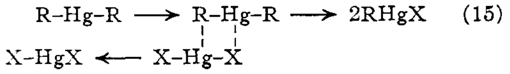
a mode of attack which seems to be supported by the retention of configuration shown by the optically active *sec*-butylmercury compounds in their reactions with $HgBr_2$,[4,5] the above facts seem consistent. Steric factors should not, within reason, markedly affect the rate of reaction by SE2. This has been vividly illustrated by the work of Winstein[13] on the cleavage of di-4-camphylmercury by HCl. In this case a bridge head mercurial reacts only 4 times slower than di-*n*-butylmercury.

The low entropies of activation and insensitivity to added water or iodide ion seem to support a molecular (four-center) or ion pair attack, while the large negative $\rho$-value for the aromatic series certainly indicates the importance of the electrophilic attack on carbon as compared to possible nucleophilic attack on mercury and points to the ready polarization of the attacking species.

The increase in rate observed in going along the sequence R, cyclopropyl, phenyl seems to be related to the entropy term. In light of the electrophilic nature of the attack this is probably related to the increased availability of electrons at the attacked position, either due to the increasing amount of delocalized $\pi$-electrons along the series or to steric factors related to hybridization of the attacked position.

It should be noted again that unlike reaction 10 which required both $\sigma + \sigma^+$ in a Hammett plot, the present reaction requires only $\sigma$. One possible explanation[14] is that the Hg atom in the attacking $HgX_2$ species is a very weak electrophile. It would be expected then that the rate would be quite sensitive to substituent effects, as is noted ($\rho = -5.87$); the Hg atom of the $HgX_2$ is apparently incapable of eliciting the latent electromeric properties of the substituted benzene ring ($\sigma^+$).

The linearity of the Hammett plot would seem to indicate that the effect of only one substituent is felt in the rate-determining step. If a four-center system were visualized as the activated complex



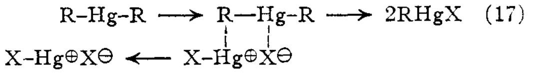
$$\begin{array}{ccc} R\text{-}Hg\text{-}R \longrightarrow & R\text{-}Hg\text{-}R & \longrightarrow 2RHgX \qquad (15) \\ & \vdots \qquad \vdots & \\ X\text{-}HgX \longleftarrow & X\text{-}Hg\text{-}X & \end{array}$$

it would seem obvious that the Hammett equation relationship would be best expressed by

$$\log k/k^0 = \sigma\rho + \sigma\rho' \qquad (16)$$

since it would not be expected that $\rho$ and $\rho'$ would be of the same value, or even sign. Such behavior is not noticed. Initial attack of $X^{\ominus}$ on $R_2Hg$ seems unlikely for reasons already pointed out—the lack of effect of added $I^{\ominus}$ or $H_2O$. The only remaining possibility appears to be either electrophilic attack on carbon by some species with the Hg absorbing or blocking the effect of the substituent on the other ring, or a four-center system in which $\rho' << \rho$, perhaps because of the hybridization of mercury other than sp.[7]

Whether one pictures the transition state as in equation 15, or as



$$\begin{array}{ccc} R\text{-}Hg\text{-}R \longrightarrow & R\text{—}Hg\text{-}R & \longrightarrow 2RHgX \qquad (17) \\ & \vdots \qquad \vdots & \\ X\text{-}Hg^{\oplus}X^{\ominus} \longleftarrow & X\text{-}Hg^{\oplus}X^{\ominus} & \end{array}$$

is probably immaterial, but the latter is consistent with the fact that the ease of ionization of the Hg–Z bond in $HgZ_2$ parallels the reactivity with $R_2Hg$ compound, thus favoring ion pair attack over molecular attack.

**Acknowledgments.**—The authors wish to acknowledge support of this work by a National Science Foundation Grant NSF G-5911, and to thank Miss Carol Woodruff for some of the measurements involving Job's method.

CINCINNATI, OHIO

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[13] S. Winstein and T. G. Traylor, THIS JOURNAL, **78**, 2597 (1956).

[14] The authors wish to thank referee no. 1 for suggesting this possibility.

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[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO]

# The Reduction of Amides to Amines *via* Nitriles by Lithium Aluminum Hydride[1]

BY MELVIN S. NEWMAN AND TADAMICHI FUKUNAGA[2]

RECEIVED JULY 7, 1959

The isolation of nitriles in lithium aluminum hydride reductions of amides indicates that part, if not all, of the reduction involves dehydration of amide to nitrile followed by reduction of nitrile to amine.

The reduction of unsubstituted amides to primary amines has often been accomplished by lithium aluminum hydride.[3] In discussion as to possible mechanisms for this type of reduction, attention has been directed to the nature of the complex hydride rather than to the organic moiety. With regard to the latter, it has been assumed that some species added to the carbonyl group as a first step.

In an attempt to reduce triisopropylacetamide to 2,2,2-triisopropylethylamine an absorption band at 4.55 $\mu$, indicative of nitrile, was noted in the crude product.[4] When the amide was treated with about one-half mole of lithium aluminum hydride, 55–66% yields of triisopropylacetonitrile were obtained, in addition to recovered amide. When excess reducing agent was used 2,2,2-triisopropylethylamine was obtained in almost quantitative yield from the corresponding nitrile.

To see whether reduction *via* the nitrile was due to the extreme steric hindrance in the amide, a similar experiment was carried out with benzamide.

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[1] This research was supported by the United States Air Force under Contract No. AF 33(616)-3412, monitored by the Aeronautical Research Laboratory, Wright Air Development Center.

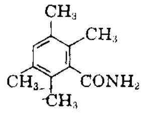
[2] The material herein presented was taken from the Ph.D. thesis, Ohio State University, 1959, of T. Fukunaga.

[3] N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, p. 544 ff.; also for stoichiometry of these reductions.

[4] A band in the 4.5–4.6 $\mu$ region is characteristic for nitriles; L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 263.

### TABLE I

### LITHIUM ALUMINUM HYDRIDE REDUCTIONS

| Run | Compound | Molar ratio[a] | H₂, moles | Solvent[b] | Reacn. temp.[c] | Reacn. time, hr. | Yield, % (crude) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Nitrile | Aldimine | Amine | Amide |
| 1[d] | $(i\text{-}C_3H_7)C\cdot CONH_2$ | 0.67 | ..[e] | THF | Refl. | 48 | 55 | ... | Trace | 25 |
| 2[d] |  | .52 | ..[e] | E | Refl. | 120 | 66 | ... | Trace | 26 |
| 3[f] | | .50 | ..[e] | THF | Refl. | 40 | 20[g] | ... | Trace | 62 |
| 4[f] | | 1.5 | 2.0 | E | Room | 70 | Trace[g] | ... | 50 | 20 |
| 5[f] | | 0.38 | 1.2 | THF | Refl. | 4 | 45[g] | 4[h] | ... | 35 |
| 6[f] | $C_6H_5\cdot CONH_2$ | 1.4 | 2.0 | THF–E | Room | 2 | Trace[g] | Main | Trace | Trace[i] |
| 7[d] | $(i\text{-}C_3H_7)_3C\cdot CN$ | 1.3 | 0 | THF | Refl. | 96 | ... | ... | 97 | |
| 8[d] | | 1.0 | 0 | THF | Refl. | 24 | 7 | 46[j] | 47[k] | |

[a] Molar ratio of lithium aluminum hydride to substrate. [b] THF = tetrahydrofuran and E = ether. [c] Refl. = reflux temperature: 65° for THF, 35° for E. [d] In these cases suspensions of LAH were used. [e] Qualitatively measured. [f] In these experiments clear solutions of LAH were used. [g] Remaining reaction mixtures, after several aliquots had been removed, were worked up and the yields of products were calculated. [h] Isolated as benzoic acid after oxidation with permanganate. [i] Not isolated as pure component but amount was estimated by suitable procedure. See Experimental. [j] Isolated as triisopropylacetaldehyde 2,4-dinitrophenylhydrazone. [k] Calculated by substracting the yield of aldehyde (corresponding to imine) from that of total picrate (imine and amine).

In this case also an appreciable yield of benzonitrile was obtained when an insufficient amount of lithium aluminum hydride was used.

The above facts suggest that reduction of amides to primary amines proceeds *via* a base-induced dehydration of amide to nitrile, followed by reduction of the nitrile formed to amine, as

$$RCONH_2 + {}^1/_2M_4H_4 \longrightarrow RCN + M_2O + 2H_2 \quad (1)$$

$$RCN + {}^1/_2M_4H_4 \longrightarrow RCH_2NM_2 \quad (2)$$

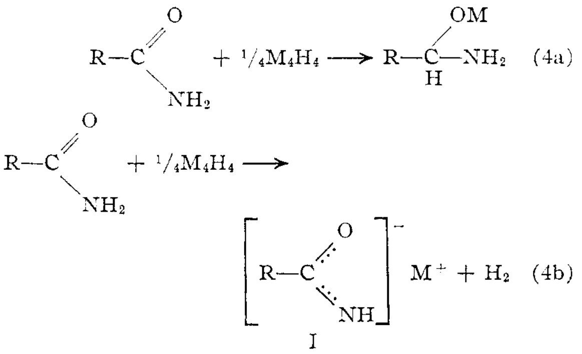
$$RCH_2NM_2 + H_2O \longrightarrow RCH_2NH_2 + M_2O \quad (3)$$

where $M = \frac{LiAl}{4}$

In support of equation 1 above the following facts are cited: I, In those experiments (see Table I) in which measurements were made two equivalents of hydrogen were evolved.[5] II, Good yields of nitriles have been obtained during attempts at alkaline hydrolysis at 190-200° of highly hindered aromatic amides.[6] III, A small amount of nitrile was formed on attempting to react a hindered acid chloride with sodium amide in liquid ammonia.[7] The nitrile undoubtedly arose from a base induced dehydration of the initially-formed amide. IV, Methyldipropylacetonitrile was obtained from the reaction of sodium amide with methyldipropylacetophenone in boiling benzene.[8] This nitrile undoubtedly arose from the amide formed in the cleavage. V, Benzonitrile has been isolated in small amount on treatment of thiobenzamide with lithium aluminum hydride.[9]

The reduction of nitriles to amines (*via* aldimine) requires no comment[10] other than that the reduction of highly hindered nitriles, such as triisopropylacetonitrile, to amine would be expected to be quite slow (see Table I). On the other hand, reduction of benzonitrile is extremely rapid, as a sample of the reaction products taken almost immediately after mixing ethereal solutions of benzonitrile and lithium aluminum hydride at 0–5° did not have any absorption band at 4.50 μ characteristic of benzonitrile.[4] Although benzonitrile is very rapidly reduced to the imine, the latter is more slowly reduced to benzylamine.

At first glance the ready formation of nitrile from amide under the influence of lithium aluminum hydride appears surprising. However, we believe that the results may be rationalized by taking into consideration the fact that lithium aluminum hydride is a very strong base[11] in addition to being a powerful reducing agent. The first step in the reaction of an amide may either be a reductive attack by hydride ion[12] (equation 4a) or an acid–base reaction involving the formation of an amide salt[13] I and a molecule of hydrogen (equation 4b). It appears from our results that reaction 4b predominates.[14]



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(5) Two equivalents of hydrogen were obtained on reaction of 2-ethylhexanoamide; see J. A. Krynitsky, J. E. Johnson and H. W. Carhart, THIS JOURNAL, **70**, 486 (1948).

(6) L. Tsai, T. Miwa and M. S. Newman, *ibid.*, **79**, 2530 (1957).

(7) E. Wenkert and B. G. Jackson, *ibid.*, **80**, 211 (1958).

(8) J. Leroid, *Ann. chim.*, [9] **16**, 377 (1921).

(9) M. W. Cronyn and J. E. Goodrich, THIS JOURNAL, **74**, 3936 (1952).

(10) See ref. 3, p. 731 ff., for a review.

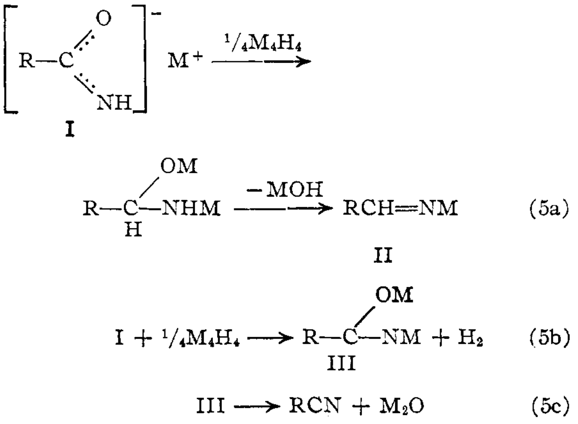
(11) See ref. 3 above, p. 92.

(12) In this discussion simple hydride ion attack will be used although it is realized that the nature of the reagent is complex. Similarly the symbol M will be used (for LiAl/4) as an indication of ignorance as to the nature of the metallic cation involved.

(13) R. L. Hinman, THIS JOURNAL, **78**, 2463 (1956), reports that the first step in reduction of acylhydrazines containing the grouping, RCONHN<, is anion formation with hydrogen evolution.

(14) That the acid–base reaction does not always win out over the reduction reaction is shown by the facts that treatment of ethyl acetoacetate and diethyl malonate with lithium aluminum hydride indicates that they are only 50-70% enolized (see J. A. Krynitsky, J. E. Johnson and H. W. Carhart, THIS JOURNAL, **70**, 486 (1948); F. A. Hochstein, *ibid.*, **71**, 305 (1949); E. Hofling, H. Lieb and W. Schoniger, *Monatsh.*, **83**, 60 (1952)), whereas with the Grignard reagent they are 100% enolized; T. Zerewitinoff, *Ber.*, **41**, 2233 (1908); W. Fuchs, N. H. Ishler and A. G. Sandhoff, *Ind. Eng. Chem., Anal. Ed.*, **12**, 507 (1940).

The amide salt I may react further in two ways: it may be reductively attacked to yield an aldehyde–ammonia type intermediate which is dehydrated (or the equivalent, loss of MOH) to aldimine salt II (equation 5a); or it may undergo another acid–base type reaction with hydride ion to yield another molecule of hydrogen and a double salt III (equation 5b) which then loses $M_2O$ to yield nitrile (equation 5c)



$$[\mathrm{RC(O)NH}]^- M^+ \xrightarrow{1/4\,M_4H_4}$$

I

$$\mathrm{R{-}CH(OM){-}NHM} \xrightarrow{-MOH} \mathrm{RCH{=}NM} \quad (5a)$$

II

$$\mathrm{I} + {}^1/_4\mathrm{M_4H_4} \longrightarrow \mathrm{R{-}C(OM){=}NM} + \mathrm{H_2} \quad (5b)$$

III

$$\mathrm{III} \longrightarrow \mathrm{RCN} + \mathrm{M_2O} \quad (5c)$$

Judging from our results, reaction according to equations 5b and 5c predominates.[15,16] The ready formation of dianions reported[17] supports the idea that the salt I might be as readily robbed of a proton (equation 5b) as reductively attacked by a hydride reagent (equation 5a). Certainly, it would be expected that the larger the steric requirement in the group R the greater the preference of reaction according to equation 5b,[18] but there may be a natural tendency in this direction anyway.

One might expect that proton abstraction from I (equation 5b) might lead directly to nitrile without the intervention of a salt III (*i.e.*, III would merely represent a transition state). However, since starting amide was recovered in appreciable quantity from an experiment (no. 4, Table I) in which two equivalents of hydrogen were evolved and an excess of reducing agent was present, we have shown that a salt such as III may have appreciable stability. How generally true this is must await further study.

It is conceivable that III might be reductively attacked by metal hydride. However, in view of the double salt character of III, we deem this possibility unlikely.

## Experimental[19]

**Reagents.**—Triisopropylacetamide was prepared in 93% yield by adding the acid chloride to a solution of sodamide in liquid ammonia.[20]

Triisopropylacetonitrile[21] and 2,3,5,6-tetramethylbenzamide[6] were prepared as described.

Tetrahydrofuran, kept over potassium hydroxide pellets, was distilled from lithium aluminum hydride (LAH). Ether was dried with calcium hydride followed by distillation from ethyl Grignard reagent.

Suspensions of LAH were used in experiments 1, 2, 7 and 8, whereas solutions of LAH in ether (0.5 *M*) or in tetrahydrofuran (0.25 *M*) were prepared as described[22] and used in experiments 3–6.

**Reduction Experiments.**—A solution of substrate was added to suspensions or solutions of LAH except in experiment 5 where a LAH solution was added to a benzamide solution. In experiments in which the volume of hydrogen was quantitatively measured, the addition was carried out at such a rate that moderate gas evolution occurred. Under these conditions all the gas was evolved during the course of addition. The volumes of gas evolved were corrected for gas evolved from solvent alone (blank experiments).

The progress of reaction (expts. 3–6) was followed by taking infrared spectra of samples withdrawn after known periods of time and treated in a suitable manner.

After stirring for various periods of time at specified temperatures, the reaction mixtures were cooled in an ice-bath and decomposed by the successive addition of water, 15% sodium hydroxide and water as recommended[16c] for amide reductions. Precipitates were filtered and washed with ether (or tetrahydrofuran) several times. After drying the solutions over anhydrous magnesium sulfate the solvent was removed to give products.

**Triisopropylacetonitrile (Expts. 1 and 2).**—The reaction product was distilled through a glass helices-packed column to give triisopropylacetonitrile, b.p. 75–78° at 4 mm. (reported[21] b.p. 220–221°), the identity of which was established by infrared analysis. The starting amide was recovered by washing the solid residue of distillation with cold petroleum ether (b.p. 35–55°). Treatment of the washings with hydrogen chloride afforded traces of 2,2,2-triisopropylethylamine hydrochloride.

**2,3,5,6-Tetramethylbenzonitrile (Expt. 3).**—Aliquots of this reaction mixture yielded products which had an absorption band at 4.55 $\mu$ (nitrile), the intensity of which increased as the reaction proceeded, while a band at 6.0 $\mu$ (amide) decreased.

The organic product was recrystallized from benzene to give a 62% yield of the starting amide. Distillation of the mother liquor gave a 20% yield of low melting substance, b.p. 100–110° at 2 mm., which was recrystallized from hot water to give 2,3,5,6-tetramethylbenzonitrile, m.p. 73–74° (reported[6] m.p. 73–74°). The basic fraction obtained from the distillation residue yielded a trace of 2,3,5,6-tetramethylbenzylamine hydrochloride after treatment with concentrated hydrochloric acid. Identity was established by infrared spectral analysis.

**2,3,5,6-Tetramethylbenzylamine (Expt. 4).**—In no sample of the reaction mixture was a nitrile absorption band observed. Although shifts of absorption bands in the vicinity of 6 $\mu$ (amide and imine) were noticed, no attempt was made to follow the reaction by infrared analysis.

When an ether–benzene solution of the reaction products was washed with 2 *N* hydrochloric acid a voluminous white precipitate was formed. After adding more concentrated hydrochloric acid, the precipitate was filtered and recrystallized from alcohol to give 2,3,5,6-tetramethylbenzylamine hydrochloride (50%), m.p. near 300° (w. dec. in a sealed tube).

*Anal.* Calcd. for $C_{11}H_{18}NCl$: C, 66.2; H, 9.1; N, 7.0; Cl, 17.8. Found: C, 66.0, 66.2; H, 9.0, 9.1; N, 7.0, 7.2; Cl, 17.6, 17.8.

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(15) A mechanism similar to that pictured in the successive equations 4b, 5b, 5c is probably involved in the conversions of amide to nitrile mentioned above in references 6, 7, 8 and 9.

(16) Although in the present cases the acid-base reaction is more rapid, the reductive attack of metal hydride on a salt-like intermediate, such as I, is also probably rapid. In the cases of reduction of amides of primary amines, the salt formed (equation 4a) is readily reduced to form $RCH_2NHR$, and when amides of secondary amines are involved, the intermediate $RCHOMNR_2$ is rapidly reduced to $RCH_2NR_2$. Cleavage reactions leading to alcohols (by further reduction) and aldehydes often occur with such amides and are more important in the cases of amides of secondary amines. See (a) F. Weygand and D. Tietjen, *Ber.*, **84**, 625 (1951); (b) S. Chiavarelli, F. F. Rogers and G. B. Marini-Bettolo, *Gazz. chim. ital.*, **83**, 347 (1953); and (c) V. M. Micovic and M. L. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953).

(17) See C. R. Hauser and T. M. Harris, THIS JOURNAL, **81**, 1154 1160 (1959), and references therein.

(18) See footnote 12 in ref. 7.

(19) Analyses were performed by the Galbraith Microanalytical Laboratories, Knoxvile, Tenn. Melting points of pure compounds are corrected.

(20) M. S. Newman and T. Fukunaga, to be reported.

(21) M. S. Newman, T. Fukunaga and T. Miwa, THIS JOURNAL, **82**, in press (1960).

(22) W. G. Brown, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 484.

From the neutral fraction the starting amide (20%) was recovered. The small amount of remaining liquid showed a medium infrared absorption band at 4.55 μ (nitrile).

A small sample of the amine hydrochloride was refluxed with *p*-nitrobenzoyl chloride in benzene–pyridine for several hours to give N-(2,3,5,6-tetramethylbenzyl)-*p*-nitrobenzamide, m.p. 218.0–218.6° (recrystallized from alcohol).

*Anal.* Calcd. for $C_{18}H_{20}N_2O_3$: C, 69.2; H, 6.5; N, 9.0. Found: C, 69.1, 69.3; H, 6.4, 6.7; N, 8.9, 8.9.

**Benzonitrile (Expt. 5).**—The sample withdrawn as soon as possible after the addition had a weak absorption band at 4.5 μ (nitrile). The intensity of this band increased as the reaction proceeded while a band at 6.0 μ (amide) became weaker.

The reaction product was mixed with petroleum ether (b.p. 35–55°) and cooled in a Dry Ice–acetone-bath to separate the starting amide (35%). The mother liquor was washed with 6 *N* hydrochloric acid and distilled to give a mixture of benzonitrile and benzaldehyde. The distillate was then oxidized with alkaline permanganate according to a conventional method[23] to give benzoic acid (4%) and benzonitrile (45%), b.p. 75–76° at 20 mm.

In experiment 6, samples withdrawn after various periods of time had no infrared absorption band at 4.5 μ (nitrile). Although no pure component was isolated from the reaction mixture the neutral fraction had a weak band at 4.5 μ (nitrile) and a strong band at 5.9 μ (aldehyde).

**2,2,2-Triisopropylethylamine (Expt. 7).**—Distillation of the reaction product gave crude 2,2,2-triisopropylethylamine (97%), b.p. 87–90° at 8 mm., which solidified into a wax-like solid, m.p. 40–45°. N-(2,2,2-Triisopropylethyl)-*p*-nitrobenzamide, m.p. 124.5–125.5° (recrystallized from alcohol), was prepared by refluxing with *p*-nitrobenzoyl chloride in benzene for 20 minutes.

*Anal.* Calcd. for $C_{18}H_{28}N_2O_3$: C, 67.5; H, 8.8; N, 8.7. Found: C, 67.3; 67.5; H, 8.7, 8.9; N, 8.8, 8.8.

Treatment of the crude amine with concentrated hydrochloric acid caused an exothermic reaction, followed by precipitation of crystalline amine hydrochloride. Recrystallization from hot water afforded 2,2,2-triisopropylethylamine hydrochloride, m.p. in the region of 355° in a sealed tube.

*Anal.* Calcd. for $C_{11}H_{26}NCl$: C, 63.6; H, 12.6; N, 6.7; Cl, 17.1. Found: C, 63.6, 63.7; H, 12.9, 12.7; N, 6.7, 6.7; Cl, 17.0, 17.3.

**Triisopropylacetaldehyde (Expt. 8).**—The reaction product was distilled to give a colorless oil, b.p. 105–110° at 4 mm. A part of the distillate was refluxed with 2,4-dinitrophenylhydrazine and a small amount of concentrated hydrochloric acid in alcohol. The crystals were dissolved in benzene and chromatographed on alumina. On evaporating the benzene the 2,4-dinitrophenylhydrazone in 46% yield of triisopropylacetaldehyde, m.p. 152.0–152.8° (recrystallized from alcohol), was obtained.

*Anal.* Calcd. for $C_{17}H_{26}N_4O_4$: C, 58.3; H, 7.5; N, 16.0. Found: C, 58.4, 58.4; H, 7.7, 7.6; N, 15.9, 16.0.

A part of the distillate yielded a mixture of picrates, m.p. 185–197°, after treatment with picric acid in alcohol. This mixture contained picrates of both imine and amine. The amount of amine listed in Table I was obtained by subtracting the weight of imine picrate calculated on the basis of aldehyde isolated above.

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[23] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 170.

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[CONTRIBUTION FROM THE ORGANIC CHEMISTRY DEPARTMENT, RESEARCH DIVISION, ABBOTT LABORATORIES]

# Synthesis of Primary 1,2-Diamines by Hydrogenation of α-Aminonitriles[1]

BY MORRIS FREIFELDER AND RICHARD B. HASBROUCK

RECEIVED JULY 6, 1959

In the catalytic hydrogenation of α-aminonitriles to 1,2-diamines, hydrogenolysis is a competing reaction. Successful low pressure reduction of unsubstituted α-aminonitriles in alcoholic hydrogen chloride in the presence of platinum oxide is reported.

Catalytic hydrogenation of α-aminonitriles has not led directly to primary diamines. Reduction has been accomplished only when at least one alkyl substituent has been present on the amino nitrogen.[2a,b] Yields as high as 50% have been obtained when a tertiary aminonitrile has been hydrogenated.[2a,c] There are a few instances of better than average yields.[3a–d]

The difficulty in obtaining good yield is due to the small difference between the rates of hydrogenation and hydrogenolysis. That hydrogenolysis is a problem is shown by Winans and Adkins,[4] who report a 37% yield of β-diethylaminoethylamine from high pressure reduction of diethylaminoacetonitrile with Raney nickel. They also found in the case of four different α-piperidinonitriles that rapid hydrogenolysis of the nitrile group occurred without any of the desired β-piperidinoethylamines being formed. In this Laboratory we have attempted to hydrogenate piperidinoacetonitrile under various conditions with palladium and platinum catalysts and have obtained only piperidine.

Reitsema[5] reports a 37% yield of N-β-aminoethylpyrrolidine from high pressure reduction of pyrrolidinoacetonitrile with a nickel catalyst. In the work of Leonard and his co-workers[6] extensive hydrogenolysis is encountered in the reduction of α-acetanilinophenylacetonitrile. They obtained a 20% yield of desired product I plus 60% of aniline and 10% of benzylaniline.

Reduction leading to primary diamines involves acylation of the aminonitrile, followed by

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[1] Presented at the Atlantic City Meeting, American Chemical Society, September, 1959.

[2] (a) W. L. Hawkins and B. J. Biggs, THIS JOURNAL, **71**, 2530 (1949); (b) R. A. Turner, *ibid.*, **68**, 1607 (1946); (c) I. G. Farbenind., German Patent 561,156, Sept. 22, 1932, reports yields of 20–40% in high pressure reductions of various mono- and di-N-substituted α-aminonitriles using nickel-on-kieselguhr.

[3] (a) F. E. King and R. M. Acheson, *J. Chem. Soc.*, 683 (1946), obtained a 61% yield of β-diethylaminoethylamine by a high pressure reduction of diethylaminoacetonitrile in ether in the presence of Raney nickel. (b) Union Carbide and Carbon Corp., British Patent 745,684, Feb. 29, 1946, noted 90% yields after successful high pressure hydrogenation of dialkylaminoacetonitriles with a cobalt catalyst. (c) J. Corse, J. T. Bryant and H. A. Shonle, THIS JOURNAL, **68**, 1907 (1946), obtained yields ranging from 34–88% in catalytic reductions of mixed dialkylsubstituted-α-aminonitriles in ether in the presence of Raney nickel and ammonia at 125°. (d) H. Baganz and H. Milster, *Arch. Pharm.*, **291**, 118 (1958), report 82 and 79% yields of N-β-aminoethylmorpholine and N-β-aminoethylpiperidine by reduction of the corresponding nitriles with nickel and ammonia.

[4] C. F. Winans and H. Adkins, THIS JOURNAL, **55**, 4172 (1933).

[5] R. H. Reitsema, U. S. Patent 2,496,955, Feb. 7, 1950.

[6] N. J. Leonard, G. W. Leubner and E. H. Burk, Jr., *J. Org. Chem.*, **15**, 982 (1950).