acetone and oxygen was bubbled through the solution for three days, acetone being added from time to time to replace that lost by evaporation. The solvent was evaporated and the solid residue extracted with a solution of potassium bicarbonate. Acidification of the carbonate solution, however, yielded no organic acid. Extraction of the residue with 5% sodium hydroxide yielded isodurenol melting at 78–79°.[7] The only compound which was isolated from the neutral fraction was unchanged enol (4.4 g.).

Summary

It has been shown that stable vinyl alcohols can be made by the condensation of Grignard reagents with suitable α,β-unsaturated ketones.

Urbana, Illinois

Received July 3, 1944

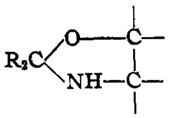
[7] Hey, *J. Chem. Soc.*, 1590 (1931).

[Contribution from the Department of Chemistry, Columbia University]

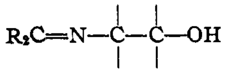
Condensation Products of Aldehydes and Ketones with *o*-Aminobenzyl Alcohol and *o*-Hydroxybenzylamine

By Frederick W. Holly and Arthur C. Cope

The condensation products of ketones with ethanolamine and other 1,2-alkanolamines have been shown to be oxazolidines (I) or azomethines (Schiff bases) (II), depending on the structure of the ketone.[1]



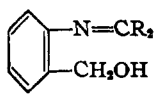
I



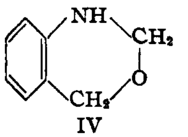
II

In general, the anhydro compounds derived from reactive, unhindered ketones proved to be oxazolidines, while corresponding compounds obtained from the sterically hindered diisobutyl ketone were azomethines. Interconversion of the two forms was evident for the condensation product of methyl propyl ketone with ethanolamine, which rapidly established an equilibrium between the two structures ($I \rightleftarrows II$) by ring-chain tautomerism. In other cases molecular refraction data indicated a predominance of one form, but did not exclude the possibility that the other was present in smaller amount. Similar observations have been made concerning the structure of anhydro compounds obtained from ketones and 3-amino-1-propanol.[2] The present paper is concerned with the structure of condensation products of aldehydes and ketones with *o*-aminobenzyl alcohol and *o*-hydroxybenzylamine.

Paal and Laudenheimer[3] have described the condensation products of acetone and a number of aldehydes with *o*-aminobenzyl alcohol as azomethines (III), and did not consider a possible cyclic structure (IV).



III



IV

They obtained amorphous products from *o*-aminobenzyl alcohol and formaldehyde or methylal, while methyl ethyl ketone and less reactive ketones failed to condense.

We have condensed *o*-aminobenzyl alcohol with a number of aldehydes and ketones by refluxing the reactants in benzene solution, and removing the water continuously as it formed. Glacial acetic acid was added as a catalyst except with aldehydes, acetone and cyclohexanone, which required no catalyst. Properties of the condensation products are listed in Table I. Evidence for their structure has been obtained by absorption spectrum and molecular refraction measurements.

Ultraviolet absorption spectra of compounds 3, 4, 5 and 11 (Table I) are shown in Figs. 1 and 2. Each has the two absorption maxima characteristic of a secondary aromatic amine, at 2940–2975 Å. (log ε 3.34–3.20) and 2445–2450 Å. (log ε 3.96–3.72). These wave lengths and extinction coefficients correspond closely to the data for N-ethyl-*o*-toluidine (Fig. 1), which has maxima at 2910 Å. (log ε 3.39) and 2440 Å. (log ε 3.86). The 2-phenyl derivative (12, Table I) has a maximum at 2450 Å. (log ε 3.93) and an inflection point at

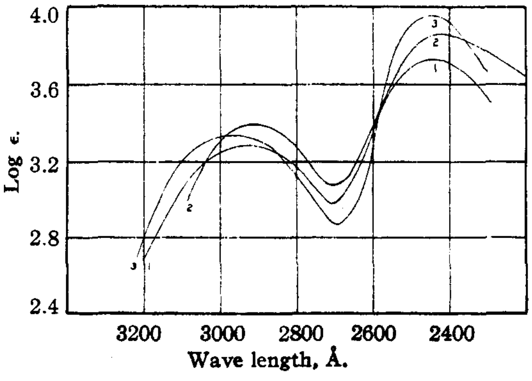


Fig. 1.—Curve 1, absorption spectrum of 2-propyl-1,2-dihydro-3,1,4-benzoxazine (3, Table I); curve 2, N-ethyl-*o*-toluidine; curve 3, spiro-[cyclohexane-2-(1,2-dihydro-3,1,4-benzoxazine)] (11, Table I).

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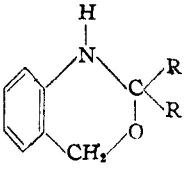
[1] Cope and Hancock, This Journal, 64, 1503 (1942); 66, 1453 (1944); Hancock and Cope, *ibid.*, 66, 1738 (1944).

[2] Hancock, Hardy, Heyl, Wright and Cope, *ibid.*, 66, 1747 (1944).

[3] Paal and Laudenheimer, *Ber.*, 25, 2967 (1892).

TABLE I

2-SUBSTITUTED-1,2-DIHYDRO-3,1,4-BENZOXAZINES,



No.	R	R′	Yield,[a] %	M. p., ° C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
1	Hydrogen	Hydrogen	74[b] A	43–44[g]	C_8H_9NO	71.09	71.02	6.71	6.90
2	Ethyl	Hydrogen	94[b] B	42.5–43.5[h]	$C_{10}H_{13}NO$	73.59	73.81	8.03	8.04
3	Propyl	Hydrogen	57[c] B	55–56[i]	$C_{11}H_{15}NO$	74.54	74.46	8.53	8.59
4	Hexyl	Hydrogen	87[d] B	42[j]	$C_{14}H_{21}NO$	76.66	76.57	9.65	9.40
5	Methyl	Methyl	56[i]	123–124.5[k]	$C_{10}H_{13}NO$				
6	Methyl	Ethyl	69[e] C	41.5–43[h]	$C_{11}H_{15}NO$	74.54	74.80	8.53	8.33
7	Methyl	Propyl	65[c] C	60–61[i]	$C_{12}H_{17}NO$	75.35	75.16	8.96	9.02
8	Methyl	Amyl	52[d] C	52–53[i]	$C_{14}H_{21}NO$	76.66	76.48	9.65	9.63
9	Methyl	Hexyl	64[f] C	49–50[i]	$C_{15}H_{23}NO$	77.24	77.14	9.94	9.90
10	Ethyl	Ethyl	64[d] C	[l]	$C_{12}H_{17}NO$	75.35	75.04	8.96	8.71
11	Spiro-cyclohexane		93[d] B[m]	95–96[n]	$C_{13}H_{17}NO$	76.81	76.97	8.43	8.64
12	Phenyl	Hydrogen	57[c] B	120–120.5[i,o]	$C_{14}H_{13}NO$				

[a] The capital letter following the yield refers to the procedure in the experimental part by which the compound was prepared. The following molar ratio of aldehyde or ketone to *o*-aminobenzyl alcohol was used in the condensation: [b] 1.5, [c] 1.0, [d] 1.1, [e] 1.4, [f] 1.2. [g] B. p. 78° (0.5 mm.). [h] Purified by sublimation at 0.07–0.15 mm. [i] Crystallized from alcohol. [j] B. p. 110° (0.08 mm.). [k] The procedure of Paal and Laudenheimer was followed (ref. 3) except that anhydrous calcium sulfate was added to remove the water formed. They report m. p. 120°. [l] B. p. 95° (0.35 mm.). [m] Refluxed six hours. [n] Crystallized from petroleum ether. [o] Ref. 3 reports m. p. 115°.

2875 Å. (log ε 3.38) (Fig. 3). N-Benzyl-*o*-toluidine, examined as a reference compound, has maxima at 2440 Å. (log ε 4.14) and 2925 Å. (log ε 3.46) (Fig. 3). In the absorption spectrum of benzylidene *o*-toluidine (Fig. 3), used as a reference compound for structure III, conjugation of the carbon–nitrogen double bond with the benzene ring results in a shift of the maxima to longer wave lengths and higher extinction values, and the maxima appear at 2600 Å. (log ε 4.19) and 3225 Å. (log ε 3.90). These data indicate the presence of a secondary aromatic amine group and the absence of a carbon–nitrogen double bond conjugated with the ring in five of the compounds listed in Table I, and consequently support structure IV. Infrared absorption spectra of compounds 3 and 12 (Table I) showed absorption peaks at 2.92 μ and 2.91 μ, respectively, in carbon tetrachloride solution.[4] These data are consistent with structure IV, since absorption peaks at about 2.9 μ are characteristic of NH groups, while OH groups show absorption peaks at about 2.8 μ. Substantiating evidence was obtained from molecular refraction data for compounds 1, 4, 9 and 10 (Table I), which are summarized in Table II. The observed molecular refractions are uniformly lower (by 0.30 to 0.48 unit) than the values calculated for the 1,2-dihydro-3,1,4-benzoxazine structure (IV), indicat-

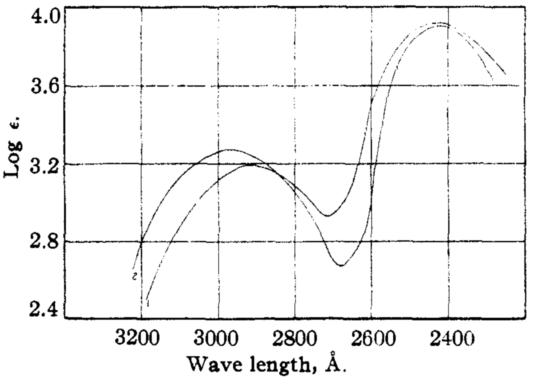


Fig. 2.—Curve 1, absorption spectrum of 2-hexyl-1,2-dihydro-3,1,4-benzoxazine (4, Table I); curve 2, 2,2-dimethyl-1,2-dihydro-3,1,4-benzoxazine (5, Table I).

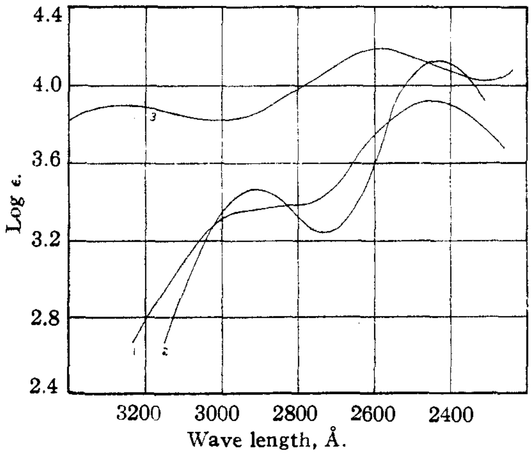


Fig. 3.—Curve 1, absorption spectrum of 2-phenyl-1,2-dihydro-3,1,4-benzoxazine (12, Table I); curve 2, N-benzyl-*o*-toluidine; curve 3, benzylidene-*o*-toluidine.

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[4] We are indebted to Drs. Ephraim Shorr and Robert F. Furchgott, The New York Hospital, New York City, for these data.

ing a characteristic optical depression.[5] The observed molecular refractions are lower by 2.14–3.47 units than the values calculated for the azomethine structure (III).

TABLE II

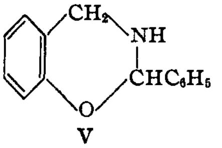
MOLECULAR REFRACTIONS OF 2-SUBSTITUTED-1,2-DIHYDRO-3,1,4-BENZOXAZINES

Compound no.[a]	n^{25}_D	d^{25}_4	Molecular refractions[b] Calcd. for III	Calcd. for IV	Found
1	1.5843[c]	1.1569	41.24	39.58	39.12
4	1.5278[c]	1.0057	69.83	67.40	67.10
9	1.5262[c]	1.0014	74.58	72.02	71.55
10	1.5502	1.0548	61.25	58.16	57.78

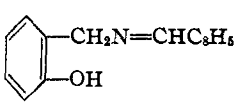
[a] See Table I for the structure of these compounds. [b] The following atomic refractions were used: C, 2.42; H, 1.10; O, 1.64 (Eisenlohr, *Z. physik. Chem.*, **75**, 605 (1910)). Nitrogen (in III), 4.10, as in alkylidene amines (von Auwers, *ibid.*, **147**, 436(1930)); nitrogen (in IV), 3.59, as in secondary aromatic amines, Brühl, *ibid.*, **16**, 503 (1895). Conjugated double bond (in III), 0.93 × mol. wt./100, (von Auwers, *ibid.*, **147**, 446(1930)). [c] Refractive indices and densities were determined on the supercooled liquids.

Chemical evidence also supports the cyclic structure for the condensation products. It was possible to isolate a crystalline condensation product from formaldehyde and *o*-aminobenzyl alcohol (1, Table I). The molecular weight of this compound in boiling chloroform shows that it is a monomer (calcd. 135, found 132). The corresponding 2-propyl derivative (3, Table I) is also monomeric (mol. wt. calcd. 177, found 177). A number of azomethines of the type (ArN=CHR)$_n$ have been shown to be dimeric or polymeric.[6] Consequently, the fact that compounds 1 and 3 (Table I) are monomers is evidence for the cyclic structure. The formation of this heterocyclic ring system is analogous to the formation of cyclic hemi-acetals from hydroxycarbonyl compounds, such as the sugars. Like their oxygen analogs, the dihydrobenzoxazines are readily hydrolyzed by dilute aqueous acids.

The condensation product of *o*-hydroxybenzylamine and benzaldehyde was prepared and examined in order to determine whether it had structure V or VI. Its ultraviolet absorption spectrum (Fig. 4) is nearly identical with the absorption spectrum of the *p*-isomer, benzylidene *p*-hydroxybenzylamine (Fig. 4). The absorption spectrum of *o*-methoxydibenzylamine (Fig. 4), prepared as a model compound for structure V, is strikingly variant. It is concluded from these data that the condensation product has the azomethine structure VI. The fact that VI does not cyclize to V may be related to the difficulty with which phenols add to the carbonyl group in acetal formation.



V



VI

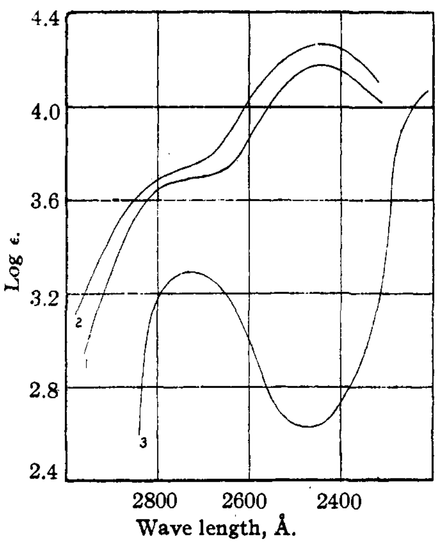
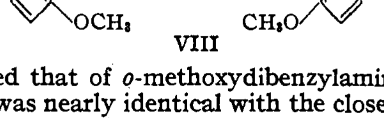
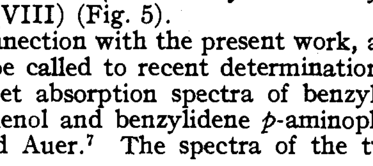


Fig. 4.—Curve 1, absorption spectrum of benzylidene-*o*-hydroxybenzylamine (VI); curve 2, benzylidene-*p*-hydroxybenzylamine; curve 3, *o*-methoxydibenzylamine.

The condensation product of formaldehyde with *o*-hydroxybenzylamine proved to be a white, crystalline solid with the empirical formula $C_{17}H_{18}N_2O_2$. Its molecular weight by the Rast method (276) was in agreement with this molecular formula. Acid hydrolysis gave a 94% yield of formaldehyde as the methone derivative, and a 62% yield of *o*-hydroxybenzylamine, both calculated on the basis of structure VII (methylene-bis-(3,4-dihydro-1,3,2-benzoxazine). The ultraviolet absorption spectrum of VII (Fig. 5) closely resembled that of *o*-methoxydibenzylamine (Fig. 4), and was nearly identical with the closer model methylene-bis-(*o*-methoxy-N-methylbenzylamine) (VIII) (Fig. 5).



VII



VIII

In connection with the present work, attention should be called to recent determinations of the ultraviolet absorption spectra of benzylidene *o*-aminophenol and benzylidene *p*-aminophenol by Kiss and Auer.[7] The spectra of the two com-

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[5] Optical depression has been observed in unsaturated heterocyclic compounds by Brühl, *Z. physik. Chem.*, **79**, 38 (1912), and von Auwers, *Ber.*, **57**, 461 (1924); also in oxazolidines (ref. 1).

[6] Kharasch, Richlin and Mayo, THIS JOURNAL, **62**, 494 (1940); Stein and Day, *ibid.*, **64**, 2569 (1942).

[7] Kiss and Auer, *Z. physik. Chem.*, **A189**, 344 (1941).

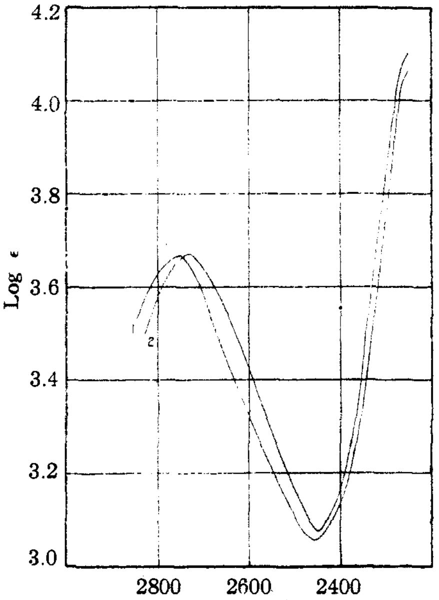

Fig. 5.—Curve 1, absorption spectrum of methylene-bis-(3,4-dihydro-1,3,2-benzoxazine) (VII); curve 2, methylene-bis-(N-methyl-*o*-hydroxybenzylamine) (VIII).

pounds are similar and divergent from those of aromatic secondary amines, indicating that they are azomethines. The infrared absorption spectrum of benzylidene *o*-aminophenol, however, is stated to indicate that the compound has a cyclic structure.[8]

Experimental[9]

Condensation of Aldehydes and Ketones with *o*-Aminobenzyl Alcohol.—*o*-Aminobenzyl alcohol was prepared by the method of Coleman and Johnson.[10] The following experimental conditions were used for the condensations. Properties and yields of the products are recorded in Table I.

A. Formaldehyde.—Five ml. of a 37% U. S. P. formaldehyde solution (equivalent to 0.06 mole of formaldehyde) was added slowly with cooling to 5 g. (0.04 mole) of *o*-aminobenzyl alcohol suspended in 25 ml. of water. The mixture was then stirred vigorously with 25 ml. of benzene. The benzene layer was separated, and the aqueous layer was extracted twice with 25-ml. portions of benzene. The combined benzene solutions were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The brown oil which remained was distilled through a short Vigreux column.

B. Other Aldehydes.—The liquid aldehydes were purified by distillation before use. To a solution of 0.08–0.10 mole of *o*-aminobenzyl alcohol in 75 ml. of benzene, 1.0–1.5 molar equivalents of aldehyde was added. The solution was refluxed under a constant water separator[11] for thirty minutes. The benzene was removed *in vacuo*, and the residue was purified by distillation, sublimation, or crystallization.

C. Ketones.—Procedure B was used with the following modifications, except in the case of acetone and cyclohexanone. Glacial acetic acid (0.03–0.05 mole) was used as a catalyst to condense 0.02–0.21 mole of *o*-aminobenzyl alcohol with 1.0–1.4 molar equivalents of the ketone. After the solution had refluxed under a continuous water separator for two to three hours, it was cooled, washed free of acetic acid with 5% aqueous sodium bicarbonate and dried over anhydrous sodium sulfate. The products were isolated as in procedure B.

***o*-Hydroxybenzylamine.**—*o*-Hydroxybenzaldoxime was prepared by an adaptation of the method described by Bousquet[12] for preparing heptaldoxime. The crude oxime was purified by distillation, b. p. 155° (24 mm.), m. p. 57°. *o*-Hydroxybenzylamine was obtained from the oxime in good yield by catalytic reduction. In preliminary trials, the oxime was hydrogenated in alcohol saturated with ammonia and in dioxane solution in the presence of Raney nickel catalyst at room temperature and eighty atmospheres pressure. Impure products were obtained. Hydrogenation of 10 g. of the oxime in 90 ml. of glacial acetic acid in the presence of 1 g. of palladinized charcoal[13] gave 4 g. of bis-*o*-hydroxybenzylamine, m. p. 166–167°. The procedure of Hartung[13] for reducing aromatic oximes was satisfactory except that a large volume of absolute alcohol was required to dissolve the oxime hydrochloride and keep the amine hydrochloride which was formed in solution. The ethylsulfates of both the oxime and *o*-hydroxybenzylamine were found to be more soluble than the hydrochlorides, so that a smaller volume of absolute alcohol could be used, as illustrated in the following procedure.

To 150 ml. of absolute alcohol, 24 ml. of concd. sulfuric acid was added with cooling. *o*-Hydroxybenzaldoxime (20 g.) was dissolved in the solution, and 0.5 g. of palladinized charcoal[13] was added. Reduction was carried out at one to two atmospheres pressure and the temperature inside the bottle was kept between 20 and 30° by cooling with dry ice or cold water. Below 20°, the salts began to crystallize and reduction stopped. Hydrogenation was complete in two to three hours. The catalyst was removed by filtration, 75 ml. of benzene was added, and the solvent was distilled *in vacuo*. The crystalline residue of the ethylsulfate was dissolved in 100 ml. of water and 60 ml. of 28% aqueous ammonia was added. The solution was cooled and the precipitate which formed slowly was filtered, washed with 3-50 ml. portions of water to remove ammonium sulfate, and dried, yielding 14 g. of *o*-hydroxybenzylamine, m. p. 126–127°. Extraction of the filtrate with methylene chloride in a continuous extractor gave an additional 3.5 g., m. p. 120–123°, making the total yield 98%. *o*-Hydroxybenzaldoxime has been reduced to *o*-hydroxybenzylamine in excellent yield by Raiford and Clark[14] with sodium amalgam in a slightly alkaline solution.

Benzylidene *o*-Hydroxybenzylamine (VI).—A solution of 2 g. of *o*-hydroxybenzylamine and 3 g. of benzaldehyde in 50 ml. of benzene was allowed to remain at room temperature for one hour and refluxed for one hour under a constant water separator. The benzene was removed *in vacuo* and the residue was extracted with petroleum ether to remove excess benzaldehyde. One crystallization from 80% alcohol gave 2.4 g. (70%), m. p. 106–108°. After three additional crystallizations the m. p. was 106–107°.

Anal. Calcd. for $C_{14}H_{13}NO$: C, 79.59; H, 6.20. Found: C, 79.63; H, 6.27.

***m*-Nitrobenzylidene *o*-Hydroxybenzylamine.**—*o*-Hydroxybenzylamine (5 g.) and *m*-nitrobenzaldehyde (6.2 g.) were condensed by the above procedure. The yellow product was crystallized from benzene to give 9.5 g. (90%), m. p. 123–125°. The analytical sample was recrystallized twice from alcohol, m. p. 125.5–126°.

Anal. Calcd. for $C_{14}H_{12}N_2O_3$: C, 65.61; H, 4.72. Found: C, 65.68; H, 4.81.

Methylene-bis-(3,4-dihydro-1,3,2-benzoxazine) (VII).—U. S. P. formalin (15 ml.) was added with vigorous shaking

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[8] Snyder, Levin and Wiley, THIS JOURNAL, **60**, 2025 (1939), quoting unpublished data of Rodebush, Buswell and Roy.

[9] Boiling points and melting points are uncorrected.

[10] "Organic Syntheses," Vol. 21, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 10.

[11] Any small constant water separator may be used, such as the one described in THIS JOURNAL, **63**, 3452 (1941).

[12] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 313.

[13] Hartung, THIS JOURNAL, **50**, 3370 (1928).

[14] Raiford and Clark, *ibid.*, **45**, 1740 (1923).

to a suspension of 9 g. of *o*-hydroxybenzylamine in 50 ml. of water and 50 ml. of benzene in a separatory funnel. The emulsion that formed was filtered, thus removing a white solid (4.6 g.), m. p. 152–153°. The benzene layer in the filtrate was separated and the aqueous layer was extracted twice with 25-ml. portions of benzene. The combined benzene extracts were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. Five grams of light brown crystals remained, m. p. 136–147°. Recrystallization of this material from absolute alcohol gave 2.8 g. of white crystals, m. p. 152–154°, making the total yield 7.4 g. (72%). The analytical sample was crystallized from absolute alcohol, m. p. 154–155°.

Anal. Calcd. for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N 9.92; mol. wt., 282. Found: C, 72.28; H, 6.61; N, 9.77; mol. wt. (Rast method in camphor), 277, 267, 284.

Acid hydrolysis was carried out under the following conditions. A 0.151-g. sample of V was dissolved in 50 ml. of water containing 1 ml. of concd. sulfuric acid and the solution was distilled slowly into an excess of methone dissolved in 5% alcohol. The formaldehyde-methone was filtered on a sintered glass crucible and washed with water; m. p. 187–188°, yield 0.440 g. (94%). An excess of potassium carbonate solution was added to the distillation residue from a similar hydrolysis. A solid precipitated, and the suspension was extracted continuously with methylene chloride. Removal of the methylene chloride gave a 62% yield of *o*-hydroxybenzylamine, m. p. 120–125°. After sublimation it had a m. p. and mixed m. p. with a known sample of 127.5–128°.

In absolute alcohol solution V reacted with picric acid to yield the picrate of *o*-hydroxybenzylamine, which was crystallized from an absolute alcohol–ether–pentane mixture, m. p. and mixed m. p. with a known sample 221–222° (dec.).

Anal. Calcd. for $C_{13}H_{12}N_4O_8$: N, 15.91. Found: N, 16.05.

Ultraviolet Absorption Spectra.—A Hilger medium quartz spectrograph with a rotating sector was used to obtain the absorption spectra. A hydrogen discharge tube was employed as the light source. In every determination absolute ethanol was the solvent. In Figs. 1–5 the logarithms of the molar extinction coefficients are plotted against the wave lengths in ångström units. Compounds used for the absorption spectra measurements which are not described earlier in the Experimental Part were prepared as follows. Benzylidene *o*-toluidine[15] was prepared from benzaldehyde and *o*-toluidine by procedure B and distilled through a Widmer column; b. p. 133° (1.2 mm.). N-Benzyl-*o*-toluidine[16] was prepared by hydrogenation of benzylidene-*o*-toluidine in the presence of Raney nickel at 65–125° and purified by crystallization from petroleum ether, m. p. 59.5–60.0°. N-Ethyl-*o*-toluidine was distilled through a Widmer column, b. p. 91° (10 mm.).

***o*-Methoxydibenzylamine.**—To 13.6 g. of *o*-methoxybenzaldehyde dissolved in 25 ml. of absolute alcohol, 10.7 g. of benzylamine in 25 ml. of absolute alcohol was added slowly with cooling. Platinum oxide (0.5 g.) was suspended in 25 ml. of absolute alcohol, hydrogenated, and the above solution was added. The mixture was hydrogenated during thirty-five minutes at one to two atmospheres pressure. The catalyst was removed by filtration and rinsed with benzene. The filtrate was distilled through a Widmer column. The yield of *o*-methoxydibenzylamine was 19.4 g. (86%); b. p. 154° (1.3 mm.); $n^{25}D$ 1.5735; d^{25}_4 1.0678; *M*D calcd. 69.42, found 70.19.

Anal. Calcd. for $C_{15}H_{17}NO$: C, 79.26; H, 7.54. Found: C, 79.43; H, 7.30.

Methylene-bis-(N-methyl-*o*-methoxybenzylamine) (VIII).—A solution of 27.2 g. of *o*-methoxybenzaldehyde and 24 ml. of a 35% aqueous solution of methylamine in 75 ml. of alcohol was reduced by the method described above. N-Methyl-*o*-methoxybenzylamine[17] was obtained in 98% yield, 29.6 g., b. p. 103° (10 mm.); $n^{25}D$ 1.5299; d^{25}_4 1.0175; *M*D calcd. 45.41, found 45.90.

Anal. Calcd. for $C_9H_{13}NO$: C, 71.49; H, 8.6. Found: C, 71.66; H, 8.86.

A solution of 18.8 g. of N-methyl-*o*-methoxybenzylamine in 50 ml. of benzene was shaken with 8.5 ml. of formalin and 15 ml. of water for fifteen minutes. The benzene solution was separated, washed once with 15 ml. of water, dried over anhydrous sodium sulfate, and filtered. Distillation through a Widmer column gave 15.8 g. of a yellow oil, b. p. 195° (2.5 mm.). Redistillation of 8 g. through a short insulated Vigreux column yielded 6 g. of a light yellow oil, b. p. 165° (0.6 mm.); $n^{25}D$ 1.5538; d^{25}_4 1.0632; *M*D calcd. 91.90, found 93.24.

Anal. Calcd. for $C_{19}H_{26}N_2O_2$: C, 72.58; H, 8.34. Found: C, 72.94; H, 8.29.

Benzylidene *p*-Hydroxybenzylamine.—*p*-Hydroxybenzaldoxime, m. p. 110–112°, was hydrogenated in the presence of palladinized charcoal. Concd. sulfuric acid (12 ml.) was added slowly with cooling to a solution of 10 g. of the oxime in 100 ml. of absolute alcohol. On shaking in the presence of 0.5 g. of palladinized charcoal, two molar equivalents of hydrogen were absorbed in thirty minutes. The catalyst was removed by filtration, and the filtrate was evaporated to dryness *in vacuo*. Upon cooling, the ethylsulfate of *p*-hydroxybenzylamine crystallized. It was filtered on a sintered glass funnel and used directly for preparing the benzylidene derivative.

This salt (6 g.) was dissolved in 15 ml. of water and brought to a *p*H of 9 with a solution of potassium carbonate. To this mixture was added 5 ml. of benzaldehyde in 25 ml. of ether. An additional 25 ml. of water was added and the aqueous layer was extracted with three 25 ml. portions of ether. Unreacted *p*-hydroxybenzylamine, m. p. 105–107°[18] (1 g.) was recovered from the aqueous layer by filtration. The ether layer was dried over anhydrous calcium sulfate, filtered, and concentrated *in vacuo*. One gram of benzylidene *p*-hydroxybenzylamine, m. p. 137–140°, was obtained. After one crystallization from alcohol it melted at 143–144°. The m. p. was unchanged on sublimation at 0.05 mm.

Anal. Calcd. for $C_{14}H_{13}NO$: N, 6.63. Found: N, 6.35.

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Summary

The condensation products of aldehydes and ketones with *o*-aminobenzyl alcohol have been shown to be 2-substituted-1,2-dihydro-3,1,4-benzoxazines (IV), rather than azomethines (III). The condensation product of benzaldehyde and *o*-hydroxybenzylamine is benzylidene *o*-hydroxybenzylamine (VI), while the product obtained from formaldehyde and *o*-hydroxybenzylamine is the cyclic compound, methylene-bis-(3,4-dihydro-1,3,2-benzoxazine) (VII). These structures are based upon ultraviolet absorption spectra, supported in some cases by molecular refraction data and chemical evidence.

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[15] von Auwers and Ottens, *Ber.*, **57**, 446 (1924).

[16] Mailhe, *Compt. rend.*, **172**, 280 (1921); Courtot and Peticolas, *Bull. soc. chim.*, **39**, 452 (1926).

[17] Prepared recently by another method by Wojahn and Erdelmeier, *Arch. Pharm.*, **280**, 223 (1942).

[18] Jones and Pyman, *J. Chem. Soc.*, **127**, 2588 (1925).