(calcd. 34 g.). Aqueous dilution of the alcohol solution was followed by separation of the water-insoluble layer which was dried and fractionated. There was obtained 20 g. of low boiling material and 21 g. of the methyl ether which boiled at 88–92° at 30 mm.; $n^{20}_{D}$ 1.4928; $d^{20}_{4}$ 1.0239; $M_R$ calcd. 40.10; $M_R$ found, 41.57.

*Anal.* Calcd. for $C_7H_{11}ClO$: C, 57.35; H, 7.51. Found: C, 56.91; H, 7.74.

**Action of Sodium Acetate on Dichloro-1,3-hexadiene-2,4. Preparation of Acetoxy-1-chloro-3-hexadiene-2,4.**[5]—One hundred grams of the dichloro compound, 100 g. of fused sodium acetate, and 300 cc. of glacial acetic acid were refluxed together for four hours. The acetic acid was neutralized with 20% sodium hydroxide and the mixture was extracted with ether. The ether extract was dried with calcium chloride, and then distilled. Three fractionations gave 55 g. of colorless liquid boiling at 84 to 85° at 3 mm.; $d^{20}_{4}$ 1.0915; $n^{20}_{D}$ 1.4890; $M_R$ calcd., 44.61; $M_R$ found, 46.14.

*Anal.* Calcd. for $C_8H_{11}O_2Cl$: Cl, 20.31. Found: 20.58, 20.78.

## Summary

The action of aqueous hydrochloric acid on divinylacetylene yields a dihydrochloride. The compound is oxidized by permanganate with the formation of acetic acid and chloroacetic acid, and this fact together with a consideration of the probable mechanism of its formation, indicates that it has the structure dichloro-1,3-hexadiene-2,4 and that it results from two successive acts of 1,4 addition. When treated with sodium acetate its reactive (terminal) chlorine is replaced by acetoxy, and the action of methyl alcoholic potash similarly leads to the formation of a methyl ether.

(5) We are indebted to Dr. W. F. Talbot for this experiment.

WILMINGTON, DELAWARE

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[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

# The Preparation of Amines by Catalytic Hydrogenation of Derivatives of Aldehydes and Ketones

BY CHARLES F. WINANS AND HOMER ADKINS

The preparation of amines through the hydrogenation of reaction products of aldehydes or ketones with ammonia or a substituted ammonia has attracted attention for several years. For example, the catalytic hydrogenation of oximes should be a practical process for the preparation of amines. There have been a number of papers bearing on this transformation, among which the following may be noted. Mailhe used nickel for a vapor phase hydrogenation and obtained a variety of products. Wassiljew by the use of two to four times as much nickel as oxime obtained in the liquid phase small quantities of amines which he did not isolate but determined as the platinum or gold derivatives. Mignonac has several patents on the hydrogenation of oximes over nickel. Hartung used palladium for the hydrogenation of oximes in a hydrochloric acid solution and obtained good yields of various primary amines. Skita and Keil reported poor yields from the hydrogenation of several oximes over platinum and palladium.[1] In so far as the authors are aware there is no process described in the literature for the hydrogenation of oximes over nickel which has been shown to be satisfactory in the preparation of amines.

There is presented in Table I a summary of the results obtained in submitting a variety of oximes to hydrogenation for approximately one hour over nickel at approximately 100°, under a pressure of 100 atmospheres of hydrogen. It is important that the catalyst be sufficiently active so that the temperature need not be higher nor the time of reaction much longer than that specified above. It may be seen that yields of 62 to 75% of primary and of 10 to 27% of secondary amines were obtained from the oximes derived from acetone, valeraldehyde, heptaldehyde and benzaldehyde. The primary amine is a result of direct hydrogenation while the secondary amine no doubt results from the reaction of primary amine with an intermediate product, an aldimine or ketimine, *i. e.*

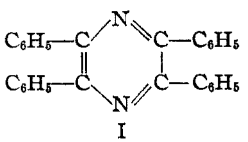
$$\mathrm{RCH{=}NOH} \xrightarrow{\mathrm{H_2}} \mathrm{RCH{=}NH} \xrightarrow{\mathrm{H_2}} \mathrm{RCH_2NH_2}$$

$$\mathrm{RCH{=}NH + RCH_2NH_2} \xrightarrow{-\mathrm{NH_3}} \mathrm{RCH{=}NCH_2R} \xrightarrow{\mathrm{H_2}} \mathrm{(RCH_2)_2NH}$$

This scheme was suggested by von Braun[2] and has been supported by results obtained in this Laboratory in the hydrogenation of cyanides.[3]

The oximes of benzophenone and camphor were hydrogenated almost quantitatively to the corresponding primary amines, no detectable amounts of secondary amines being formed. In contrast to these results the oxime of $\gamma$-phenylpropionaldehyde gave nearly equal molecular amounts of the primary and secondary amines. The oxime of cinnamaldehyde gave low yields of amines and high yields of tar.

The hydrogenation of an $\alpha$-hydroxy oxime and of an $\alpha,\beta$-dioxime also gave considerable yields of products other than the primary amines. The oxime of benzoin gave a 64% yield of $\alpha,\beta$-diphenylethanolamine accompanied by a 20% yield of tetraphenylpyrazine,[4] I. The pyrazine became the predominant product when the dioxime of benzil was submitted to hydrogenation. In this connection it should be reported that Covert in this Laboratory has found that small amounts (0.1 mole) of isonitrosopropiophenone were hydrogenated over nickel at 75–90° rapidly and almost quantitatively to 1-phenyl-2-amino-



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[1] For complete references to 1930 see Ellis, p. 274 *et seq.*, "Hydrogenation of Organic Substances," D. Van Nostrand Company, 250 Fourth Ave., New York City, 1930; Mailhe and Murat, *Bull. soc chim.*, [4] **9**, 464 (1911); Mailhe, *ibid.*, [3] **33**, 963 (1905); Wassiljew, *Ber.*, **60B**, 1122 (1930); Mignonac *Chem. Abstr.*, **23**, 154, 2446 (1929); Hartung, THIS JOURNAL, **50**, 3370 (1928); *ibid.*, **53**, 2248 (1931) Skita and Keil, *Ber.*, **65**, 428 (1932).

[2] Von Braun, Blessing and Zobel, *Ber.*, **56**, 1988 (1923).

[3] Winans and Adkins, THIS JOURNAL, **54**, 307 (1932).

[4] Braun and Meyer, *Ber.*, **21**, 1270 (1888).

propanol-1. When larger quantities (0.5 mole) were used the rate of hydrogenation was such that it was not possible to keep the temperature sufficiently low (below 95°) to prevent the formation of compounds of higher molecular weight. (The rate of hydrogenation may be lowered, and thus the rise in the temperature of the reaction mixture, by decreasing the ratio of catalyst to isonitrosopropiophenone or by interrupting the shaking of the reactants, but both of these procedures were shown to be disadvantageous.) It thus appears that the hydrogenation of the oximes of $\alpha$-keto alcohols or of $\alpha,\beta$-diketones must be very carefully controlled to avoid the interaction of amino or of amino and hydroxy groups.

Certain compounds other than oximes containing a carbon to nitrogen double bond were also submitted to hydrogenation, a summary of the data being given in Table I. The phenylhydrazone of butyraldehyde was readily hydrogenated to aniline and mono- and di-butylamines. Hydrogenolysis of the nitrogen to nitrogen bond must have preceded hydrogenation of the carbon to nitrogen double bond for the yield of dibutylamine was high, indicating the intermediate formation of butyraldimine. Azobenzene was readily converted into aniline at 90°, or at 200° into mono- and dicyclohexylamine. At the latter temperature the formation of the secondary amine is probably dependent upon the reaction of two molecules of the primary amine with the liberation of ammonia.[3] Benzaldazine underwent a smooth hydrogenation primarily to benzylamine, accompanied by dibenzylamine and a small amount of tribenzylamine. The latter is the only tertiary amine isolated from the hydrogenations reported in this paper. It seems probable that it was formed as suggested by von Braun through the interaction of benzaldimine and previously formed dibenzylamine, *i. e.*

$$C_6H_5CH{=}NH + (C_6H_5CH_2)NH \longrightarrow C_6H_5CH(NH_2)N(CH_2C_6H_5)_2 \xrightarrow[+H_2]{-NH_3} (C_6H_5CH_2)_3N$$

The preparation of amines through the hydrogenation of the reaction products of aldehydes or ketones with ammonia was first utilized by Mignonac,[5] who submitted ammoniacal solutions of aldehydes or ketones to the action of hydrogen over nickel. However, much better results have been obtained in this Laboratory if the reaction product of the aldehyde or ketone with ammonia were isolated before hydrogenation was attempted. The reaction of ammonia and various aldehydes may result in the formation of several types of compounds each of which behaves very differently when submitted to hydrogenation, so that the structure of the aldehyde plays an important role in determining the nature and ratio of products.

Furfural reacts with ammonia with the formation of hydrofuramide (II). The latter when submitted to the action of hydrogen over nickel underwent hydrogenolysis at one of the carbon to nitrogen linkages and hydrogenation

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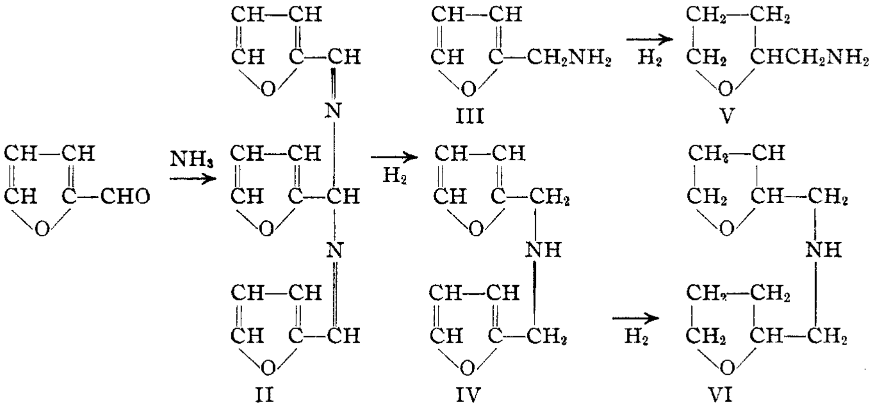
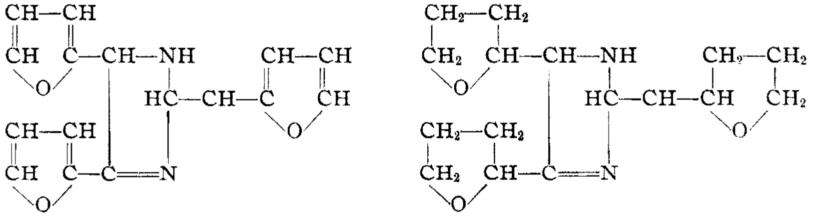
(5) Mignonac, *Compt. rend.*, **172**, 223 (1921).

at the carbon to carbon and carbon to nitrogen double bonds. The final products were equimolecular amounts of mono- and di-tetrahydrofurfurylamine (V and VI), although the corresponding furfurylamines (III and IV) were found among the products of incomplete hydrogenation.



This conversion of an aldehyde by means of ammonia and hydrogen to equimolecular amounts of the corresponding primary and secondary amines goes smoothly with benzaldehyde and trimethylacetaldehyde as well as with furfural. The yields reported in Table I for amines from the hydroamide of trimethylacetaldehyde were low not because of any side reactions but because of the mechanical losses incident to the hydrogenation of so small a quantity.

Quite different products may also be obtained from benzaldehyde or furfural with ammonia and hydrogen. Hydrofuramide when heated with alkali is converted to furfurin or 2,4,5-trifuryldihydroimidazole[6] (VII), which when submitted to hydrogenation was converted into the corresponding tri-(tetrahydrofurfuryl)-dihydroimidazole (VIII). The carbon to nitrogen double bond in the latter compound was resistant to hydrogenation even at 200°.



VII VIII

In a similar fashion benzaldehyde was converted into amarin and then into hydrolophine or tricyclohexyldihydroimidazole.

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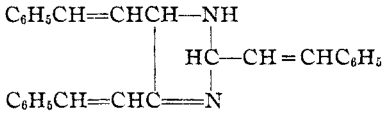
(6) Bahrmann, *J. prakt. Chem.*, [2] **27**, 311 (1883).

Cinnamaldehyde shows a somewhat different behavior because when treated with ammonia it does not give a true hydroamide (II) but a compound of the type of VII.[7] It thus appears that if the hydroamide is formed it immediately rearranges to the tri-β-styryldihydroimidazole (IX) which was readily hydrogenated to the corresponding tri-β-phenylethyldihydroimidazole.



IX

According to Schiff[8] heptaldehyde reacts with ammonia with the formation of a hydroamide. This is hardly to be expected from an aldehyde such as *n*-heptaldehyde. However, the hydrogenation of a product, prepared as described by Schiff, gave *n*-heptylamine and di-*n*-heptylamine in similar molecular amounts, as would be the case if the compound undergoing hydrogenation were really a hydroamide. For the reasons given below the yields were relatively low because of the formation of compounds of high molecular weight.

An aldehyde of the type $RCH_2CHO$ may react with ammonia to give at least two products other than of the hydroamide type. In addition aldolization may occur, perhaps followed by dehydration.

$$C_2H_5CH_2CHO + NH_3 \longleftrightarrow C_2H_5CH_2CH(OH)NH_2 \longleftrightarrow C_2H_5CH_2CH{=}NH + H_2O$$

$$2C_2H_5CH_2CHO \longleftrightarrow C_3H_7CHOHCH(C_2H_5)CHO \longleftrightarrow C_3H_7CH{=}C(C_2H_5)CHO + H_2O$$

A combination and repetition of these reactions results in the formation of complex compounds among the simpler of which are the substituted pyridine and piperidine referred to below.

The yields of amines obtained by the hydrogenation of reaction products of ammonia and an aldehyde of the type $RCH_2CHO$ were not very satisfactory. "Butyraldehyde-ammonia-hydrate," butyraldehyde in an alcoholic solution of ammonia, and heptaldehyde ammonia, were converted to the extent of 47 to 55% into compounds of relatively high molecular weight. The yields of primary amines were 32 to 36% and of secondary amines 12 to 21%. A fair yield, 23 to 26% of one of the higher molecular weight condensation products, *i. e.*, 2-propyl-3,5-diethylpyridine[9] was also obtained from butyraldehyde. Another application of this type of reaction is in the conversion of acetone and ammonia into 2,2,6,6-tetramethylpiperidone-4,[10] and the hydrogenation of the latter into 2,2,6,6-tetramethyl-4-hydroxypiperidine. The relationship of the pyridine (X) and piperidine

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[7] Delépine, *Bull. soc. chim.*, [3] **19**, 270 (1898).

[8] Schiff, *Ann.* (Spl.), **3**, 367 (1864).

[9] Tschitschibabin, *J. Chem. Soc.*, **90**, 451 (1906).

[10] Francis, *J. Chem. Soc.*, 2897 (1927); Heintz, *Ann.*, **183**, 308 (1876).

TABLE I

HYDROGENATION$^{a}$ OF OXIMES, ETC.

| Moles and name of hydrogen acceptor | Yield, name, and b. p. or m. p. product |
|---|---|
| 0.41 Acetoneoxime | 67% Isopropylamine$^{b}$ 30–32°, 10% di-isopropylamine$^{c}$ 80–84° |
| .17 *n*-Valeraldoxime | 62% *n*-Pentylamine$^{d}$ 100–104°, 27% di-*n*-pentlyamine$^{e}$ 200–210° |
| .23 *n*-Heptaldoxime | 61% *n*-Heptylamine$^{f}$ 152–155°, 20% di-*n*-heptylamine$^{g}$ 130–140° (10 mm.) |
| .27 Cinnamaldoxime | 32% γ-Phenylpropylamine$^{h}$ 78–83° (2 mm.), 12% di-γ-phenylpropylamine$^{i}$ 170–180° (2 mm.) |
| .11 γ-Phenylpropanaldoxime | 48% γ-Phenylpropylamine$^{h}$ 95–100° (8 mm.), 43% di-γ-phenylpropylamine$^{i}$ 200–210° (8 mm.) |
| .15 Benzophenoneoxime | 95% Benzhydrylamine$^{j}$ 164–167° (13 mm.) |
| .18 Camphoroxime | 94% Bornylamine$^{k}$ m. p. 160° |
| .16 *p*-Nitrosophenol | 85% *p*-Aminophenol$^{l}$ m. p. 180° |
| .09 Benzoinoxime | 64% α,β-Diphenylethanolamine$^{m}$ m. p. 160–162°, 20% tetraphenylpyrazine$^{4}$ m. p. 242–243° |
| .06 *Syn*-benzildioxime | 44.5% α,β-Diphenylethylenediamine$^{o}$, 51% tetraphenylpyrazine$^{n}$ m. p. 242–243° |
| .33 α-Benzaldoxime (I) | 77% Benzylamine 47–50° (1 mm.), 19% dibenzylamine 164–167° (7 mm.) |
| .33 α-Benzaldoxime (II) | 73% Benzylamine 71–74° (15 mm.), 20% dibenzylamine 175–180° (15 mm.) |
| .11 Azobenzene (I) | 22% Cyclohexylamine$^{p}$ 130–133°, 21% aniline$^{q}$ 175–185°, 48% dicyclohexylamine$^{r}$ 245–255° |
| .22 Azobenzene (II) | 95% Aniline$^{q}$ 70–75° (10 mm.) |
| .15 Butyraldehyde phenylhydrazone | 57% *n*-Butylamine$^{s}$ 76–80°, 40% di-*n*-butylamine$^{t}$ 155–165°, 95% aniline$^{q}$ 175–185° |
| .10 Diazoaminobenzene | 78% Aniline$^{q}$ 70–75° (10 mm.) |
| .12 Benzaldazine | 68% Benzylamine$^{u}$ 70–75° (12 mm.), 26% dibenzylamine$^{v}$ 175–180° (12 mm.), 2% tribenzylamine$^{w}$ m. p. 90–91°. |
| .56 Trifurfurylidene-diamine (hydrofuramide) | 88% Tetrahydrofurfurylamine$^{x}$ 146–149°, 90% di-tetrahydrofurfurylamine$^{y}$ 115–120° (6 mm.) |
| .03 Tri-(trimethylethylidene)-diamine (hydropinalamide) | 79% *Tert*-butylcarbinylamine$^{z}$ 80–82°, 62% di-*tert*-butylcarbinylamine$^{aa}$ 150–160° |
| .13 Triheptylidene-diamine$^{kk}$ (hydroenanthamide) | 43% *n*-Heptylamine$^{f}$ 150–160°, 49% di-*n*-heptylamine$^{g}$ 140–150° (11 mm.) |
| .20 Hexahydrobenzaldimine (polymer) | 61% Hexahydrobenzylamine$^{bb}$ 55–60° (14 mm.), 33% di-hexahydrobenzylamine$^{cc}$ 150–155° (14 mm.) |
| .04 Isobutyraldimine (polymer) | 70% Isobutylamine$^{dd}$ 60–70°, 24% di-isobutylamine$^{ee}$ 130–138° |
| .56 Butyraldehyde ammonia hydrate | 32% *n*-Butylamine$^{s}$ 76–80°, 13% di-*n*-butylamine$^{t}$ 158–165°, 23% 3,5-diethyl-2-*n*-propylpyridine 103–106° (10 mm.) |
| .23 Heptaldehyde ammonia$^{ll}$ | 32% *n*-Heptylamine$^{f}$ 152–156°, 12% di-*n*-heptylamine$^{g}$ 120–125° (7 mm.) |
| .28 Butyraldehyde and alcoholic ammonia | 32% *n*-Butylamine$^{s}$ 76–80°, 21% di-*n*-butylamine$^{t}$ 158–165°, 26% 3,5-diethyl-2-*n*-propylpyridine 240–250° |
| .10 2,2,6,6-Tetramethylpiperidone-4 (triacetone amine) | 81% 2,2,6,6-Tetramethyl-4-hydroxypiperidine (triacetone alkamine) m. p. 128–128.5° |
| .07 2,4,5-Triphenyldihydroimidazole (amarin) | 85% 2,4,5-Tricyclohexyldihydroimidazole$^{hh}$ (hydrolophine) m. p. 205–206° |
| .07 2,4,5-Trifuryldihydroimidazole$^{oo}$ (furfurin) | 82% 2,4,5-Tri-(tetrahydrofuryl)-dihydroimidazole$^{ii}$ (hydrofurfurin) 200–205° (4 mm.) |
| .06 2,4,5-Tri-β-styryldihydroimidazole | 83% 2,4,5-Tri-β-phenylethyldihydroimidazole$^{jj}$ 300–310° (6 mm.) |

### FOOTNOTES TO TABLE I

(*a*) The hydrogenations were in general carried out under a pressure of 100–150 atmospheres of hydrogen at 100–125° with 2–3 g. of an ammonium carbonate type nickel catalyst on a kieselguhr support using 50–100 ml. of ether, alcohol or methylcyclohexane as solvent. Hydrogenations usually required one to two hours. The following exceptions should be noted: azobenzene (I) was hydrogenated for 8.5 hours at 200° and azobenzene (II) for half an hour at 90°; diazoaminobenzene required a temperature of 150°; hydrofuramide, *p*-nitrosophenol, triheptylidenediamine, triacetoneamine, amarin (200°), furfurin, and 2,4,5-tri-$\beta$-styryldihydroimidazole required three to five hours. Ten grams of Raney catalyst gave the same rate and proportion of products in $\alpha$-benzaldoxime II as did the nickel on kieselguhr in $\alpha$-benzaldoxime (I). [Covert, Connor and Adkins, THIS JOURNAL, **54**, 1651, 4116 (1932).] The reported yield of tetrahydrofurylamines is that obtained after rehydrogenation at 125° of the mixture of amines from hydrofuramide.

The amines were in general characterized through the formation of solid derivatives. The ones referred to in this paragraph have been previously described so that only the observed melting points will be given: benzenesulfonamide (*b*) 99°; *p*-bromobenzenesulfonamide (*s*) 58°; picrate (*h*) 152–153°, (*k*) 252–254°; hydrochloride (*j*) 268–270°; (*m*) 207–209°, (*r*) 333 d, (*hh*) 250–253°; nitroso (*c*) 148°; phenyl isocyanate (*f*) 61–62°, (*t*) 85–86°, (*ee*) 104–105°; benzoyl (*q*) 160°, (*u*) 105°, (*v*) 111°, (*bb*) 105–106°, (*dd*) 55°; dibenzoyl (*l*) 233°; carbaminate (*o*) 106–108°; dimethyl oxalate (addition) (*z*) 163–164°.

A number of derivatives not hitherto described have been prepared:

(*d*) *p*-Brom benzene sulfonamide, m. p. 60–61°. *Anal.* Calcd. for $C_{11}H_{16}O_2NSBr$: N, 4.14. Found: N, 4.10.

(*e*) Crystalline hydrochloride from water. *Anal.* Calcd. for $C_{10}H_{24}NCl$: Cl, 18.31. Found: Cl, 18.24.

(*g*) Crystalline hydrochloride from water. *Anal.* Calcd. for $C_{14}H_{32}NCl$: Cl, 14.22. Found: Cl, 13.91.

(*p*) Benzene sulfonamide, m. p. 88–89°. *Anal.* Calcd. for $C_{12}H_{17}O_2NS$: N, 5.86. Found: N, 5.81.

(*x*) Phenyl isocyanate der., m. p. 147–147.5°. *Anal.* Calcd. for $C_{12}H_{16}O_2N_2$: N, 12.70. Found: N, 12.62.

(*y*) Picrate, m. p. 104–105°. *Anal.* Calcd. for $C_{10}H_{18}O_2N \cdot C_6H_3O_7N_3$: picric acid, 55.30. Found: picric acid, 55.37.

(*aa*) *p*-Bromobenzene sulfonamide, m. p. 128–129°. *Anal.* Calcd. for $C_{16}H_{26}O_2NSBr$: N, 3.73. Found: N, 3.88.

(*cc*) Hydrochloride, m. p. 298–299°. *Anal.* Calcd. for $C_{14}H_{28}NCl$: Cl, 14.44. Found: Cl, 14.30.

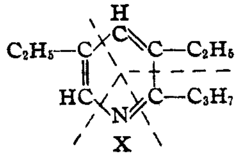
(*ii*) Picrate, m. p. 202–203°; neutral equivalent calcd., 280.2; found: 279. *Anal.* Calcd. for $C_{15}H_{24}O_3N_2$: N, 9.99. Found: N, 10.05.

(*jj*) Picrate, m. p. 130–132°. *Anal.* Calcd. for $C_{38}H_{33}N_5O_7$: N, 11.45. Found: N, 11.43. The viscous oil solidified to a yellow crystalline mass on standing for two months at room temperature, but the material could not be recrystallized.

(*kk*) Triheptylidenediamine (hydroenanthamide) was prepared by bubbling dry ammonia for ten hours into 80 g. of heptaldehyde [Schiff, *Ann.*, Suppl., **3**, 367 (1864)]. The water was removed in a separatory funnel, and the oily layer after drying with sodium sulfate weighed 64.2 g.

(*ll*) Heptaldehyde ammonia was prepared [Erlenmeyer and Sigel, *Ann.*, **176**, 343 (1875)] by adding 80 g. of heptaldehyde to 150 ml. of chilled aqueous ammonia and allowing to stand overnight. The oily layer was separated and after being dried under reduced pressure weighed 85 g.

(XI) derivative to butyraldehyde and acetone, respectively, is obvious from a consideration of their formulas.



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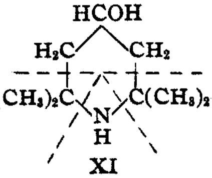

XI

Aldehydes of the type $R_2CHCHO$ such as hexahydrobenzaldehyde and isobutyraldehyde while capable of aldolization do not suffer from this reaction under the conditions necessary for the reaction with ammonia and hydrogen. Hexahydrobenzaldehyde reacts with ammonia to form the imine almost exclusively which then polymerizes to give a stable compound $(C_6H_{11}CH{=}NH)_x$. Upon hydrogenation this polymer is converted almost quantitatively into mono- and di-hexahydrobenzylamines, the ratio of the former to the latter being approximately 2 to 1. The reaction product of isobutyraldehyde and ammonia is less stable than that for hexahydrobenzaldehyde.

Lipp[11] upon the basis of this analyses of this compound has assigned to it what seems to be an improbable structure, containing six nitrogens, seven carbons and one oxygen in a ring. It is probable that Lipp's product was a slightly impure polymer of isobutyraldimine analogous to the polymer of hexahydrobenzaldimine referred to above. The compound as prepared in this Laboratory was almost quantitatively hydrogenated to mono- and di-isobutylamines in the ratio of almost three molecules of the primary to one of the secondary amine.

## Summary

A method has been given whereby a number of oximes may be hydrogenated so that good yields of the corresponding primary amines may be obtained. There is a considerable variation in the yields and ratios of primary and secondary amines produced depending upon the structure of the aldehyde or ketone from which the oxime is formed. Representative phenylhydrazones, azines and azo compounds have also been submitted to catalytic hydrogenation under similar conditions. The various types of reaction products obtained from representative aldehydes or ketones and ammonia, such as hydroamides, dihydroimidazoles and aldimines, have been submitted to hydrogenation and in several cases excellent yields of primary and secondary amines have been obtained.

MADISON, WISCONSIN

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[11] Lipp, *Ann.*, **205**, 4 (1880).