

is slightly lower than that of toxicarol. The velocity of fatality of deguelin increases with increase in concentration at a higher rate than that of toxicarol (half again as high), but this rate is lower for tephrosin (less than half that of toxicarol). The rate of increase for rotenone is double that of toxicarol. At higher concentrations, when the rate of increase decreases, toxicarol is slightly more toxic than deguelin and tephrosin is considerably less toxic; for example, at a concentration of 0.20 mg. per liter the survival times are, respectively, 139, 175 and 274 minutes. Rotenone at higher concentrations is considerably more toxic than toxicarol; at a concentration of 0.20 mg. per liter the survival time is sixty-five minutes. According to Powers' formula, which is an expression of relative toxicity considering the first two factors only, the three substances studied have the following decreasing order of toxicity: toxicarol, deguelin and tephrosin. Their toxicities are 65, 56 and 23%, respectively, of that of rotenone.

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[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY AND  
THE LABORATORY FOR PURE RESEARCH OF MERCK AND COMPANY]

## CATALYTIC REDUCTION OF MIXTURES OF PARA-NITRO- AND NITROSOPHENOLS WITH ALDEHYDES AND KETONES

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In connection with an attempt to prepare certain O-arylhydroxylamines it was noted that when the product that was formed by the catalytic reduction of 2,4-dinitrophenol in solution in acetone was benzoylated by the usual method of Schotten-Baumann, the compound expected, (2,4-bis-benzaminophenyl) benzoate, m. p. 233°,<sup>1</sup> was not obtained. Analyses indicated that the new compound contained one C<sub>3</sub>H<sub>6</sub> group more than does (2,4-bis-benzaminophenyl) benzoate. When, however, the solvent that was used was either dioxane or isopropyl alcohol instead of acetone the expected (2,4-bis-benzamino-phenyl) benzoate was formed.

These facts pointed to the probability of a condensation taking place between acetone and the phenol during the reduction.

A solution of 2,4-dinitrophenetole<sup>2</sup> was then catalytically reduced and benzoylated. The compound that was obtained was found to be the expected new compound (2,4-bis-benzamino)-phenetole.

Thinking that the phenol group might have something to do with the peculiar course of the reduction in the first case mentioned, ortho, meta and para nitrophenols were catalytically reduced in solution in acetone.

When *p*-nitrophenol was catalytically reduced in the presence of acetone

<sup>1</sup> Post and Stuckenberg, *Ann.*, 205, 69 (1880).

<sup>2</sup> Willgerodt, *Ber.*, 12, 764 (1879).

some *p*-aminophenol was formed, but there was also obtained another product which was soluble in alkalis and acids and which could be separated from *p*-aminophenol by shaking a solution of the two in acids with benzaldehyde, which combined with and precipitated the *p*-aminophenol.<sup>3</sup> This other product was shown to be the same compound that was formed by the catalytic reduction of 4-(isopropylidene-amino)-phenol,  $(\text{CH}_3)_2\text{C}=\text{NC}_6\text{H}_4\text{OH}$ ,<sup>4</sup> and corresponded in every way to 4-(isopropyl-amino)-phenol which had previously been prepared by the action of isopropyl chloride on *p*-aminophenol.<sup>5</sup> Various derivatives were made, including the hydrochloride, dibenzoyl derivative, the nitroso derivative and the phenyl isocyanate addition product.

When, however, *o*-nitrophenol was catalytically reduced in the presence of acetone no (2-isopropylamino)-phenol was formed but when the reduction product was benzoylated (2-benzamino-phenyl) benzoate<sup>6</sup> was obtained. Also when *m*-nitrophenol was reduced in the presence of acetone, no *m*-isopropylaminophenol could be detected.

Obviously, therefore, the compound that was formed by the benzoylation of the reduction product of the mixture of 2,4-dinitrophenol and acetone was (2-benzamino-4-benzoyl-(isopropyl)-amino)-phenyl benzoate,  $2,4-(\text{C}_6\text{H}_5\text{CONH})(\text{C}_6\text{H}_5\text{CONCH}(\text{CH}_3)_2)\text{C}_6\text{H}_4\text{-OCOC}_6\text{H}_5$ .

The course of the reaction was not simply a condensation between the *p*-aminophenol formed during the reduction and the acetone which was present, followed by further reduction. This was shown by catalytically reducing a mixture of *p*-aminophenol and of acetone. No 4-(isopropyl-amino)-phenol was obtained.

By a similar process (4-*sec*-butylamino)-phenol was formed by the reduction of a mixture of *p*-nitrophenol and methyl ethyl ketone, and 4-(*amyl*-3-amino)-phenol hydrochloride,  $p-(\text{C}_2\text{H}_5)_2\text{CHNHC}_6\text{H}_4\text{OH}\cdot\text{HCl}$ , was formed from the reduction products of a mixture of *p*-nitrophenol and diethyl ketone.

However, when *p*-nitrophenol was reduced in the presence of acetophenone or menthone, only *p*-aminophenol was obtained.

Also, when nitrobenzene was catalytically reduced in the presence of acetone, no *n*-isopropylaniline was formed.

On the other hand, good yields of 4-(isopropylamino)-phenol were obtained by the reduction of *p*-nitrosophenol in the presence of acetone.

Attention was next directed to the possibility of condensation between 4-nitrophenols and aldehydes during reduction. No definite, crystalline

<sup>3</sup> German Patent 208,434.

<sup>4</sup> Haegel, *Ber.*, **25**, 2755 (1892); Michaelis and Luxembourg, *ibid.*, **27**, 3006 (1894).

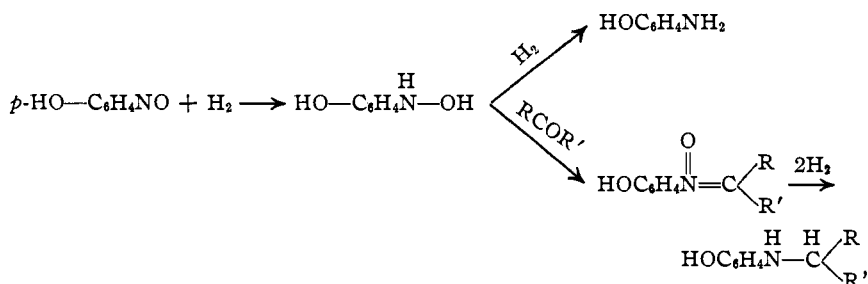
<sup>5</sup> Buc, U. S. Patent 1,555,452, September 29, 1925.

<sup>6</sup> (a) Ladenburg, *Ber.*, **9**, 1529 (1876). (b) Hinsberg and Udranszky, *Ann.*, **254**, 256 (1889).

condensation products were isolated when *p*-nitrophenol was catalytically reduced in the presence of either formaldehyde or acetaldehyde. However, when a mixture of *p*-nitrophenol, benzaldehyde and an inert solvent such as methanol was catalytically reduced, a considerable yield of 4-(dibenzylamino)-phenol<sup>7</sup> was obtained.

It was also found that reduction of a mixture of *p*-aminophenol and benzaldehyde gave a good yield of 4-(dibenzylamino)-phenol.

A complete explanation of the rather peculiar reactions that have been recorded is not at present clear. However, in the case of the reduction of mixtures of ketones and *p*-nitro- and nitrosophenols it seems clear that some intermediate product formed during reduction of the substituted phenols condensed with the ketone and the condensation product was, in turn, reduced. The most likely intermediate products that could behave in this way are the corresponding hydroxylamines. It has been shown by Hoffmann and Victor Meyer that hydroxylamines are formed as intermediate products in the reduction of many nitro compounds.<sup>8</sup> According to this conception the reaction must proceed in the following manner



Apparently a hydroxy group in the para position to the nitrogen atom must increase the chemical activity of the hydroxylamine group which is formed during the reduction. That this is probably true is indicated by the fact that while zinc dust and water reduce nitrobenzene and most of its derivatives to phenyl hydroxylamines,<sup>9</sup> the same agents reduce *p*-nitrophenols to *p*-aminophenols.<sup>10</sup>

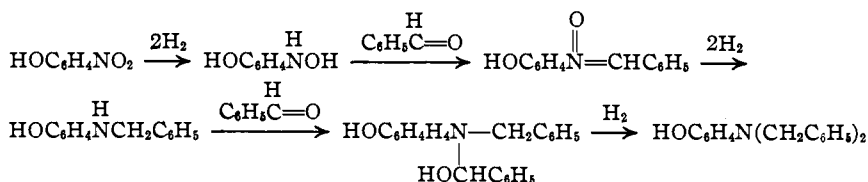
In the case of the reduction of a mixture of *p*-nitrophenol and benzaldehyde, the same sort of reaction probably occurred at first and then due to the greater activity of aldehydes as compared with ketones condensation took place between the aldehyde and the secondary amine which had been formed. Finally, there was reduction of the new condensation product. The reaction may be represented as follows

<sup>7</sup> Bakunin, *Gazz. chim. ital.*, II, 36, 211 (1906); *Chem. Centr.*, II, 1413 (1906).

<sup>8</sup> Hoffmann and V. Meyer, *Ber.*, 24, 3528 (1891).

<sup>9</sup> Bamberger, *ibid.*, 27, 1348, 1548 (1894); Wohl, *ibid.*, 27, 1432 (1894).

<sup>10</sup> Bamberger, *ibid.*, 28, 250 (1895).



### Experimental Part

**General Method of Reduction.**—All of the reductions described in this paper were carried out in a Burgess-Parr Reduction Apparatus.<sup>11</sup> The hydrogenation catalyst was in every case platinum oxide.<sup>12</sup>

**Reduction Followed by Direct Benzoylation of the Reduction Product.**—The appropriate mixtures shown in Table I were reduced. The reduction products were diluted with water and benzoylated with a mixture of benzoyl chloride and sodium hydroxide.

TABLE I  
REDUCTION EXPERIMENTS

Solid	Mixture reduced	Solvent	Solid product obtained		Formula	Nitrogen, %	
			M. p., °C.	Crystallized from		Calcd.	Found
2,4-Dinitrophenol		Acetone	171	Alc.	C <sub>30</sub> H <sub>26</sub> O <sub>4</sub> N <sub>2</sub>	5.86	6.11
2,4-Dinitrophenol		Isopropyl alc.	233 <sup>b</sup>	.. <sup>c</sup>	.....	..	..
2,4-Dinitrophenetole		Acetone <sup>a</sup>	189	Alc.	C <sub>22</sub> H <sub>20</sub> O <sub>2</sub> N <sub>2</sub>	7.78	7.80 7.57 <sup>d</sup>

<sup>a</sup> The same compound was obtained when other solvents such as 1,4-dioxane, methanol and glacial acetic acid were used in place of acetone. <sup>b</sup> Post and Stuckenberg, Ref. 1, give 231–233° as the m. p. of 2,4-(bis-benzamino)-phenyl benzoate and state that the compound is insoluble in alcohol. <sup>c</sup> Insoluble in alcohol. <sup>d</sup> *Mol. wt.* Calcd. for C<sub>22</sub>H<sub>20</sub>O<sub>2</sub>N<sub>2</sub>: 360. Found: 362, 365 (Menzies-Wright method).<sup>13</sup>

**Hydrolysis of 2,4-(Bis-benzamino)-phenetole.**—A solution of 2.5 g. of 2,4-(bis-benzamino)-phenetole in concentrated hydrochloric acid was heated in a sealed tube at 155–160° for four hours. After the tube had been cooled long needle-like crystals were found in the solution. These were filtered and the filtrate extracted with ether. The solid which was left after the ether had been evaporated and the above-mentioned solid precipitate were identified as benzoic acid by their solubility in organic solvents and alkalies, relatively slight solubility in water and the melting point of 121–122°,<sup>14</sup> yield 71%.

The acid filtrate described above was evaporated to dryness *in vacuo*. One gram of solid remained. To 0.3 g. of this was added a dilute aqueous solution of picric acid.

A pale yellow precipitate formed which was recrystallized from dilute alcohol; decomposition point 120°.<sup>15</sup>

Another portion of the solid left after excess of hydrochloric acid had been evaporated was dissolved in water and benzoylated with benzoyl chloride and sodium hydroxide. A

<sup>11</sup> Manufactured by the Burgess-Parr Company, Moline, Illinois.

<sup>12</sup> Adams and Shriner, *THIS JOURNAL*, **45**, 2171 (1923).

<sup>13</sup> Menzies and Wright, Jr., *ibid.*, **43**, 2314 (1921).

<sup>14</sup> Reissert, *Ber.*, **23**, 2244 (1890), gives 121.25° as the m. p. of benzoic acid.

<sup>15</sup> Lumière and Seyewetz, *Bull. soc. chim.*, [III] **9**, 597 (1893), give 120° as the decomposition point of 2,4-diaminophenol picrate.

solid was obtained which was relatively insoluble in alcohol; m. p. 233°. A mixture with 2,4-(bis-benzamino)-phenyl benzoate also melted at 233°.

**Reduction of a Mixture of *p*-Nitrophenol and Acetone.**—A solution of 0.18 mole of *p*-nitrophenol in one mole of acetone was reduced. When the reduction was complete the solution was evaporated to dryness. The residue was then extracted with hot benzene. The portion which did not dissolve was soluble in hot acetone, m. p. 184° with decomposition.<sup>16</sup>

When the above-mentioned solution in hot benzene was cooled, a solid precipitated which melted with decomposition at 143°. The filtrate from this was evaporated to dryness. An oil remained, most of which was insoluble in dilute acids. It was accordingly washed with dilute hydrochloric acid and extracted with ether. Evaporation of the ether left a solid which was recrystallized from benzene; m. p. 115°. A mixture of *p*-nitrophenol with this compound also melted at 115°. It was soluble in dilute alkalis.

The above-mentioned solid, m. p. 143°, was dissolved in dilute acetic acid and the solution shaken with an excess of benzaldehyde for ten minutes. The excess benzaldehyde and any condensation product with it was extracted with ether. The acid layer was neutralized with sodium carbonate. A cream colored precipitate formed which was recrystallized from benzene; m. p. 155–156° with some decomposition; yield, 45%. It occurred in the form of fine white needles.

*Anal.* Calcd. for C<sub>9</sub>H<sub>10</sub>ON: C, 71.47; H, 8.67; N, 9.27; mol. wt., 151.11. Found: C, 71.4, 71.72; H, 8.95, 8.77; N, 9.64; mol. wt. (Menzies-Wright method),<sup>13</sup> 150.

**4-(Isopropyl-(nitroso)-amino)-phenol, *p*-C<sub>6</sub>H<sub>7</sub>N(NO)C<sub>3</sub>H<sub>7</sub>OH.**—A cold solution of 0.5 g. of 4-(isopropylamino)-phenol in dilute hydrochloric acid was treated with an aqueous solution of 0.25 g. of sodium nitrite in water. After standing for a short while, salt solution was added and the solution was extracted with ether. When the ether was evaporated a yellow solid was left which was soluble in dilute alkalis but insoluble in acids. It gave the Liebermann nitroso reaction.<sup>17</sup> It was recrystallized from benzene; m. p. 112–113°.

*Anal.* Calcd. for C<sub>9</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: N, 15.54. Found: N, 15.05.

**4-(Phenylcarbamino-(isopropyl)-amino)-phenol.**—A solution of 0.4 g. of *p*-isopropylamino-phenol and 0.6 g. of phenyl isocyanate in dry benzene was heated to boiling. A white precipitate formed. The solution was cooled and the solid was filtered off. It was insoluble in dilute acids but soluble in dilute alkali. It was recrystallized from benzene; m. p. 214–215° with some decomposition.

*Anal.* Calcd. for C<sub>16</sub>H<sub>18</sub>O<sub>2</sub>N<sub>2</sub>: N, 10.38. Found: N, 10.80, 10.79.

**4-Isopropylamino-phenol.**—A solution of 2.5 g. of 4-(isopropylidene-amino)-phenol in alcohol was reduced. After completion of the reduction the alcohol was evaporated. A solid remained which was recrystallized from benzene; m. p. 155–156°. A mixture of this solid with the compound, m. p. 155–156°, obtained by the catalytic reduction of a mixture of *p*-nitrophenol and acetone also melted at 155–156°.

**Reduction of a Mixture of a Nitrophenol and a Ketone Followed by Treatment of the Reduction Product with Nitrous Acid.**—A solution of the nitrophenol in the ketone, and methanol, also when the ketone was diethyl ketone, was reduced. The volatile material was then evaporated *in vacuo* at room temperature. The residue was dissolved in cold dilute hydrochloric acid. A cold aqueous solution of sodium nitrite was then added. The nitroso derivative of the *sec*-alkylaminophenol precipitated.

<sup>16</sup> Lossen, *Ann.*, **175**, 296 (1875), gives 184° as the decomposition point of *p*-amino-phenol.

<sup>17</sup> Liebermann, *Ber.*, **7**, 248, 806, 1098 (1874).

TABLE II  
 RESULTS OF EXPERIMENTS

Nitrophenol	Ketone	Nitroso derivative yield, %	M. p., °C.	Formula	Nitrogen, %	
					Calcd.	Found
Ortho	Acetone	Negl. <sup>a</sup>	....	.....	...	.....
Para	Diethyl	60	89-90 <sup>b</sup>	C <sub>11</sub> H <sub>16</sub> O <sub>2</sub> N <sub>2</sub>	13.44	13.21 13.57

<sup>a</sup> A portion of the residue left after acetone had been evaporated was benzoylated with a mixture of benzoyl chloride and dilute sodium hydroxide. A solid formed which was recrystallized from alcohol; m. p. 182°. <sup>b</sup> Purified by dissolving in alcohol, treating with decolorizing carbon, filtering and reprecipitating with water. It was then twice recrystallized from a one to one mixture of benzene and petroleum ether and finally dissolved in glacial acetic acid and reprecipitated with water.

**Separation of the Alkyl Aminophenols by Treatment of the Reduction Products with Benzaldehyde.**—After the reduction was complete the volatile solvents were evaporated *in vacuo*. The residue was dissolved in dilute acetic acid. The solution was shaken with a slight excess of benzaldehyde and then extracted with ether. The aqueous solution was then made neutral with sodium carbonate. Any alkylaminophenol which had been formed during the reduction precipitated. These phenols darkened when they were exposed to air and light. All were soluble in acids and alkalies.

 TABLE III  
 EXPERIMENTAL DATA

Solid	Mixture reduced	Ketone	Product obtained		Formula	Nitrogen, %	
			Yield, %	M. p., °C.		Calcd.	Found
<i>m</i> -Nitrophenol	Acetone	Acetone	Negl.	....	.....	..	.....
<i>p</i> -Aminophenol	Acetone	Acetone	No	....	.....	..	.....
<i>p</i> -Nitrophenol	Methyl ethyl <sup>a</sup>	Methyl ethyl <sup>a</sup>	34	118-119 <sup>c</sup>	C <sub>10</sub> H <sub>16</sub> ON	8.50	8.80 8.68
<i>p</i> -Nitrophenol	Menthone <sup>a</sup>	Menthone <sup>a</sup>	No	....	.....	..	.....
Nitrobenzene	Acetone	Acetone	No <sup>b</sup>	....	.....	..	.....
<i>p</i> -Nitrosophenol	Acetone	Acetone	54	155-156 <sup>d</sup>	C <sub>9</sub> H <sub>13</sub> ON	9.27	9.12 9.22

<sup>a</sup> The mixture to be reduced was diluted with methyl alcohol.

<sup>b</sup> No oil precipitated when the acid solution was treated with sodium carbonate, nor could any be extracted with ether. Another portion of the oily residue from the reduction was treated with benzoyl chloride and sodium hydroxide. The solid which formed was recrystallized from alcohol. White platelets were obtained; m. p. 161°. A mixture of this compound with pure benzanilide also melted at 161°. The last portion of the oily residue was distilled. After a small amount of acetone and other low-boiling material had distilled over, the rest all distilled at about 184°, <sup>19</sup> and the temperature of the distilling liquids never rose to the boiling point of *N*-isopropylaniline. <sup>20</sup>

<sup>c</sup> Recrystallized three times from toluene.

<sup>d</sup> Recrystallized from benzene.

**Reduction of a Mixture of *p*-Nitrophenol and Acetophenone.**—A solution of 0.05 mole of *p*-nitrophenol, and 0.05 mole of acetophenone in alcohol was reduced. A precipitate formed. It was filtered off; m. p. 184° with decomposition; <sup>18</sup> yield, 4 g. Water

<sup>18</sup> Hinsberg and Udranszky, Ref. 6 b, give 182° as the m. p. of 2-(benzamino)-phenyl benzoate.

<sup>19</sup> Thorpe, *J. Chem. Soc.*, 37, 221 (1880), gives 184° as the b. p. of aniline.

<sup>20</sup> Pictet and Crepieux, *Ber.*, 21, 1109 (1888), give 209-210° as the b. p. of *N*-isopropylaniline.

was added to the filtrate and the mixture benzoylated with benzoyl chloride and sodium hydroxide. The solid which formed was recrystallized from alcohol; m. p. 233°. <sup>21</sup>

**4-(Isopropylamino)-phenol Hydrochloride.**—Dry hydrogen chloride was passed into a solution of 4-(isopropylamino)-phenol in a mixture of chloroform and dry ether. The solid which formed was dissolved in absolute alcohol and reprecipitated with dry ether. The 4-(isopropylamino)-phenol from the reduction of 4-(isopropylidene-amino)-phenol and that formed by the reduction of a mixture of *p*-nitrophenol and acetone both gave hydrochlorides which melted at 189°; a mixture of the two also melted at 189°.

**Hydrochloride of the 4-(Isopropylamino)-phenol Obtained by the Reduction of a Mixture of *p*-Nitrophenol and Acetone.**—*Anal.* Calcd. for C<sub>9</sub>H<sub>14</sub>ONCl: Cl, 18.91. Found: Cl, 19.31, 19.18.

**Hydrochloride of the 4-(Isopropylamino)-phenol Obtained by the Reduction of 4-(Isopropylidene-amino)-phenol.**—*Anal.* Calcd. for C<sub>9</sub>H<sub>14</sub>ONCl: Cl, 18.91. Found: Cl, 18.88.

**4-(*Sec.*-alkylamino)-phenol Hydrochloride.**—A solution of 4-(*sec.*-alkylamino)-phenol or its nitroso derivative in concentrated hydrochloric acid was evaporated to dryness *in vacuo* at room temperature. Of course, oxides of nitrogen were evolved when acid was added to the nitroso derivative. The solid residue was dissolved in absolute alcohol and reprecipitated with dry ether. These hydrochlorides had no definite melting point but decomposed when heated.

TABLE IV  
EXPERIMENTAL DATA

Substituted phenol dissolved	Formula	Nitrogen, % of chloride	
		Calcd.	Found
4-( <i>Sec.</i> -butylamino)-phenol	C <sub>10</sub> H <sub>16</sub> ONCl	6.96	6.93 6.96
4-(Amyl-3-(nitroso)-amino)-phenol	C <sub>11</sub> H <sub>18</sub> ONCl	6.51	6.39 6.23

**Reduction of a Mixture of *p*-Nitrophenol and Benzaldehyde.**—A solution of 0.1 mole of *p*-nitrophenol and 0.3 mole of benzaldehyde in methanol was catalytically reduced in the usual manner. The reduced solution was then evaporated *in vacuo* to remove methanol. Ether was added to the residue. White crystals remained which decomposed at 184°, <sup>16</sup> were insoluble in water but soluble in acids and alkalis and were darkened by standing in the air in the light. The ethereal filtrate from these crystals was washed with sodium bisulfite and then sodium carbonate in order to remove benzaldehyde and acids. The ether solution was then extracted with dilute hydrochloric acid. During this extraction a solid precipitated. It was treated with dilute sodium carbonate solution and this solution was extracted with ether. Evaporation of the ether left a solid which was recrystallized from 75% alcohol; m. p. 127–128°. The same solid was obtained by addition of sodium carbonate to the extract in hydrochloric acid described above. In that case an oil precipitated which was extracted with ether. This solution was evaporated and the residue was recrystallized from 75% alcohol; m. p. 127–128°. <sup>22</sup>

*Anal.* Calcd. for C<sub>20</sub>H<sub>18</sub>ON: N, 4.85. Found: N, 5.05.

**Benzoylation of Substituted *p*-Aminophenols.**—A solution of the substituted *p*-aminophenol in sodium hydroxide was shaken for several minutes with benzoyl chloride. A solid benzoate was formed.

**Reduction of a Mixture of *p*-Aminophenol and Benzaldehyde.**—A solution of 0.05 mole of *p*-aminophenol and 0.15 mole of benzaldehyde in 20 cc. of methanol and 50

<sup>21</sup> Hinsberg and Udranszky, Ref. 6 b, give 231° as the m. p. of 4-(benzamino)-phenyl benzoate.

<sup>22</sup> Bakunin, *Gazz. chim. ital.*, II, 36, 211 (1906); *Chem. Centr.*, II, 1413 (1906), gives 127° as the m. p. of 4-(dibenzylamino)-phenol.

TABLE V  
 EXPERIMENTAL DATA

Substance	M. p., °C.	Recrystallized from	Nitrogen, %	
			Calcd.	Found
4-(Benzoyl-(isopropyl)-amino)-phenyl benzoate, $C_6H_5CON(C_3H_7)C_6H_4OCOC_6H_5$	174-175 <sup>a</sup>	EtOH	3.90	3.97
4-(Dibenzylamino-phenyl) benzoate	143-144	Iso-PrOH	3.56	3.84 3.63

<sup>a</sup> Occurred in the form of white needles.

cc. of 1,4-dioxane was reduced. When reduction was complete the solution was evaporated to dryness. An oil remained which was dissolved in ether. The ethereal solution was shaken for some time with an aqueous solution of sodium bisulfite. The ethereal layer was then washed with a solution of sodium carbonate. The ether was then evaporated. An oil remained which solidified. The solid was twice recrystallized from 75% ethyl alcohol. Needle-like almost colorless crystals were obtained, m. p. 127°; yield 73%. A mixture of these crystals with 4-dibenzylaminophenol also melted at 127°.

*Anal.* Calcd. for  $C_{20}H_{19}ON$ : N, 4.85. Found: N, 5.07, 5.08.

A study of the condensation which takes place between ketones and aldehydes with *p*-nitroaniline and *p*-phenylenediamine during reduction has also been made and will shortly be submitted for publication.

The author wishes to express his appreciation to Mr. Douglass F. Hayman for many of the analyses which are recorded in this paper.

### Summary

1. Catalytic reduction of a mixture of *p*-nitrophenol or *p*-nitrosophenol and an aliphatic ketone led to the formation of 4-(*sec*-alkyl-amino)-phenols.

2. Various derivatives of 4-(*sec*-alkyl-amino)-phenols have been prepared.

3. Catalytic reduction of 2,4-dinitrophenol and acetone led to the formation of 2-amino-4-isopropylamino-phenol.

4. There is no appreciable condensation between ketones and any of the following nitro compounds during catalytic reduction: nitrobenzene, *p*-nitrophenetole, *o*-nitrophenol, and *m*-nitrophenol.

5. There was no appreciable condensation between *p*-nitrophenol and either acetophenone or menthone during catalytic reduction.

6. 4-(Dibenzylamino)-phenol was prepared by the catalytic reduction of a mixture of benzaldehyde and *p*-nitrophenol, and also of a mixture of benzaldehyde and *p*-aminophenol.

RAHWAY, NEW JERSEY