greatly reduced this negative polarity or actually changed it to positive.

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Preparation of Substituted Bis-phenols

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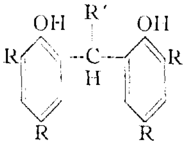
Since the original synthesis[1] of Baeyer, numerous papers on phenol–aldehyde condensations have appeared in the literature.[2] More recently, an increasing interest has been shown by various investigators of this type compound as intermediates for phenolic resins,[3] as antioxidants for wax,[4] as rubber chemicals,[5] as bacteriocides,[6] and as fungicides.[7]

The present work was directed toward the preparation of bis-phenols of the general formulas



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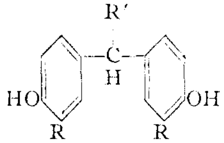

in which R = alkyl, aryl or chlorine and R′ = alkyl or aryl, for use as rubber antioxidants and bacteriostatic agents. A search of the literature revealed a surprisingly small number of bis-phenols other than derivatives of phenol and the cresols with formaldehyde[3] and chloral.[6]

This paper describes the preparation of 35 polyalkylated and chlorinated phenol–aldehyde condensation products not reported previously. They are white crystalline compounds in all cases except 4,4′-(*p*-hydroxybenzylidene)-bis-(6-*t*-butyl-*m*-cresol), #9, which is lemon yellow.

The wide applicability and versatility of the described procedures can readily be seen from the following tables. The reaction time, as given, was the point at which resin formation was observed and the batch quenched with the designated precipitant. The reaction times are, therefore, not true measures of the reaction rates but they do definitely indicate the wide variations observed by changing the structure of the phenols and aldehydes. Since the formation of bis-phenol and resin is a competitive reaction, the low yields can be attributed to either insufficient reaction time for bis-phenol formation or, conversely, not quenching quickly enough to prevent the bis-phenols formed from condensing further to resinous products. The reported yields have no quantitative significance, since in most cases the figures given are the results of a single run.

The compounds described in Table I are 4,4′-alkylidene or arylidene bis-phenols since they do not form nitroso derivatives as does the unreacted 6-*t*-butyl-*m*-cresol. The specific preference for 4,4′-linkage in ortho–para competition is probably a result of partial steric hindrance,[8] although condensation in the ortho position does occur, if the para position is occupied. Examples are given in compounds 20, 28 and 34 in which 4,6-di-*t*-butyl-*m*-cresol is condensed in the one available ortho position with three different aldehydes.

TABLE I

BIS-PHENOLS FROM 6-*t*-BUTYL-*m*-CRESOL[a]

No.	Aldehyde	Precipitant[b]	Time, hr.	M.p., °C.	Yield, %	Recrystallizing solvent	Empirical formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Chlorine Calcd.	Chlorine Found
1	Formaldehyde	1	2	178.7–179.2	39.0	Heptane	$C_{23}H_{32}O_2$	81.12	81.01	9.47	9.53		
2	Acetaldehyde	1	1/4	201.1–201.5	87.0	Heptane	$C_{24}H_{34}O_2$	81.31	80.93	9.67	9.99		
3	Chloroacetaldehyde	1	1/4	228.5–229.5	45.9	Heptane	$C_{24}H_{33}ClO_2$	74.09	73.93	8.55	8.58	9.12	8.95
4	Propionaldehyde	1	4	190.0–190.4	43.4	Heptane	$C_{25}H_{36}O_2$	81.48	81.29	9.85	9.92		
5	Butyraldehyde	2	8	210.0–210.7	62.8	Heptane	$C_{26}H_{38}O_2$	81.64	81.91	10.01	10.23		
6	Isobutyraldehyde	1	24	229.8–230.7	50.8	Heptane	$C_{26}H_{38}O_2$	81.64	81.47	10.01	9.94		
7	Heptaldehyde	2	12	160.2–160.4	24.5	Heptane	$C_{29}H_{44}O_2$	82.03	81.85	10.44	10.61		
8	Benzaldehyde	1	1/2	199.3–199.8	43.3	Heptane	$C_{29}H_{36}O_2$	83.62	83.54	8.71	8.55		
9	*p*-Hydroxybenzaldehyde	3	1/2	262.4–263.1	35.2	Acetic acid	$C_{29}H_{36}O_3$	80.53	80.33	8.39	8.10		
10	Salicylaldehyde	1	1/2	216.7–217.0	18.9	Toluene	$C_{29}H_{36}O_3$	80.53	80.37	8.39	8.59		
11	2,4-Dichlorobenzaldehyde	1	4	209.9–210.4	59.6	Heptane	$C_{29}H_{34}Cl_2O_2$	71.73	71.91	7.06	6.96	14.61	14.65
12	5-Chlorosalicylaldehyde	1	6	214.2–215.9	29.2	Benzene	$C_{29}H_{35}ClO_3$	74.58	74.86	7.55	7.49	7.59	7.58
13	*o*-Chlorobenzaldehyde	1	1/2	226.3–226.9	23.5	Toluene	$C_{29}H_{35}ClO_2$	77.22	77.20	7.82	7.76	7.86	8.02
14	Veratraldehyde	1	1/2	231.2–231.9	52.5	Heptane	$C_{31}H_{40}O_4$	78.12	78.17	8.46	8.60		
15	Pyruvic aldehyde	2	1/4	196.2–197.1	34.8	Benzene	$C_{25}H_{34}O_3$	78.50	78.38	8.96	8.78		
16	Chloral	2	6	218.8–219.3	65.6	Toluene	$C_{24}H_{31}Cl_3O_2$	62.94	63.28	6.82	7.01	23.23	23.05
17	2-Methyl-2-pentenal	1	18	190.1–190.5	18.5	Heptane	$C_{28}H_{40}O_2$	82.30	82.15	9.87	9.52		
18	2-Ethyl-2-hexenal	1	3	210.2–210.6	38.4	Heptane	$C_{30}H_{44}O_2$	82.46	82.46	10.16	9.89		
19	2-Thiophenaldehyde	1	1/4	223.3–223.7	42.0	Heptane	$C_{27}H_{34}O_2S$	76.75	76.68	8.11	8.41	[c]	

[a] The compounds in Table I were all prepared following Procedure A. [b] 1, Heptane; 2, benzene; 3, glacial acetic acid; 4, water. [c] Sulfur, %: calcd. 7.57; found 7.64.

Experimental[9]

The compounds described in this paper have been prepared by two procedures—modifications of the original Baeyer synthesis. In both cases, the choice of precipitant was determined by spot testing during the initial reaction period. One ml. of the reaction mix was added to 3 ml. of each of the four selected precipitants and when crystal formation was noted, the reaction mixture was quenched with the chosen precipitant as indicated in the tables.

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(9) All melting points are corrected.

TABLE II

BIS-PHENOLS FROM FORMALDEHYDE

No.	Phenol	Procedure	Precipitant[a]	Time, hr.	M.p., °C.	Yield, %	Recrystallizing solvent	Empirical formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Chlorine Calcd.	Chlorine Found
20	4,6-Di-*t*-butyl-*m*-cresol	A	3	1/4	215.3–216.3	92.0	Acetic acid	$C_{31}H_{48}O_2$	82.26	82.38	10.69	10.65		
21	α^4-Phenyl-2,4-xylenol	A	1	1	121.5–121.9	22.0	Heptane	$C_{29}H_{28}O_2$	85.26	84.96	6.91	7.02		
22	4-Chloro-*o*-cresol[b]	B	4	1/4	195.2–196.4	83.7	Benzene	$C_{15}H_{14}Cl_2O_2$	60.61	60.91	4.75	4.49	23.86	23.80
23	6-Chloro-*o*-cresol	B	4	2	157.0–157.3	78.7	Benzene	$C_{15}H_{14}Cl_2O_2$	60.61	60.67	4.75	5.02	23.86	23.86
24	4-*t*-Butyl-*o*-chlorophenol	B	4	3	123.2–123.7	51.5	Acetic acid	$C_{21}H_{26}Cl_2O_2$	66.12	66.17	6.87	6.85	18.62	18.85
25	6-*t*-Butyl-4-chloro-*m*-cresol	A	4	18	181.6–182.5	72.2	Heptane	$C_{23}H_{30}Cl_2O_2$	67.47	67.54	7.39	7.45	17.32	17.25
26	4-Chloro-α^2-phenylisopseudocumenol	B	4	1/4	191.7–192.1	72.0	Heptane	$C_{31}H_{30}Cl_2O_2$	73.64	73.57	5.98	6.17	14.03	13.96

[a] 1, Heptane; 2, benzene; 3, glacial acetic acid; 4, water. [b] Shown in (7) as having m.p. 188°.

TABLE III

BIS-PHENOLS FROM BUTYRALDEHYDE

27	Thymol	A	1	3	165.1–165.8	98.5	Heptane	$C_{24}H_{34}O_2$	81.31	81.57	9.67	9.79
28	4,6-Di-*t*-butyl-*m*-cresol	A	3	14	123.5–124.1	26.0	Butanol	$C_{34}H_{54}O_2$	82.51	82.40	11.00	10.95
29	4-*t*-Butyl-*o*-cresol	A	3	14	130.8–131.5	89.1	Acetic acid	$C_{26}H_{38}O_2$	81.64	81.69	10.01	10.15
30	2-*t*-Butyl-*p*-cresol	A	1	18	126.4–127.2	88.5	Heptane	$C_{26}H_{30}O_2$	81.64	81.30	10.01	9.75
31	α-4-Phenyl-2,4-xylenol	A	1	5	108.8–109.2	76.5	Heptane	$C_{32}H_{34}O_2$	85.31	85.55	7.61	7.75
32	6-*t*-Amyl-*m*-cresol	A	1	14	162.8–163.6	43.0	Heptane	$C_{28}H_{42}O_2$	81.90	81.60	10.31	10.35
33	6-*n*-Butyl-*m*-cresol	A	1	2	121.4–122.0	53.5	Heptane	$C_{26}H_{38}O_2$	81.64	81.96	10.01	10.08

[a] 1, Heptane; 2, benzene; 3, glacial acetic acid; 4, water.

TABLE IV

MISCELLANEOUS BIS-PHENOLS

No.	34	35
Phenol	4,6-Di-*t*-butyl-*m*-cresol	2,4-Xylenol
Aldehyde	Isobutyraldehyde	2,4-Dichlorobenzaldehyde
Procedure	A	A
Precipitant[a]	3	1
Time, hours	16	1
M.p., °C.	118.1–118.6	193.7–194.1
Yield, %	22.0	52.0
Recrystallizing solvent	Butanol	Heptane
Empirical formula	$C_{34}H_{54}O_2$	$C_{23}H_{22}Cl_2O_2$[b]
Analyses, % Carbon Calcd.	82.51	68.83
Analyses, % Carbon Found	82.33	68.66
Analyses, % Hydrogen Calcd.	11.00	5.53
Analyses, % Hydrogen Found	11.31	5.79

[a] 1, Heptane; 2, benzene; 3, glacial acetic acid; 4, water. [b] Chlorine, %; calcd. 17.67; found 17.65.

Procedure A. 4,4′-Propylidenebis-(6-*t*-butyl-*m*-cresol).—Approximately 4 ml. of concentrated HCl was added to a well-stirred solution of 82.1 g. of 6-*t*-butyl-*m*-cresol (0.5 mole) and 14.5 g. of propionaldehyde (0.25 mole). The reaction was exothermic and the temperature rose from 30 to 75° within 5 minutes. The reaction mixture was further heated and held at 95° for 4 hours, 100 ml. of heptane was added and the mixture cooled and held 1 hour at 30°. The crystalline product was filtered, washed with two 20-ml. portions of cold heptane and recrystallized from the same solvent at boiling; yield 43.4% of fine white needles, m.p. 190.0–190.4°.

Procedure B. 2,2′-Methylenebis-(4-chloro-*o*-cresol).—Concentrated H_2SO_4 was added dropwise to a well-stirred solution of 71.3 g. of 4-chloro-*o*-cresol (0.5 mole) and 7.5 g. of trioxymethylene (0.25 mole) in 50 ml. of glacial acetic acid. The temperature rose rapidly to 95° and the mixture solidified after 8 ml. of acid had been added. After standing 15 minutes, 200 ml. of water was added and the mixture cooled to 30° The solids were filtered and washed with cold water until free of acidity. The crude product was taken up in 200 ml. of benzene and following decolorization with 10 g. of Darco G-60 gave fine white plates; m.p. 195.2–196.4°, yield 83.7%.

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[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

Alcoholysis of Cellulose with 2-Methoxyethanol[2,3]

BY MARY GRACE BLAIR

Methanolysis of cellulose or its derivatives has been used a very few times as a tool in structural studies of cellulose.[4,5] Partial methanolysis, or alcoholysis with other alcohols as well, has been suggested to replace hydrolysis or oxidation for the shortening of cellulose chains without the introduction of reducing end-groups in the production of industrial materials.[6] Some data were given concerning the extent of reactions by the normal alcohols with from one to five carbon atoms. The present study is concerned with the extent of cleavage which can be obtained with a new alcohol—2-methoxyethanol—which does not appear to have been used previously for the alcoholysis of any polysaccharide. Its high reactivity makes this alcohol worth consideration as an alcoholytic reagent for polysaccharides, particularly since the use of an autoclave is not required in order for the optimal reaction temperature to be reached.

That cellulose acetate is converted by acidic 2-

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(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture, New Orleans 19, La. Article not copyrighted.

(2) Known also as ethylene glycol monomethyl ether and as Methyl Cellosolve.

(3) Report of a study made under the Research and Marketing Act of 1946.

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