bearing of these investigations on the structure and formation of phenol-formaldehyde resins is briefly discussed.

In a preceding paper (this vol., p. 109) a method of nuclear methylation of aromatic amines (in their *p*-positions) was described, *p*-anhydroaminoaryl alcohols being caused to undergo disproportionation by heating above 300°, *e.g.*, by dry distillation. We thought it possible that anhydro-*o*- or -*p*-hydroxyaryl alcohols of the general type (I, X = O) or (II, X = O) would undergo a similar disproportionation to form nuclear-methylated phenols.



o- and *p*-Hydroxyaryl alcohols, known to be the first reaction products between phenols and formaldehyde in the presence of alkaline catalysts, possess a great tendency in absence or presence of alkalis and acids to form polyphenolic substances containing methylene linkages between the several phenolic groups, such as the crystalline dihydroxydiarylmethanes and the more complicated high-molecular phenol-formaldehyde resins. Conditions had to be found under which anhydrohydroxyaryl alcohols would be formed and in addition would not undergo the further condensation of the phenol-formaldehyde type at the high temperatures (250—500°) required for a reaction similar to that observed in the case of the anhydro-*p*-aminoaryl alcohols.

3 : 5-Bishydroxymethyl-*p*-cresol was chosen for detailed investigation because it can be obtained readily and in high yield by reaction between *p*-cresol and formaldehyde (2 mols.) in presence of an alkaline catalyst (von Auwers, *Ber.*, 1907, 40, 2531). Preliminary experiments showed that, when heated above 250°, this substance decomposes with the formation of small amounts of *m*-4-xyleneol and mesitol, the two theoretically possible methylated phenols, in addition to considerable amounts of *p*-cresol. The heating was carried out as a distillation, although heating under pressure is also possible. In presence of alkalis, the yield of *m*-4-xyleneol and mesitol varies considerably, but is generally higher than that obtained without such additions. In order to compare the effect of different alkalis, the amount of mesitol was determined by treatment of the phenolic distillate with formaldehyde and alkali, any *p*-cresol and *m*-4-xyleneol forming non-volatile products and so allowing the separation of the unchanged mesitol by steam-distillation. Its weight was determined, and a correction made for the amount dissolved in water. In all cases, 1 mol. (168 g.) of 3 : 5-bishydroxymethyl-*p*-cresol was distilled. The experimental error should not exceed 2—3 g. Some typical results are shown in Table I, where the type and amount of added material, and the approximate weights of distillate and of mesitol are given.

The best results are obtained in presence of mild alkalis, *i.e.*, oxides and hydroxides of the alkaline earths

and magnesium and the borates of the alkali metals, which neutralise the phenols without making the reaction mixture too alkaline.

When 3 : 5-bishydroxymethyl-*p*-cresol is heated alone or in presence of too weakly alkaline substances, only small amounts of mesitol but considerable amounts of *p*-cresol (and *m*-4-xylenol) are obtained, accompanied by much formaldehyde. This is due to the intermediate formation of condensation products consisting of two or more phenolic groups connected by methylene linkages, which substances decompose above 400° to give mainly the original phenols; e.g., 2 : 2'-dihydroxy-5 : 5'-dimethyldiphenylmethane and 4-hydroxy-3 : 5-bis-(6-hydroxy-3-methylbenzyl)toluene (Koebner, *Z. angew. Chem.*, 1933, **46**, 251) decompose under such conditions in presence or absence of alkalis to give *p*-cresol and traces of *m*-4-xylenol and mesitol. Similarly, 4 : 4'-dihydroxy-2 : 2'-dimethyldiphenylmethane (Eberhardt and Welter, *Ber.*, 1894, **27**, 1814) and 2 : 2'-dihydroxy-1 : 1'-dinaphthylmethane (Fries and Hübner, *Ber.*, 1906, **39**, 440) form almost exclusively *o*-cresol and 2-naphthol, only traces of mesitol and 1-methyl-2-naphthol, respectively, being detected. Distillation of the so-called phenol-formaldehyde resins derived from phenol, *o*-, *m*-, or *p*-cresol, or *m*-5-xylenol also yields, as already found in absence of alkalis (Megson, *Trans. Faraday Soc.*, 1935, **32**, 336), mainly the original phenols, and, even in presence of alkalis, only traces of methylated phenols.

The analogous behaviour of 3 : 5-bishydroxymethyl-*p*-cresol and *p*-aminoaryl alcohols is apparent. Both form anhydrides which at high temperatures undergo disproportionation (with the probable intermediate formation of radicals) (III) to afford methylated phenols and amines, respectively, and oxidised resins serving as a source of hydrogen. Both condense to a varying degree (controlled by the presence of alkalis) to form high-molecular substances containing methylene linkages, which spontaneously decompose to form mainly the original amines or phenols.

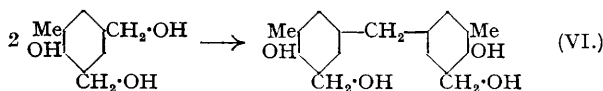
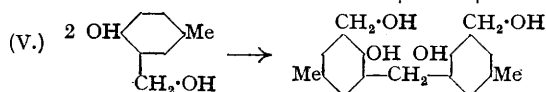
TABLE I.

Added substance, g.	Distillate, g.	Mesitol, g.	Added substance, g.	Distillate, g.	Mesitol, g.
(i) —	60	3.5	(xx) { CaSO ₃ 180		
(ii) ZnO 122	49	5	{ Ca(OH) ₂ 168	60	22
(iii) Al ₂ O ₃ 51	50	5	CaO 84	57	20
(iv) CaCO ₃ 150	53	5	(xxii) Ca(OH) ₂ 111	64	32
(v) { CaCO ₃ 150			(xxiii) Ca(OH) ₂ 168	77	27
{ Ca(OH) ₂ 111	75	30	(xxiv) MgO 60	64	29
(vi) MgCO ₃ 126	47	6	(xxv) Mg(OH) ₂ 87	54	14
(vii) BaCO ₃ 296	50	4	(xxvi) Sr(OH) ₂ 100	46	20
(viii) { BaCO ₃ 197			(xxvii) Ba(OH) ₂ 90	67	6
{ Ca(OH) ₂ 168	32	16	(xxviii) „ 257	40	15
(ix) Na ₂ CO ₃ 159	54	4	(xxix) „ 514	19	14
(x) Na ₂ CO ₃ 530	46	4	(xxx) { Ba(OH) ₂ 257		
(xi) { Na ₂ CO ₃ 159			{ Ca(OH) ₂ 168	13	11
{ Na ₂ B ₄ O ₇ 302	78	20	(xxxi) Na salt 45	45	14
(xii) NaOH 40	15	3	(xxxii) { Na salt 1		
(xiii) NaOH 120	2	1	{ Ca(OH) ₂ 168	51	15
(xiv) Na ₂ SO ₃ 189	15	6	(xxxiii) { Na salt 40	10	3
{ Na ₂ SO ₃ 189			{ NaOH 120		
(xv) { Ca(OH) ₂ 168	60	22	(xxxiv) { Na salt 2	2	1
(xvi) Na ₂ B ₄ O ₇ 168	79	9	{ NaOH 60	60	25
(xvii) Na ₂ B ₄ O ₇ 302	75	19	(xxxv) Mg salt 63	63	24
(xviii) { Na ₂ B ₄ O ₇ 302			(xxxvi) Ca salt 55	55	28
{ Ca(OH) ₂ 111	63	22	(xxxvii) Sr salt 57	57	20
(xix) CaSO ₃ 180	22	3	(xxxviii) Ba salt		

The formation of mesitol from 3 : 5-bishydroxymethyl-*p*-cresol involves the introduction of two methyl groups. The reaction should take place in two stages : (i) Formation and decomposition (disproportionation) of the anhydro-compounds, giving 2 : 4-dimethyl-6-(hydroxymethyl)phenol. (ii) Formation and decomposition of anhydro-2 : 4-dimethyl-6-(hydroxymethyl)phenol, giving mesitol.

Some examples are given to show that the foregoing reaction is characteristic of all hydroxymethylphenols and other substances able to form anhydrohydroxymethylphenols at high temperatures.

Distillation of 3-hydroxymethyl-*p*-cresol (Manasse, *Ber.*, 1894, **27**, 2411) in presence of calcium hydroxide gives a good yield of *m*-4-xylenol in addition to some *p*-cresol and mesitol. As an example of substances other than hydroxymethylphenols, e.g., aminomethylphenols, which form anhydrohydroxymethylphenols



(IV) at high temperatures, 3-piperidinomethyl-*p*-cresol (von Auwers and Dombrowski, *Annalen*, 1906, **344**, 285) behaves similarly. The formation of small amounts of mesitol is doubtless due to condensation of

3-hydroxymethyl- or 3-piperidinomethyl-*p*-cresol, *e.g.*, according to (V), and subsequent decomposition of the condensation product.

3 : 5-Dihydroxymethyl-*o*-cresol [obtained according to Granger, *Ind. Eng. Chem.*, 1932, **24**, 444, from *o*-cresol (1 mol.), formaldehyde (2 mols.), and sodium hydroxide (1 mol.)] yields in presence of calcium hydroxide a mixture of 2 : 4- and 2 : 6-dimethylphenol and mesitol, the xylenols being identified and isolated as the 6- and the 4-nitro-compound, respectively. The yield of mesitol is much smaller than that obtained from 3 : 5-bishydroxymethyl-*p*-cresol owing to the great tendency of the *o*-cresol isomer to condense and form 4 : 4'-dihydroxy-3 : 3'-dimethyl-5 : 5'-bishydroxymethyldiphenylmethane (VI). This substance was obtained by Granger (*loc. cit.*) in small quantity. It is almost exclusively formed when the condensation between *o*-cresol and formaldehyde is carried out in presence of more than 1 mol. of sodium hydroxide and allowed to proceed for many days. Its structure has been established by its preparation from 4 : 4'-dihydroxy-3 : 3'-dimethyldiphenylmethane and formaldehyde in presence of alkali. When distilled alone, it yields a mixture of *o*-cresol and *m*-4- and *m*-2-xyleneol in addition to traces of mesitol, but in presence of calcium hydroxide a good yield of the two xylenols and mesitol is obtained with only a little *o*-cresol. On distillation, it combines the features of both a hydroxymethylphenol and a dihydroxydiarylmethane.

Distillation of 2-piperidinomethyl-3 : 5-dimethylphenol (von Auwers and Dombrowski, *loc. cit.*) in presence of calcium hydroxide yields mainly *m*-5-xyleneol, 2 : 3 : 5-trimethylphenol, and a small amount of 2 : 3 : 5 : 6-tetramethylphenol. 2 : 6-Bishydroxymethyl-3 : 5-dimethylphenol (von Auwers, *loc. cit.*) decomposes in presence of calcium hydroxide to form mainly 2 : 3 : 5-trimethyl- and 2 : 3 : 5 : 6-tetramethyl-phenol. The latter does not react with formaldehyde in presence of an alkaline catalyst. No trace of 3 : 4 : 5-trimethyl-, 2 : 3 : 4 : 5-tetramethyl-, or 2 : 3 : 4 : 5 : 6-pentamethyl-phenol could be found in these experiments, indicating that the above substances are not, as suggested by von Auwers (*loc. cit.*), para-substituted derivatives of *m*-5-xyleneol (cf. also Caldwell and Thompson, *J. Amer. Chem. Soc.*, 1939, **61**, 2354).

Distillation of 1-piperidinomethyl-2-naphthol (von Auwers and Dombrowski, *loc. cit.*) gives in good yield a mixture of β -naphthol and 1-methyl-2-naphthol. The yield of the latter is higher in presence of calcium carbonate, whereas, in contrast to the findings in the case of the benzene derivatives, calcium hydroxide decreases both the total amount of distilled naphthols and that of 1-methyl-2-naphthol. Small amounts of 1-methylnaphthalene have also been observed in these experiments.

The isolation and purification of the hydroxymethyl- or aminomethyl-phenols, being generally difficult and almost always accompanied by considerable loss of material, is unnecessary. The phenols can be condensed with formaldehyde according to known methods, water and unchanged phenol removed by distillation at low temperatures, and the remaining hydroxymethyl- or aminomethyl-phenols heated to the required high temperatures. The catalyst required for the condensation may be chosen from the group of alkalis which give the best yields of methylated phenols in the subsequent heating; generally, calcium hydroxide can be used. In the case of aminomethylphenols, the amine splitting off during the heating can serve as the alkaline medium, but is better supplemented by addition (before distillation) of a suitable alkali such as calcium hydroxide.

This modification permits one to start from a mixture of phenolic substances forming a mixture of hydroxymethyl- or aminomethyl-phenols : it is especially advantageous if an exhaustive methylation of the phenols is desired. For instance, *p*-cresol is condensed with formaldehyde in presence of calcium hydroxide, and the reaction mixture is distilled, the distillate, consisting of *m*-4-xyleneol, *p*-cresol, and mesitol, being again condensed with formaldehyde in presence of calcium hydroxide. The reaction mixture, consisting of the hydroxymethyl derivatives of *m*-4-xyleneol and *p*-cresol and of unchanged mesitol, is distilled, mesitol being obtained in 30% yield. Similarly, a good yield of mesitol can be obtained from *o*-cresol and phenol, a 20% yield of 2 : 3 : 4 : 6-tetramethylphenol from *m*-cresol, and a 30% yield of 2 : 3 : 5 : 6-tetramethylphenol from *m*-5-xyleneol. A mixture of mesitol and 2 : 3 : 4 : 6-tetramethylphenol is also obtained from the very cheap cresylic acids.

The above investigation throws new light on the nature and formation of phenol-formaldehyde resins. (i) It confirms the generally accepted view that these possess structures involving numerous phenolic groups connected by methylene linkages, since, like the crystalline dihydroxydiarylmethanes, they decompose at high temperatures with formation mainly of the original phenols and only traces of methylated phenols. (ii) It shows that their formation can be preceded not only by that of hydroxymethylphenols, but also that of anhydrohydroxymethylphenols, which are stable under certain conditions and, in contrast to the phenol-formaldehyde resins, decompose at high temperatures to form methylated phenols.

EXPERIMENTAL.

3 : 5-Bishydroxymethyl-*p*-cresol.—(a) The distillates in the experiments given in Table I were generally fractionated before determination of mesitol. They consist of various amounts of *p*-cresol (b. p. 200°), identified as 3 : 5-dinitro-*p*-cresol (m. p. 84°), *m*-4-xyleneol (b. p. 212°), identified as its 5-nitro-derivative (m. p. 72°), and mesitol (b. p. 219°; m. p. 72°), in addition to small amounts of substances of b. p. >300°, traces of volatile hydrocarbons, and in many cases some formaldehyde. The fractions (in g.) obtained in a few selected experiments are given in Table II, m. p.'s being added in parentheses.

(b) 3 : 5-Bishydroxymethyl-*p*-cresol (15 g.) and calcium hydroxide (15 g.) were heated in a sealed tube for 6 hours at 300°; the resulting mixture was steam-distilled, and mesitol (2 g.) collected. A similar result was obtained when heating was carried out in an autoclave at 300°.

(c) 3 : 5-Bishydroxymethyl-*p*-cresol (100 g.) was heated for 7 hours at 200°, 6 hours at 255°, and 14 hours at 360°, formaldehyde and water distilling over (15.4, 15.8, 19.7 g. respectively). The final distillate consisted of 5.8 g. of formaldehyde and 13.9 g. of water.

TABLE II.

Experiment.	(i).	(iv).	(ix).	(x).	(xi).	Experiment.	(xvi).	(xvii).	(xxiii).	(xxvii).	(xxviii).
Distillate *	60	53	54	46	78	Distillate	79	75	77	67	40
195—200°	13	7	9	8	—	195—200°	6	—	7	9	6
200—205	13	5	13	4	7	200—205	1	8	8 (6°)	4 (4°)	6 (20°)
205—210	12	15	8	17	20 (23°)	205—210	10 (20°)	13 (22°)	11 (31°)	18 (21°)	14 (25°)
210—215	4 (19°)	5 (12°)	3 (12°)	5 (13°)	31 (36°)	210—215	35 (37°)	29 (31°)	26 (46°)	12 (32°)	4 (31°)
215—230	4	6 (17°)	3 (17°)	3 (17°)	7 (45°)	215—230	12 (47°)	12 (33°)	11 (54°)	6 (41°)	3 (34°)
Residue	5	10	13	7	12	Residue	10	12	10	12	7
Mesitol	3·5	5	4	4	20	Mesitol	9	19	27	6	15

* The distillates were in all cases slightly wet.

3-Hydroxymethyl-*p*-cresol.—This substance (138 g.) and calcium hydroxide (138 g.) were distilled; yield, 57 g. Fractions (mainly *m*-4-xyleneol, little *p*-cresol and mesitol); 200—205°, 8 g.; 205—210°, 15 g.; 210—220°, 17 g.; high-boiling residue, 8 g.

3-Piperidinomethyl-*p*-cresol.—This substance (206 g.) and calcium hydroxide (206 g.) were distilled. After removal of piperidine, the residual oil (58 g.) was fractionated. Fractions (mainly *m*-4-xyleneol, some *p*-cresol and mesitol); 200—205°, 13 g.; 205—210°, 13 g.; 210—220°, 22 g.; high-boiling residue, 9 g.

2:2'-Dihydroxy-5:5'-dimethyldiphenylmethane (loc. cit.).—(a) This substance (50 g.) and sodium carbonate (50 g.) were distilled; yield, 32 g. Fractions: 195—200°, 27 g. (almost pure *p*-cresol); residue, 3 g. (b) This phenol (50 g.) and calcium hydroxide (50 g.) were distilled; yield, 20 g. Fractions (mainly *p*-cresol, traces of *m*-4-xyleneol and mesitol): 190—200°, 5 g.; 200—205°, 10 g.; residue, 5 g.

4-Hydroxy-3:5-bis-(6-hydroxy-3-methylbenzyl)toluene (loc. cit.).—This substance (100 g.) was distilled alone and in presence of sodium carbonate (100 g.) or calcium hydroxide (100 g.); yield, about 60 g. Low-boiling fractions (36—44 g.) consist mainly of *p*-cresol, with traces of *m*-4-xyleneol and mesitol.

4:4'-Dihydroxy-5:5'-dimethyldiphenylmethane (loc. cit.).—This substance (50 g.) was distilled in presence of sodium carbonate (50 g.) or calcium hydroxide (50 g.); yield, 36—38 g. of oil, mostly boiling at 183—193° (mainly *o*-cresol). Neither *m*-4- nor *m*-2-xyleneol could be detected, but traces of mesitol were present. When refluxed alone for 14 hours, the substance decomposes with a similar result.

4:4'-Dihydroxy-3:3'-dihydroxymethyl-5:5'-dimethyldiphenylmethane.—*Preparation.* *o*-Cresol (108 g.) and sodium hydroxide (50 g.) were dissolved in water (200 c.c.), and 40% formaldehyde (160 c.c.) added. After a week, the product was precipitated by means of carbon dioxide; needles, m. p. 163°, from alcohol (Found: C, 70·3; H, 6·7. Calc. for C₁₇H₂₀O₄: C, 70·8; H, 6·9%). It is also obtained by treatment of 4:4'-dihydroxy-5:5'-dimethyldiphenylmethane with formaldehyde and sodium hydroxide.

Distillation. This substance (150 g.) was distilled alone and in presence of calcium hydroxide (respective results are separated by an oblique stroke); distillate, 50/50 g. Fractions: 190—195°, 7/8 g.; 195—200°, 17/7 g.; 200—205°, 10/12 g. (m. p. 10°); 205—210°, 4 g. (m. p. 7°)/8 g. (m. p. 17°); 210—230°, 3 g. (m. p. 16°)/8 g. (m. p. 27°); high-boiling residue, 7/5 g.; mesitol, 3/8 g. (*m*-2-Xyleneol, b. p. 202°, m. p. 47°, was identified as its 5-nitro-derivative, m. p. 170°.)

3:5-Bishydroxymethyl-*o*-cresol.—*Preparation.* *o*-Cresol, sodium hydroxide, and formaldehyde were condensed exactly as in the preceding preparation. After two days, acetic acid (60 g.) was added, whereupon 3:5-bishydroxymethyl-*o*-cresol slowly separated; m. p. 94°, after crystallisation from chloroform or, better, nitrobenzene.

Distillation. The substance (168 g.) was distilled in presence of calcium hydroxide (168 g.); distillate, 48 g. Fractions: <190, 10 g.; 190—200°, 9 g. (m. p. 16°); 200—205°, 9 g. (m. p. 26°); 205—210°, 9 g. (m. p. 32°); residue, 9 g.; mesitol, 12 g.

2-Piperidinomethyl-3:5-dimethylphenol (von Auwers and Dombrowski, loc. cit.).—This substance (219 g.) was distilled in presence of calcium hydroxide (219 g.). After removal of piperidine, the distillate (68 g.) was fractionated. Fractions [containing mainly *m*-5-xyleneol (b. p. 220°; m. p. 64°), 2:3:5-trimethylphenol (b. p. 230°; m. p. 95°), and some 2:3:5:6-tetramethylphenol (b. p. 249°; m. p. 117°)]: 215—220°, 5 g.; 220—225°, 12 g. (m. p. 42°); 225—230°, 19 g. (m. p. 55°); 230—235°, 8 g. (m. p. 56°); 235—240°, 8 g. (m. p. 57°); residue, 10 g.; 2:3:5:6-tetramethylphenol, 4 g.

2:6-Bishydroxymethyl-3:5-dimethylphenol (von Auwers, loc. cit.).—This substance (183 g.) and calcium hydroxide (183 g.) were distilled; distillate, 78 g. Fractions: <225°, 9 g.; 225—230°, 6 g. (m. p. 55°); 230—235°, 12 g. (m. p. 66°); 235—240°, 8 g. (m. p. 74°); 240—250°, 8 g. (m. p. 75°); residue, 15 g.; 2:3:5:6-tetramethylphenol, 24 g.

1-Piperidinomethyl-2-naphthol (von Auwers and Dombrowski, loc. cit.).—(a) The substance (250 g.) was distilled. After removal of piperidine, the distillate (110 g.) was treated with formaldehyde and alkali, whereupon the β -naphthol present formed 2:2'-dihydroxy-1:1'-dinaphthylmethane. Steam-distillation under alkaline conditions afforded a small amount of oil, mainly 1-methylnaphthalene, identified by its picrate (m. p. 141°); the residue was acidified, and 1-methyl-2-naphthol extracted with boiling water; yield, 22 g. (b) Distillation was carried out in presence of calcium carbonate (250 g.), sodium carbonate (250 g.), and calcium hydroxide (250 g.). Distillate, 118/52/57 g.; 1-methyl-2-naphthol, 30/10/13 g.

2:2'-Dihydroxy-1:1'-dinaphthylmethane.—When this was distilled alone or in presence of sodium carbonate or calcium hydroxide, considerable amounts of β -naphthol, in addition to traces of 1-methylnaphthalene and 1-methyl-2-naphthol (in all cases less than 2%), were formed.

No. of distns.	<i>o</i> -Cresol.		<i>p</i> -Cresol.		Phenol.		
	1.	2.	1.	2.	1.	2.	3.
Distillate	66	48	68	62	40	34	30
<200°	7	—	—	—	10	—	—
200—205	9	—	—	—	3	3	1
205—210	12	2	7	—	6	4 (10°)	1 (22°)
210—215	9	7 (40°)	9 (35°)	3	10 (20°)	4 (28°)	2 (38°)
215—220	8 (45°)	14 (56°)	20 (46°)	—	—	6 (45°)	4 (49°)
220—230	4 (55°)	11 (65°)	17 (58°)	42 (63°)	—	5 (55°)	9 (59°)
Residue	8	5	10	8	3	6	5
Mesitol	14	20	26	41	4	11	13

No. of distns.	<i>m</i> -Cresol.			<i>m</i> -5-Xylenol.		Cresylic acids.	
	1.	2.	3.	1.	2.	3.	3.
Distillate	58	47	47	75	68	44	40
< 215°	8	—	—	—	—	—	—
215—220	11	—	—	—	—	6 (60°) *	2 (44°) *
220—225	11 (9°)	7	—	3 (51°)	—	14 (68°)	2 (52°)
225—230	7 (9°)	6 (19°)	4	3 (51°)	3 (58°)	3 (59°)	5 (56°)
230—235	4 (14°)	4 (24°)	4 (30°)	7 (57°)	4 (64°)	2 (49°)	4 (48°)
235—240	3 (19°)	7 (32°)	7 (39°)	19 (67°)	8 (78°)	4 (40°)	2 (40°)
240—250	4 (23°)	4 (40°)	16 (51°)	15 (84°)	28 (98°)	—	6 (58°)
250—260	—	4 (55°)	3 (56°)	10 (86°)	9 (87°)	—	—
260—280	—	—	3 (45°)	—	5 (83°)	—	—
Residue	7	8	5	9	6	—	—
Mesitol	—	—	—	—	—	32 †	23 †
2 : 3 : 4 : 6-Tetramethylphenol	5	14	29	—	—	—	—
2 : 3 : 5 : 6-Tetramethylphenol	—	—	—	28	46	—	—

* Fractions of the mixture of mesitol and 2 : 3 : 4 : 6-tetramethylphenol obtained by steam distillation in presence of alkali and formaldehyde.

† Total amounts of mixtures of mesitol and 2 : 3 : 4 : 6-tetramethylphenol.

Exhaustive Distillation.—The phenol (1 mol.), an equal quantity of calcium hydroxide, and 40% formaldehyde (3 mols.; but in the case of phenol, *m*-cresol, and the cresylic acids, 4 mols.) were mixed, with cooling; after standing overnight, the reaction mixture containing the poly(hydroxymethyl)phenols was distilled. The distillate was again treated with an equal weight of calcium hydroxide and 100 c. c. of 40% formaldehyde solution, and the reaction mixture distilled. With phenol, *m*-cresol, and the cresylic acids the process was repeated a third time, 50 c.c. of a 40% formaldehyde solution being used. The distillates were fractionated, and the amount of mesitol (m. p. 72°), 2 : 3 : 4 : 6-tetramethylphenol (m. p. 80°), or 2 : 3 : 5 : 6-tetramethylphenol (m. p. 117°) was determined by treatment of the distillates with formaldehyde and alkali and steam distillation, the volatile unchanged phenols being collected. The results are tabulated above, weights being in g.

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