under reflux with 150 ml. of glacial acetic acid 20 ml. of 40% hydrobromic acid for 20 hr. and the solution was poured on ice, made alkaline with aqueous potassium hydroxide, and the hydrocarbon was extracted with ether benzene. The crude oily product was taken up in Skellysolve C and was chromatographed over alumina to yield 3.6 g. of a yellow solid which after several recrystallizations from Skellysolve B afforded 1.57 g. (27%) of pure Vb, m.p. 142.5–143.5°, as very pale yellow needles.

Anal. Calcd. for $C_{19}H_{13}F$: C, 87.7; H, 5.0; 7.3. Found: C, 87.5; H, 5.3; F, 7.1.

(b) Cyclization of 2.6 g. of the crude methyl ketone obtained in the previous experiment with 23 g. of polyphosphoric acid as described for Va, followed by chromatographic purification of the crude hydrocarbon furnished 0.80 g. (33%) of Vb, m.p. 142.2–143.0° undepressed by the product obtained above.

4'-Fluoro-1,2-benzanthracene (IVb). A solution of 8.1 g. of finely ground IIIb in 81 ml. of concd. sulfuric acid was kept at room temperature for 2 hr. and then poured on ice. The anthrone was collected and refluxed for 7.5 hr. with a mixture of 40 g. of zinc dust (activated with copper sulfate), 500 ml. of water, and a solution of 66 g. of sodium hydroxide in 200 ml. of water. After cooling and acidifying with 180 ml. of concentrated hydrochloric acid, the solids were collected, dried, and extracted with 250 ml. of refluxing benzene. The benzene extract on cooling furnished 3.85 g. of crystalline product, m.p. 169.5–172.0°. Crystallization from benzene after treatment with charcoal furnished 2.07 g. of a I crop of very pale yellow crystals m.p. 171.5–172.0° and 1.3 g. of product, m.p. 170–172°. The latter after chromatographic purification afforded 0.95 g. pure hydrocarbon, m.p. 171.5–172°, the total yield of pure hydrocarbon amounting to 3.02 g. (42.5%). The analytical sample, m.p. 171.5–172.0°, was obtained by recrystallization from a mixture of benzene and Skellysolve B.

Anal. Calcd. for $C_{18}H_{11}F$: C, 87.8; H, 4.5; F, 7.7. Found: C, 87.9; H, 4.6; F, 7.6.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE TECHNICAL RESEARCH DEPARTMENT OF MATSUSHITA ELECTRIC WORKS, LTD.]

Synthetic Products from Methylolphenols, Formaldehyde, and Primary Aromatic Amines

MIYOSHI NODA, HIROSHI SHIMAOKA, AND SUSUMU NAGASE

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Reaction of 2,6-dimethylol-*p*-cresol with aromatic primary amines resulted in the formation of *N*-(2-hydroxy-3-methylol-5-methylbenzyl)arylamines (I). Nitroso compounds (II) were obtained upon nitrosation of I, indicating that they were secondary amines. Benzoxazine compounds (III) were prepared by reaction of I with formaldehyde. In the same manner *N*-(4-hydroxybenzyl)arylamines (IV) and their nitroso compounds (V) were obtained from 4-methylolphenol. Twenty-six new compounds, and two compounds obtained by two new methods were prepared and studied.

Aromatic amine-phenol-formaldehyde resins which are formed by the condensation of amine, phenol, and formaldehyde are noted for their high electric resistance.[1] However, it is rarely reported whether they are simple mixtures of aromatic amine-formaldehyde and phenol-formaldehyde resins or copolymers of the three constituents.

This work is a study of the initial condensation products of amines, phenols, and formaldehyde.

The condensation of phenols with formaldehyde and primary[2] or secondary[3] aliphatic amines has been studied in several laboratories. *o*-Alkylaminomethyl-*p*-substituted phenol, *N*,*N*-bis-(2-hydroxybenzyl)alkylamines and a new series of 3,4-dihydro-3,6-disubstituted-1,3,2*H*-benzoxazine were obtained directly from three reactants in the presence of alcoholic potash in certain instances.[4]

The condensation of phenols with formaldehyde and primary aromatic amines has also been studied[5] by several workers, the following products being obtained: *N*-(2-hydroxybenzyl)aniline,[6,7] *N*-(2-hydroxybenzyl)-*p*-toluidine,[6] *N*-(4-hydroxybenzyl)-aniline,[6] *N*-(4-hydroxybenzyl)-*p*-toluidine[6] and *N*-nitroso-*N*-(4-hydroxybenzyl)aniline.[8] 3,4-Dihydro-3-*p*-tolyl-6-*t*-butyl-1,3,2*H*-benzoxazine and 3,4-dihydro-3-*p*-tolyl-6-bromo-1,3,2*H*-benzoxazine were also prepared by Burke and co-workers.[9]

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[2] (a) H. A. Bruson, U. S. Patent **2,031,557** (1936); **2,114,122** (1938); (b) J. Harmon and F. M. Meigs, U. S. Patent **2,098,869** (1937); (c) H. A. Bruson, *J. Am. Chem. Soc.*, **58**, 1741 (1936).

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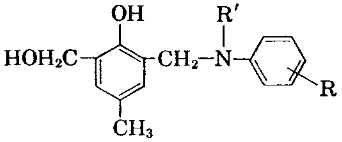
TABLE I

N-(2-HYDROXY-3-METHYLOL-5-METHYLBENZYL)ARYLAMINES FROM 2,6-DIMETHYLOL-*p*-CRESOL AND PRIMARY AMINES, AND THEIR NITROSO COMPOUNDS

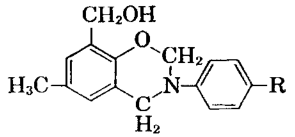


No.	R	R′	Time, (hrs.)	Yield, %	M.P., °C.	Solvent[a] for Crystal.	Molecular Formula	Mol. Wt. Calcd.	Mol. Wt. Found	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Halogen Calcd.	Halogen Found	Nitrogen Calcd.	Nitrogen Found
1	*p*-CH_3O	H	8	11.6[b]	120.0	A	$C_{16}H_{19}NO_3$	273	263	70.30	70.64	7.01	7.12			5.13	5.24
2	*p*-CH_3O	N=O	2	36.2[b]	93.0	B	$C_{16}H_{18}N_2O_4$	302	295	63.49	63.25	6.01	5.95			9.28	9.26
3	*p*-Cl	H	10	10.1[b]	106.0	C	$C_{15}H_{16}ClNO_2$	277	285	64.86	65.14	5.81	5.98	11.45	11.29	5.04	5.19
4	*p*-Cl	N=O	3	30.0[c]	131.0	B	$C_{15}H_{15}ClN_2O_3$	307	302	58.73	58.77	4.93	5.29	11.56	11.75	9.13	8.99
5	*p*-CH_3	H	8	8.2[b]	119.0	A	$C_{16}H_{19}NO_2$	257	256	74.68	74.98	7.44	7.66			5.44	5.56
6	*p*-CH_3	N=O	3	27.0[b]	101.0	B	$C_{16}H_{18}N_2O_3$	286	286	67.11	67.27	6.34	6.27			9.79	9.78
7	*p*-Br	H	9	23.0[c]	109.5	F	$C_{15}H_{16}BrNO_2$	322	314	55.91	56.20	5.00	5.20	24.83	25.03	4.34	4.62
8	*p*-Br	N=O	4	9.2[d]	135.0	B	$C_{15}H_{15}BrN_2O_3$	351	352	51.30	51.14	4.30	4.32	22.75	22.40	7.98	8.15
9	H	H	2	0.92[d]	83.0	G	$C_{15}H_{17}NO_2$	243	242	74.05	74.24	7.04	6.81			5.76	5.94
10	H	N=O	3	29.7[d]	73.0	E	$C_{15}H_{16}N_2O_3$	272	280	66.16	66.42	5.92	5.81			10.29	10.07
11	*o*-CH_3O	H	6	16.4[b]	109.0	H	$C_{16}H_{19}NO_3$	273	265	70.30	70.41	7.01	7.02			5.13	5.41
12	*p*-C_2H_5O	H	8	10.4[d]	115.9	I	$C_{17}H_{21}NO_3$	287	293	71.05	71.01	7.37	7.13			4.87	5.14
13	*p*-C_2H_5O	N=O	24	59.0[d]	101.3	H	$C_{17}H_{20}N_2O_4$	316	319	64.54	64.45	6.37	6.49			8.86	8.92

[a] A, benzene-ligroin (1:1); B, methanol; C, ethylene-dichloride–ligroin (1:1); D, acetone-water (1:1); E, methanol-water (1:1); F, ethylene-dichloride–benzene (1:1); G, ligroin. H, ethanol-water (1:1); I, ethanol; J, ligroin-benzene (4:1); K, ligroin-benzene (3:1); L, ligroin-benzene (1:2); M, ligroin-benzene (2:1). [b] After double recrystallizations. [c] Crude; [d] After recrystallization. [e] After 5 recrystallizations. [f] Compound (23) and (27) did not agree in melting points with compounds previously reported by Emerich and Bischoff and Fröhlich, Hantzsch, and Wechsler, respectively.

TABLE II*

3,4-DIHYDRO-3-ARYL-6-METHYL-8-METHYLOL-1,3,2H-BENZOXAZINES FROM FORMALDEHYDE AND *N*-(2-HYDROXY-3-METHYLOL-5-METHYLBENZYL)ARYLAMINES

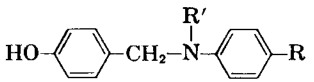


No.		Time, (hr.)	Yield, %	M.P., °C.	Solvent[a] for Crystal.	Molecular Formula	Mol. Wt. Calcd.	Mol. Wt. Found	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Halogen Calcd.	Halogen Found	Nitrogen Calcd.	Nitrogen Found
14	*p*-CH$_3$O	2	32.0[b]	108.0	B	$C_{17}H_{19}NO_3$	285	278	71.56	71.78	6.72	6.62			4.91	4.97
15	*p*-Cl	2	35.0[b]	107.0	D	$C_{16}H_{16}ClNO_2$	290	283	66.32	66.54	5.58	5.85	12.24	11.95	4.83	5.08
16	*p*-CH$_3$	2	31.8[b]	83.0	E	$C_{17}H_{19}NO_2$	269	278	75.81	76.10	7.11	7.04			5.20	5.33
17	*p*-Br	2	48.2[b]	108.5	B	$C_{16}H_{16}BrNO_2$	334	326	57.50	57.78	4.83	4.77	23.91	24.20	4.19	4.24
18	*p*-C$_2$H$_5$O	0.5	96.5[d]	94.3	A	$C_{18}H_{21}NO_3$	299	302	72.21	72.09	7.07	7.18			4.68	4.59

* See Table I for key to footnotes.

TABLE III*

N-(4-HYDROXYBENZYL)ARYLAMINES FROM 4-METHYLOLPHENOL AND PRIMARY AMINES; AND THEIR NITROSO COMPOUNDS



No.	R	R′	Time (hrs.)	Yield, %	M.P., °C.	Solvent[a] for Crystal.	Molecular Formula	Mol. Wt. Calcd.	Mol. Wt. Found	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Halogen Calcd.	Halogen Found	Nitrogen Calcd.	Nitrogen Found
19	*p*-Br	H	10	19.0[e]	86.4	J	$C_{13}H_{12}BrNO$	278	274	56.13	56.10	4.31	4.20	28.73	28.47	5.03	4.99
20	*p*-Br	N=O	5	77.0[d]	131.4	A	$C_{13}H_{11}BrN_2O_2$	307	299	50.83	51.03	3.61	3.77	26.53	26.25	9.12	9.07
21	*p*-Cl	H	10	18.0[d]	70.5	K	$C_{13}H_{12}ClNO$	234	226	66.81	66.56	5.18	5.46	15.17	14.87	5.99	6.01
22	*p*-Cl	N=O	4	81.0[d]	118.6	L	$C_{13}H_{11}ClN_2O_2$	263	269	59.41	59.71	4.22	4.55	13.50	13.25	10.66	10.44
23	*p*-CH$_3$	H	10	21.0[d]	90.0[f]	K	$C_{14}H_{15}NO$	213	214	78.84	78.72	7.09	7.06			6.57	6.63
24	*p*-CH$_3$	N=O	3	59.0[d]	110.6	M	$C_{13}H_{14}N_2O_2$	242	236	69.40	69.34	5.82	6.16			11.56	11.43
25	*p*-CH$_3$O	H	10	57.0[d]	111.1	J	$C_{14}H_{15}NO_2$	229	224	73.34	73.29	6.59	6.84			6.11	5.89
26	*p*-CH$_3$O	N=O	4	88.0[d]	118.8	J	$C_{14}H_{14}N_2O_3$	258	261	65.10	64.93	5.46	5.63			10.86	11.03
27	*p*-C$_2$H$_5$O	H	8	16.0[d]	97.4[f]	K	$C_{15}H_{17}NO_2$	272	269	74.05	73.98	7.04	6.91			5.76	5.75
28	*p*-C$_2$H$_5$O	N=O	12	53.0[d]	98.8	M	$C_{15}H_{16}N_2O_3$	272	269	66.16	66.50	5.92	5.99			10.29	10.57

* See Table I for key to footnotes.

The present study deals with the condensation of primary aromatic amines (*i.e.*, *o*-anisidine, *p*-anisidine, *p*-chloroaniline, *p*-bromoaniline, *p*-toluidine, *p*-phenetidine, and aniline) with 2,6-dimethylol-*p*-cresol or 4-methylolphenol in ethanol solution by Burke's method. *N*-(2-hydroxy-3-methylol-5-methylbenzyl)arylamines (I) and *N*-(4-hydroxybenzyl)arylamines (IV) were obtained as initial condensation products respectively. The alcoholic hydroxyl of the methylol group was detected by Nessler's reagent,[10] and the phenolic hydroxyl in the product from the 2,6-dimethylol-*p*-cresol was identified with the ferric chloride test[11] and the phenolic hydroxyl in the product from the 4-methylolphenol with Linter's[12] reagent.

The amines I and IV reacted with sodium nitrite in the presence of hydrochloric acid to yield nitroso compounds whose analysis and chemical behavior revealed the presence of one nitroso group joined to the methylolphenol and showed a secondary amine property. I reacted quantitatively with formaldehyde to form 3,4-dihydro-3-aryl-6-methyl-8-methylol-1,3,2*H*-benzoxazine which was unstable when heated.

Each structural formula was established by elementary analysis, measurement of molecular weight, and behavior of each radical.

In Tables I, II, and III are listed the properties and results of chemical analyses of the new products obtained.

EXPERIMENTAL

The 2,6-dimethylol-*p*-cresol and 4-methylolphenol used herein were synthesized according to Auwers' method[13] (m.p. 129.0°) and Manasse's method[14] (m.p. 120.0°), respectively.

N-(2-Hydroxy-3-methylol-5-methylbenzyl)-p-anisidine (*1*). A mixture of 33.6 g. of 2,6-dimethylol-*p*-cresol (0.2 mole), 24.6 g. of *p*-anisidine (0.2 mole) and 300 ml. of ethanol containing 1.2 g. of potassium hydroxide was gently refluxed for 8 hr. The reaction mixture was then allowed to cool and neutralized with acetic acid. Unreacted *p*-anisidine was removed by steam distillation. The resulting solid product was dissolved in benzene and allowed to stand for one day. A white solid was obtained; crystallization from benzene-ligroin (1:1), yielded 6.3 g., m.p. 120.0°, Nessler's reagent positive, ferric chloride test positive.

Compounds 3, 5, 7, 9, 11, and 12 were synthesized in a manner similar to that described above. For their properties, see Table I.

N-Nitroso-N-(2-hydroxy-3-methylol-5-methylbenzyl)-p-anisidine (*2*). To a solution of 2.5 g. of compound 1 in dilute hydrochloric acid at a temperature below 5°, was added 0.6 g. of sodium nitrite with stirring. A light reddish resinous product was obtained. It was dissolved in ether and neutralized with sodium carbonate solution. After washing with water, a light reddish-brown, crystalline solid was obtained upon removal of ether at room temperature; recrystallization from methanol yielded 1.0 g. of tabular crystals, m.p. 93.0°, Nessler's reagent positive, Liebermann's[15] reaction positive, ferric chloride test positive.

Compounds 4, 6, 8, 10, and 13 were synthesized in a manner similar to that described above. For their properties, see Table I.

3,4-Dihydro-3-p-anisyl-6-methyl-8-methylol-1,3,2H-benzoxazine (*14*). To 3.0 g. of compound 1 dissolved in 50 ml. of methanol was added 1.6 ml. of 37% formaldehyde solution. The mixture was gently refluxed on a water bath for 2 hr. After some water was added, the reaction mixture was allowed to cool to room temperature. A white solid substance was obtained, filtered, and recrystallized from methanol to give 1.0 g. of white leaflet crystals, m.p. 108.0°, Nessler's reagent positive, ferric chloride test negative.

Compounds 15, 16, 17, and 18 were synthesized in a manner similar to that described above. For their properties, see Table II.

N-(4-Hydroxybenzyl)-p-bromoaniline (19). This compound was prepared essentially in the same manner as compound 1 except that 12.4 g. of 4-methylolphenol (0.1 mole) and 17.2 g. of *p*-bromoaniline (0.1 mole) were used: recrystallization from ligroin-benzene (4:1); white granular crystals, yield 5.2 g., m.p. 86.4°, readily soluble in acetone, alcohol, benzene, ether, and chloroform; slightly soluble in ligroin, insoluble in water, Nessler's reagent negative, Linter's reaction positive.

Compounds 21, 23, 25, and 27 were synthesized in a manner similar to that described above. For their properties, see Table III.

N-Nitroso-N-(4-hydroxybenzyl)-p-bromoaniline (*20*). This compound was prepared essentially in the same manner as compound 2 except that 3.5 g. of compound 19 was used in place of compound 1: recrystallization from ligroin-benzene (1:1) gave 3.0 g. of light yellow granular crystals, m.p. 131.4°, readily soluble in acetone, alcohol, benzene, chloroform, and ether; slightly soluble in ligroin, insoluble in water, Liebermann's reaction positive, Linter's reaction positive.

Compounds 22, 24, 26, and 28 were synthesized in a manner similar to that described above. For their properties, see Table III.

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OSAKA PREFECTURE, JAPAN

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