pared from XXI[13] and sodium azide in the same way, to give an 84% yield of XX, m.p. 120° dec. from water.

Anal. Calcd. for $C_6H_5N_7$: N, 56.1. Found: N, 56.4.

1,4-Dihydrazinophthalazine (XXII). A mixture of 52 g. of phthalonitrile, 200 ml. of dioxane, and 100 ml. of 95% hydrazine was treated with 18 ml. of acetic acid below 30°, then heated on the steam bath for 3 hr. The orange-colored solid was broken up, filtered and washed with ethanol, and dried; yield, 69 g.; m.p. 185–190° dec. A sample was recrystallized from water, m.p. 190° dec., to a red liquid.

Anal. Calcd. for $C_8H_{10}N_6$: C, 50.5; H, 5.3; N, 44.2. Found: C, 51.6; H, 5.3; N, 43.6.

5-(2-Formylhydrazino)-1,2,3a,4-tetrazabenz[e]indene (XXV). A solution of 5 g. of XXII in 25 ml. of formic acid was refluxed for 3 hr.; water (50 ml.) was added and the solution was chilled. The product separated in the form of white crystals which were crystallized first from dimethylformamide, then from water, to give 4.0 g. of XXV, m.p. 300° dec.

Anal. Calcd. for $C_{10}H_8ON_6$: C, 52.5; H, 3.5; N, 36.8. Found: C, 52.5; H, 3.5; N, 36.6.

(13) C. F. H. Allen, H. R. Beilfuss, D. M. Burness, G. A. Reynolds, J. F. Tinker, and J. A. VanAllan, *J. Org. Chem.* **24**, 790 (1959).

5-Azido-1,2,3a,4-tetrazabenz[e]indene (XXVI). A suspension of 4 g. of XXV in 25 ml. of concentrated hydrochloric acid, and 25 ml. of water was refluxed for 1 hr. Complete solution ensued. The solution was concentrated to about 15 ml., filtered with Norit, and the filtrate made alkaline with sodium carbonate solution. The precipitate, 5-hydrazino-1,2,3a,4-tetrazabenz[e]indene (XXVa), m.p. >298°, weighed 3.0 g.

Anal. Calcd. for $C_9H_7N_6$: N, 42.1. Found: N, 41.8.

A solution of 4 g. of XXVa in 35 ml. of water containing 4 ml. of concentrated hydrochloric acid and 8 ml. of acetic acid was treated with 4 g. of sodium nitrite in 20 ml. of water at 10°. A precipitate which formed was filtered off and crystallized from alcohol to give 3.1 g. of XXVI, m.p. 195°.

Anal. Calcd. for $C_9H_4N_7$: C, 51.4; H, 1.9; N, 46.7. Found: C, 51.5; H, 2.5; N, 46.8.

5-Azido-1,2,3,3a,4-pentazacyclopent[e]indene (XXIII). This was prepared by treatment of XXII with nitrous acid as just described. It melted at 152° and showed no depression of melting point when mixed with a sample prepared according to the directions given in Ref. 7.

ROCHESTER, N. Y.

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

N,N-Bis(2-hydroxybenzyl)arylamines: Condensation of Saligenin with Primary Aromatic Amines[1]

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Condensation of saligenin with primary aromatic amines and formaldehyde resulted in N-(2-hydroxybenzyl)arylamines. Nitroso and formaldehyde derivatives were obtained from N-(2-hydroxybenzyl)arylamines on treatment with sodium nitrite and formaldehyde, respectively. N,N-Bis(2-hydroxybenzyl)arylamines were also prepared by reaction with equimolar quantities of saligenin and N-(2-hydroxybenzyl)arylamines and they were also obtained from direct reaction of saligenin and aromatic amines. Eleven new compounds were synthesized and their properties were studied.

Burke and his collaborators, in a recent paper, described the preparation of several N,N-bis(hydroxybenzyl)alkylamines[2] and new types of 3,4-dihydro-3-*p*-tolyl-6-substituted-1,3,2*H*-benzoxazines[2,3] by the direct condensation of *p*-substituted phenols with paraformaldehyde and *p*-toluidine under various conditions. Compounds of N-(2-hydroxybenzyl)-*p*-bromoaniline,[4(a)] N-(2-hydroxybenzyl)aniline,[4(b)] N-(2-hydroxybenzyl)-*p*-anisidine,[4(a),4(d)] N-(2-hydroxybenzyl)-*p*-toluidine,[4b] and N-(2-hydroxybenzyl)-*p*-chloroaniline[4(a)] were synthesized by heating saligenin and appropriate aromatic amines disolved in a small amount of alcohol in a sealed tube. N-(2-Hydroxybenzyl)aniline was also obtained by treatment of salicylal-aniline with sodium amalgam.[4(c)] Some nitroso compounds of N-nitroso-N-(2-hydroxybenzyl)arylamines were also synthesized by nitrosation of N-(2-hydroxybenzyl)arylamines in ordinary method by pioneers.[5]

In the previous reports it was shown that N-(2-hydroxybenzyl)arylamines were obtained through condensation reaction of 2,6-dimethylol-*p*-cresol with primary aromatic amines, 3,4-dihydro-3,6-substituted-1,3,2*H*-benzoxazines were prepared from reaction of N-(2-hydroxybenzyl)-arylamines with formaldehyde, and N-nitroso-N-(2-hydroxybenzyl)-arylamines were formed from treatment of N-(2-hydroxybenzyl)arylamines with sodium nitrite.[6(a)] Each type of

(1) Given in part at the 10th Annual Meeting at the Chemical Society of Japan, April 6, 1957.

(2) W. J. Burke, R. P. Smith and C. Weatherbee, *J. Am. Chem. Soc.*, **74**, 602 (1952).

(3) (a) W. J. Burke, K. C. Murdock, and Grace Ec, *J. Am. Chem. Soc.*, **76**, 1677 (1954). (b) W. J. Burke, *J. Am. Chem. Soc.*, **71**, 609 (1949). (c) W. J. Burke, C. W. Stephens, *J. Am. Chem. Soc.*, **74**, 1518 (1952).

(4) (a) C. Paal, *Arch. Pharm.*, **240**, 681, 684, 685 (1902). (b) C. Paal, H. Senninger, *Ber.*, **27**, 1802, 1804 (1894). (c) O. Emmerich, *Ann.*, **241**, 344 (1887). (d) von H. Euler and H. Nystöm; *cf.* N. J. L. Megson, *Phenolic Resin Chemistry*, Butterworths Publication Ltd., London, 1958, p. 133.

(5) (a) E. Banberger and J. Müller, *Ann.*, **313**, 105, 116 (1900). (b) A. Hantzsch and E. Wechsler, *Ann.*, **325**, 248 (1902).

(6) (a) M. Noda, H. Shimaoka, and S. Nagase, *J. Org. Chem.*, **24**, 512 (1959). (b) M. Noda, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **62**, 744, 747 (1959). (c) M. Noda, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **80**, 101, 104 (1959).

these three compounds was also formed from treatment of primary aromatic amines with 2,6-dimethylol-4-bromophenol,[6(b)] 2,6-dimethylol-4-chlorophenol,[6(b)] 2-methylol-*p*-cresol[6(c)] and 2-methylol-4-chlorophenol.[6(c)] However, the reactions between saligenin and aromatic amines appear to be rarely reported, in spite of their importance as the intermediate substance of industrially valuable aminephenolformaldehyde resins.[7]

The present study deals with condensation of saligenin with primary aromatic amines (*i.e.*, *p*-toluidine, *p*-anisidine, *p*-chloroaniline, *p*-bromoaniline, and aniline) in a molar ratio of 1:1, respectively. This procedure led to the formation of *N*-(2-hydroxybenzyl)arylamines. Yellow crystalline compounds of *N*-nitroso-*N*-(2-hydroxybenzyl)-arylamines were easily formed from *N*-(2-hydroxybenzyl)arylamines treated with sodium nitrite in good yield. The formation of these nitroso derivatives showed the presence of imino group (secondary amine properties) in father substance.

Compounds of benzoxazine type which were expected to yield from reaction of formaldehyde with —CH_2—NH— group in *ortho* position with respect to a hydroxyl group were also obtained. These compounds were prepared by condensation of *N* - (2 - hydroxybenzyl)arylamine with formaldehyde in a molar ratio of 1:1. These compounds were so unstable that recrystallization from hot methanol caused partial decomposition.

N,*N*-Bis(2-hydroxybenzyl)arylamines were obtained by reaction with saligenin and *N*-(2-hydroxybenzyl)arylamines. They could also be prepared directly by condensation of saligenin with aromatic amines under reflux in high yield.

Phenolic hydroxyl groups contained in the abovementioned compound of four types were identified with ferric chloride.[8] The *N*,*N*-bis(2-hydroxybenzyl)arylamines showed a negative reaction with this reagent, therefore infrared spectroscopy was used. The presence of the phenolic hydroxyl group was confirmed by the appearance of the absorption band near 3350 cm.$^{-1}$

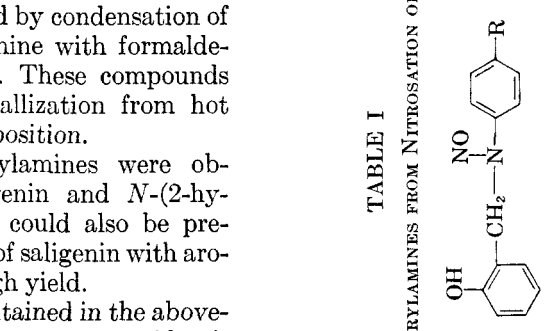
EXPERIMENTAL

N-Nitroso-N-(2-hydroxybenzyl)-p-chloroaniline (II). A solution of 2.0 g. of *N*-(2-hydroxybenzyl)-*p*-chloroaniline in 30 ml. of dilute hydrochloric acid (10%) was cooled below 3° in an ice bath, and 10 ml. of sodium nitrite solution (10%) was added dropwise with stirring. After the mixture was allowed to stand for 2 hr., a brown resinous substance was obtained. The reaction mixture was dissolved in ether and neutralized with a solution of sodium carbonate and then washed with water. After the solvent was removed by evaporation at room temperature, a brown, resinous solid was obtained; recrystallization from methanol yielded yellow tabular crystals, yield 36.0%, m.p. 119.0°, Liebermann's reaction[9] positive.

(7) F. J. Nagel, U.S. Patent **2,554,262** (1951).
(8) S. Soloway and S. H. Willen, *Anal. Chem.*, **24**, 979 (1952).
(9) C. Liebermann, *Ber.*, **7**, 247, 287, 1098 (1874).

TABLE I

N-NITROSO-*N*-(2-HYDROXYBENZYL)ARYLAMINES FROM NITROSATION OF *N*-(2-HYDROXYBENZYL)ARYLAMINES

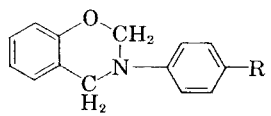


	Amines	Time, Hr.	Yield, %	M.P.	Molecular Formula	Analysis %							
						Mol. Wt.		Carbon		Hydrogen		Halogen		Nitrogen	
						Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
I	*p*-Bromoaniline	2	45.0[a]	131.6[b]	$C_{13}H_{11}BrN_2O_2$	307	305	50.83	50.92	3.61	3.62	Br 26.02	25.88	9.12	8.99
II	*p*-Chloroaniline	3	36.0[a]	119.0[c]	$C_{13}H_{11}ClN_2O_2$	263	257	59.43	59.73	4.22	4.28	Cl 13.50	13.70	10.67	10.92

[a] After crystallization. [b] Ethanol. [c] Methanol.

TABLE II

3,4-DIHYDRO-3-ARYL-1,3,2*H*-BENZOXAZINES FROM FORMALDEHYDE AND *N*-(2-HYDROXYBENZYL)ARYLAMINES

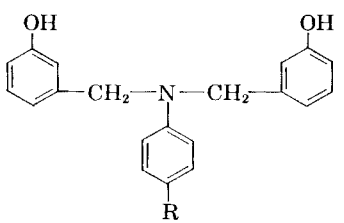


Amines	Time, Hr.	Yield, %	M.P.	Molecular Formula	Analysis %									
					Mol. Wt.		Carbon		Hydrogen		Halogen		Nitrogen	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
III *p*-Bromoaniline	2	74.0[a]	80.5[b]	$C_{14}H_{12}BrNO$	290	290	57.95	58.20	4.17	4.08	Br 27.54	27.60	4.83	4.65
IV Aniline	2	57.0[c]	55.9[b]	$C_{14}H_{13}NO$	211	208	79.59	79.67	6.20	6.38	...	...	6.63	6.86
V *p*-Toluidine	2	32.0[a]	83.9[b]	$C_{15}H_{15}NO$	225	225	79.97	79.82	6.71	6.59	...	...	6.22	6.24
VI *p*-Anisidine	2	48.0[a]	67.6[b]	$C_{15}H_{15}NO_2$	241	244	74.66	74.74	6.27	6.57	...	...	5.81	5.79
VII *p*-Chloroaniline	2	32.0[c]	51.3[b]	$C_{14}H_{12}ClNO_2$	246	240	68.43	68.19	4.92	5.20	Cl 14.43	14.71	5.70	5.90

[a] After crystallization. [b] Methanol. [c] Crude.

TABLE III

N,N-Bis(2-hydroxybenzyl)amines from Saligenin, and *N*-(2-Hydroxybenzyl)arylamines



Amines	Time, Hr.	Yield, %	M.P.	Molecular Formula	Analysis %									
					Mol. Wt.		Carbon		Hydrogen		Halogen		Nitrogen	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
VIII *p*-Bromoaniline	24	40.0[a], 5.0[b]	156.4[c]	$C_{20}H_{18}BrNO_2$	384	376	62.51	62.31	4.72	4.88	Br 20.80	20.72	3.65	3.63
IX *p*-Toluidine	14	25.0[a]	155.4[d]	$C_{21}H_{21}NO_2$	319	311	78.69	78.97	6.63	6.64	...	...	4.39	4.33
X *p*-Anisidine	12	16.0[e], 0.5[b]	160.6[d]	$C_{21}H_{21}NO_3$	335	338	75.20	75.20	6.31	6.31	...	...	4.18	4.35
XI *p*-Chloroaniline	15	31.0[f], 3.0[b]	168.4[d]	$C_{20}H_{18}ClNO_2$	340	337	70.69	70.78	5.34	5.62	Cl 10.43	10.22	4.12	4.15

[a] After crystallization. [b] Procedure B. [c] Ethanol. [d] Methanol. [e] After three recrystallizations. [f] Crude.

Compound I was prepared in a manner similar to that described above. For its properties, see Table I.

3,4-Dihydro-3-phenyl-1,3,2H-benzoxazine (IV). To a solution of 2.5 g. of *N*-(2-hydroxybenzyl)aniline in 25 ml. of methanol, 2 ml. of 37% formaldehyde solution was added. The mixture was heated on a water bath under reflux for 2 hr. The solvent was removed by distillation *in vacuo* and the residue was allowed to stand for 3 days. The product was recrystallized from warm methanol resulting in white needle crystals, yield 57.0%, m.p. 55.9°, readily soluble in acetone and ether, soluble in chloroform, alcohol, and benzene, slightly soluble in ligroin, insoluble in water.

Compounds III, V, VI, and VII were prepared in a manner similar to that described above. For their properties, see Table II.

N,N-Bis(2-hydroxybenzyl)-p-bromoaniline (VIII). Two different procedures for the preparation of this compound are given below.

Procedure A. To a solution of 2.5 g. of saligenin[10] (0.02 mole) in 2.0 ml. of ethanol, 2.8 g. of *N*-(2-hydroxybenzyl)-*p*-bromoaniline (0.01 mole) was added. After heating on a water bath for 12 hr. under reflux, the reaction mixture was cooled in an ice bath and a crystalline substance was obtained. The product was recrystallized from ethanol yielding white leaflets; yield 40.0%, m.p. 156.4°, readily soluble in acetone and ether, soluble in chloroform and alcohol, slightly soluble in ligroin, insoluble in water.

Compounds IX, X, and XI were prepared in a manner similar to that described above. For their properties, see Table III.

Procedure B. A mixture consisting of 103 g. of *p*-bromoaniline (0.6 mole), 49.6 g. of saligenin (0.4 mole) and 200 ml. of ethanol containing 0.6 g. of potassium hydroxide was heated on a water bath under reflux for 14 hr. After being allowed to cool to room temperature, the reaction mixture was neutralized with acetic acid. Unreacted *p*-bromoaniline was removed by steam distillation. The resulting brown, resinous substance was washed several times by being poured into hot water and allowed to cool. The thus formed crystals were recrystallized from methanol-water (1:1) until a constant melting point was attained, white leaflet crystals of *N*-(2-hydroxybenzyl)-*p*-bromoaniline (m.p. 125.3°, yield 36.0%) were separated.

The residue was treated with methanol-water (1:1) until a constant m.p. was obtained yielding white granular crystals; m.p. 156.4°, yield 5%. The melting point of this product was not depressed by admixture with the product prepared by procedure A.

Compounds X and XI were prepared in a manner similar to that described above.

Acknowledgment. I wish to thank Prof. M. Imoto of the Osaka City University for his encouragement throughout this work. I am also grateful to the Matsushita Electric Works, Ltd., Technical Research Department, and indebted to Mr. S. Nagase for much technical assistance.

OSAKA PREFECTURE, JAPAN

(10) S. Seto and H. Horiuchi, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, **57**, 689 (1954).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Mechanism of the Tungstic Acid Catalyzed Hydroxylation of Olefins

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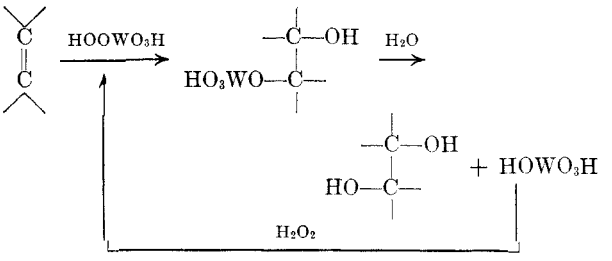
The electrophilic nature of the tungstic acid catalyzed *trans*- addition of hydrogen peroxide to an olefin has been demonstrated. One of the oxygens introduced by the tungstic acid catalyzed hydroxylation has been shown to arise from the oxidizing agent, the other from the solvent medium. These results are discussed in terms of the mechanism of the reaction, which apparently is analogous to that proposed for organic acid hydroxylations.

Since the first description[2] of tungstic acid as an effective catalyst for the addition of hydrogen peroxide to an ethylenic linkage to give a high yield of the corresponding vicinal glycol, the method has received only sporadic attention.[3,4] Mugdan and Young[3] have suggested that the hydroxylation reaction involves and ionic 1,2-*trans*-addition of an intermediate peroxy acid, $HOOWO_3H$,[5] to the double bond since in all cases thus far reported the addition of the two hydroxyl groups proceeds in the *trans*-direction. The following mechanism has been proposed.[3]



(1) Present address: Elastomer Chemicals Department, Research Division, E. I. du Pont de Nemours and Co., Wilmington 98, Del.

(2) I. Bergsteinsson, U. S. Patent **2,373,942** (April 17, 1945).

(3) M. Mugdan and D. P. Young, *J. Chem. Soc.*, 2988 (1949).

(4) J. M. Church and R. Blumberg, *Ind. Eng. Chem.*, **43**, 1780 (1951); D. P. Young, Brit. Patent **654,764** [*Chem. Abstr.*, **46**, 7115 (1952)]; L. N. Owen and P. N. Smith, *J. Chem. Soc.*, 4041 (1952); C. W. Smith, U. S. Patent **2,838,575** (June 10, 1958).

(5) Potentiometric and calorimetric measurements have established that a faint yellow solution of pertungstic acid results when tungsten trioxide was dissolved in aqueous hydrogen peroxide. A. Lottermoser, *Z. Electrochem.*, **35**, 610 (1929); F. Rivenq, *Bull. soc. chim. France*, **12**, 283 (1945).