TABLE II

RATE CONSTANTS AND ACTIVATION ENERGIES OF SILVER ION SOLVOLYSES

Compound	$k_2 \times 10^4$, l./mole sec. 63.9°	92.3 ± 0.5°[d]	109.1 ± 0.2°	E_A,[c] kcal./mole
2,2-Dimethyl-1-bromopropane	0.84,[a] 1.01[b]	11.3 ± 1(92.4)	42.5 ± 1	22.5 ± 1.3
2,2-Dimethyl-3-bromo-1-propanol		7.1 ± 0.3(91.9)	30.5 ± 1	23.7 ± 0.7
2,2-Dimethyl-3-acetoxy 1-bromopropane		3.7 ± .4(92.8)	14.9 ± 1	24.0 ± 1.2
2,2-Dimethyl-1,3-dibromopropane		0.42 ± .03(91.9)	1.75 ± 0.1	23.0 ± 0.7

[a] Extrapolated using the energy of activation. [b] Dostrovsky and Hughes, reference 11. [c] The Arrhenius energies of activation were calculated from the rate constants at the two temperatures shown. The uncertainty in the values of the activation energies negates the drawing of conclusions from these values. [d] This range is due to a steady drift of the thermostat. During a single experiment the values in parentheses were good to ±0.1°.

$2b) \log [b(a - 2x)/a(b - x)] = kt$, which assumes a slow removal of the first bromine atom and a fast hydrolysis of the second bromine atom, confirmation is obtained for the mechanism of this reaction proposed above.

Conclusions

In the absence of neighboring group participation, it is expected that the electronegative 3-substituents will retard the reaction, and that the magnitude of the retardation will be dependent on the magnitude of the electrostatic effect of the 3-substituent. The order of substituent effects on reaction rates in Table II parallels the effect of these substituents on the dissociation constants of carboxylic acids.[18] The reactions of the compounds containing the 3-bromo- and 3-hydroxy substituents show retardation of rate and rearrangement, results indicating that neighboring group participation by these 3-substituents probably does not occur. In the case of the compound containing the 3-acetoxy substituent, the kinetic result of retardation indicates that it, also, does not participate as a neighboring group. The structural result of rearrangement in this latter case does not necessarily lead to the same conclusion since most of the rearranged product is probably produced *via* the bromo alcohol.

It is interesting to compare these results with those of Lindegren and Winstein.[10] The two sets of data are in agreement concerning the role of halogen but not concerning that of the acetoxy group. The kinetic evidence for participation of the 3-acetoxy group is especially convincing since kinetic criteria are usually less sensitive than structural criteria. It is possible that the discrepancy between the two results with respect to the acetoxy group may be reconciled by a consideration of the reaction conditions employed.[19]

(18) S. Winstein, E. Grunwald and L. L. Ingraham[2b] have calculated the driving force of several neighboring groups including the *trans*-2-bromo and *trans*-2-acetoxy groups after taking into account the electrostatic effect of these groups. Comparison of these calculations with the retardations reported here for the 3-substituents indicates that electrostatic interactions will account for the present results.

(19) The referee has suggested the following possible explanation. A comparison of the solvents used in the two studies indicates that the aqueous ethanol employed in the present investigation is a better nucleophilic solvent than is the acetic acid employed by Lindegren and Winstein. However, if the comparison is made from the point of view of the *Lim.* character of the solvolysis, it is possible to say that the conditions of Lindegren and Winstein are more of the *Lim.* variety than are those of the present investigation (S. Winstein and H. Marshall, THIS JOURNAL, **74**, 1123 (1952)). One would expect that a more limiting solvolysis would favor external solvation over internal solvation and thus reduce the neighboring group participation. If one, however, considers the competition between external and internal solvation from the point of view of the variation in the nucleophilicity of the solvent, one arrives at an opposite conclusion which is in agreement with the data.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM ROHM AND HAAS CO.]

The Aminomethylation of Olefins. V. A New Synthesis of 4-Phenylpyridine and Related Compounds

BY CLAUDE J. SCHMIDLE AND RICHARD C. MANSFIELD

RECEIVED SEPTEMBER 28, 1955

A new and relatively simple synthesis of 4-phenylpyridine from α-methylstyrene, formaldehyde and ammonium chloride is reported.

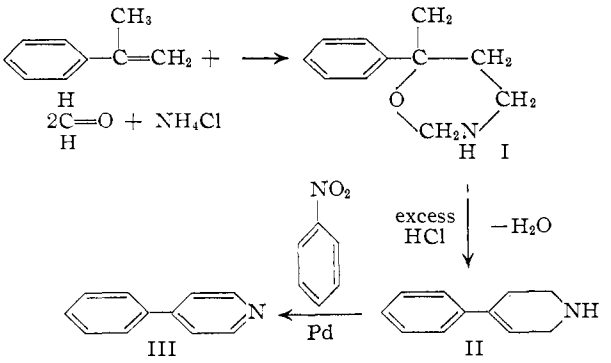
Previous methods of synthesis[1-5] of 4-phenylpyridine (III) suffer the disadvantages of low yield, involved and tedious procedures, contamination of the product by isomers and the use of relatively unavailable and expensive starting materials. Melting points for 4-phenylpyridine (III) ranging from 69–78° have been reported by previous investigators.[1-5]

We have found that 4-phenylpyridine (III) can be prepared from α-methylstyrene, formaldehyde and ammonium chloride. Hartough and co-workers[6] have reported the condensation of these materials to give 6-methyl-6-phenyltetrahydro-1,3-oxazine (I). Studies in this Laboratory have shown that the latter material can be converted with ex-

(1) A. Hantzsch, *Ber.*, **17**, 1518 (1884).
(2) R. Möhlau and R. Berger, *ibid.*, **26**, 1994 (1893).
(3) R. Forsyth and F. L. Pyman, *J. Chem. Soc.*, 2922 (1926).
(4) J. Overhoff and G. Tilman, *Rec. trav. chim.*, **48**, 993 (1929).
(5) J. W. Haworth, I. M. Heilbron and D. H. Hey, *J. Chem. Soc.*, 349 (1940).

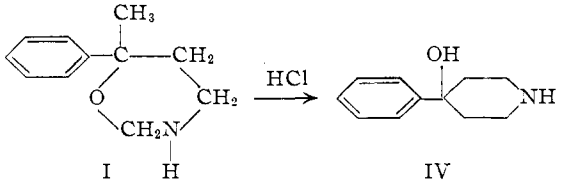
(6) H. D. Hartough, J. J. Dickert and S. L. Meisel, U. S. Patent 2,647,117 (July 28, 1953); *C. A.*, **48**, 8265 (1954).

cess acid to 4-phenyl-1,2,3,6-tetrahydropyridine (II) which can then be dehydrogenated to 4-phenylpyridine (III) using nitrobenzene and a palladium catalyst.

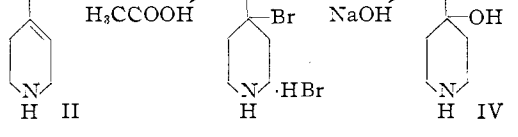


The yield of 6-methyl-6-phenyltetrahydro-1,3-oxazine (I) from α-methylstyrene, formaldehyde and ammonium chloride has been increased to 67% by treatment of the reaction mixture with methanol prior to liberation of the free base. This treatment serves to remove excess formaldehyde and to cleave methylene-bis and related compounds with the formation of methylal. Cleavage of the oxazine ring results if the methanol treatment is prolonged.

The conversion of 6-methyl-6-phenyltetrahydro-1,3-oxazine (I) to 4-phenyl-1,2,3,6-tetrahydropyridine (II) has been carried out in 52% yield by heating with excess hydrochloric acid. Under milder conditions some 4-phenyl-4-piperidinol (IV) is obtained. The latter material, 4-phenyl-4-piperidinol (IV), can be obtained directly from the



reaction of α-methylstyrene, formaldehyde and ammonium chloride. It also has been prepared by hydration of 4-phenyl-1,2,3,6-tetrahydropyridine (II) *via* the 4-bromopiperidine hydrobromide, which was prepared by the method of McElvain and Safranski.[7]



4-Phenyl-4-piperidinol (IV) can be dehydrated to 4-phenyl-1,2,3,6-tetrahydropyridine (II) by heating with excess hydrochloric acid. An obvious simplification in the preparation of 4-phenyl-1,2,3,6-tetrahydropyridine (II) from α-methylstyrene, formaldehyde and ammonium chloride is to simultaneously rearrange 6-methyl-6-phenyltetrahydro-1,3-oxazine (I) and dehydrate 4-phenyl-4-piperidinol (IV) since the conditions for both these reactions are similar. When α-methylstyrene, formaldehyde and ammonium chloride reacted and then were treated with excess hydrochloric acid before liberation of the free base, there was obtained directly 50% of 4-phenyl-1,2,3,6-tetrahydropyridine (II) based on α-methylstyrene.

The conversion of 6-methyl-6-phenyltetrahydro-1,3-oxazine (I) to 4-phenyl-1,2,3,6-tetrahydropyridine (II) and to 4-phenyl-4-piperidinol (IV) may be looked upon as cleavage of the oxazine ring followed by an intramolecular aminomethylation.[8]

4-Phenyl-1,2,3,6-tetrahydropyridine (II) has been reduced over palladium to 4-phenylpiperidine, prepared previously by Koelsch[9] from 4-phenyl-2-piperidone.

Dehydrogenation of 4-phenyl-1,2,3,6-tetrahydropyridine (II) was accomplished by heating it with excess nitrobenzene in the presence of 5% palladium-on-alumina in an atmosphere of nitrogen. In this manner, 81% of 4-phenylpyridine (III) was obtained. Nitrobenzene may be omitted from the dehydrogenation. In this event a higher reaction temperature is required to obtain a good yield of 4-phenylpyridine (III).

Pure 4-phenylpyridine (III) is a colorless solid and after recrystallization from heptane melts at 77–78°, the melting point originally reported by Hantzsch[1] in 1884.

Its ultraviolet absorption characteristics provide additional proof of the 4-phenylpyridine (III) structure. Very strong dependence on proton-donating solvents is indicated by a shift of the single absorption peak from 247 mμ in isoöctane to 257 mμ in methanol. The latter spectrum is identical with that obtained by Gillam, *et al.*,[10] for 4-phenylpyridine.

When 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine (from α-methylstyrene, formaldehyde and methylamine hydrochloride)[8] was subjected to dehydrogenation under conditions similar to those employed for the dehydrogenation of 4-phenyl-1,2,3,6-tetrahydropyridine (II) there was obtained 70% of 4-phenylpyridine (III).

Acknowledgment.—We wish to thank Dr. J. D. Stroupe and his staff for spectroscopic data and physical-chemical interpretation and Mr. C. W. Nash and his staff for analytical data reported.

Experimental

6-Methyl-6-phenyltetrahydro-1,3-oxazine (I).—A mixture of 236 g. (2.0 moles) of α-methylstyrene, 668 g. (8.25 moles) of 37% aqueous formaldehyde and 216 g. (4.04 moles) of ammonium chloride was stirred and warmed to 60°. An exothermic reaction ensued which was controlled by external cooling so that the temperature stayed at 55–60°. When the exotherm had ceased the temperature was allowed to fall to 40° during one hour. There was then added 450 g. (14.0 moles) of methanol and the mixture was stirred at room temperature for two hours and allowed to stand overnight. The alcohol was removed by distillation from a steam-bath and the mixture was made basic with ex-

(7) S. M. McElvain and J. C. Safranski, Jr., THIS JOURNAL, **72**, 3134 (1950).

(8) Claude J. Schmidle and R. C. Mansfield, *ibid.*, **78**, 425 (1956).

(9) C. F. Koelsch, *ibid.*, **65**, 2459 (1943).

(10) A. E. Gillam, D. H. Hey and A. Lambert, *J. Chem. Soc.*, 364 (1941).

cess 50% sodium hydroxide. The amine was taken up in toluene, dried and distilled to give 236 g. (67%) of 6-methyl-6-phenyltetrahydro-1,3-oxazine (I), b.p. 95–110° (1.0 mm.). This was redistilled and a center cut boiling at 92–93° (0.8 mm.) and weighing 125 g. was taken for analysis; $n^{25}D$ 1.5382.

Anal. Calcd. for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.58; H, 8.94; N, 7.74.

The hydrochloride melted at 147–149° after recrystallization from acetone containing about 5% isopropyl alcohol.

Anal. Calcd. for $C_{11}H_{16}NOCl$: C, 61.82; H, 7.55; N, 6.56; Cl, 16.6. Found: C, 61.15; H, 7.67; N, 6.62; Cl, 16.7.

4-Phenyl-1,2,3,6-tetrahydropyridine (II).—A mixture of 100 g. (1.0 mole) of concentrated hydrochloric acid and 62 g. (0.35 mole) of 6-methyl-6-phenyltetrahydro-1,3-oxazine (I) was stirred on a steam-bath for 4 hours, cooled, poured into 500 ml. of water and made basic with excess 50% sodium hydroxide. The amine was taken up in toluene, dried over potassium carbonate and distilled to give 29 g. (52%) of 4-phenyl-1,2,3,6-tetrahydropyridine (II), b.p. 95–110° (1.2 mm.), $n^{25}D$ 1.5889. This was redistilled to give a center cut, b.p. 100–105° (1.5 mm.), $n^{25}D$ 1.5882.

Anal. Calcd. for $C_{11}H_{13}N$: C, 82.97; H, 8.23; N, 8.80. Found: C, 83.18; H, 8.50; N, 8.74.

The hydrochloride melted at 200–202° after recrystallization from acetone containing about 5% isopropyl alcohol.

Anal. Calcd. for $C_{11}H_{14}NCl$: C, 67.51; H, 7.21; N, 7.16; Cl, 18.1. Found: C, 67.70; H, 7.41; N, 7.19; Cl, 18.1.

Quantitative hydrogenation of II using 5% palladium-on-alumina catalyst in 95% ethanol required 0.99 molar equivalent of hydrogen.

4-Phenyl-1,2,3,6-tetrahydropyridine (II) (Directly from α-Methylstyrene, Formaldehyde and Ammonium Chloride).—A mixture of 216 g. (4.04 moles) of ammonium chloride and 668 g. (8.25 moles) of 37% aqueous formaldehyde was stirred and heated to 65°. There was slowly added during 15 min. with stirring and cooling 236 g. (2.0 moles) of α-methylstyrene. After the exotherm had been controlled at 60–65° during the addition, the cooling bath was removed and the mixture stirred for 2 hr. while the temperature fell to 40°. There was added 500 ml. of methanol, the mixture was stirred for one hour at room temperature and allowed to stand 2 days. The methanol was removed by heating to 83° under reduced pressure during one hour. After cooling there was added 600 g. (6.0 moles) of concentrated hydrochloric acid and the mixture was stirred for 3 hr. on a steam-bath, cooled, poured into 800 ml. of water, extracted with toluene and made basic with excess 50% sodium hydroxide. The amine was taken up in toluene, dried and distilled to give 159 g. (50%) of 4-phenyl-1,2,3,6-tetrahydropyridine (II), b.p. 97–112° (1.0 mm.).

Anal. Calcd. for $C_{11}H_{13}N$: N, 8.80. Found: N, 8.69.

The hydrochloride melted at 200–201° after recrystallization from acetone containing about 5% isopropyl alcohol.

Anal. Calcd. for $C_{11}H_{14}NCl$: C, 67.51; H, 7.21; N, 7.16; Cl, 18.1. Found: C, 67.28; H, 7.25; N, 7.26; Cl, 18.0.

4-Phenylpyridine (III) A. Using Nitrobenzene.—A mixture of 88 g. (0.55 mole) of 4-phenyl-1,2,3,6-tetrahydropyridine (II), about 5 g. of 5% palladium-on-alumina catalyst and 435 g. (3.53 moles) of nitrobenzene was stirred at 135° for 6 hr. with removal of water in an atmosphere of nitrogen and then cooled. There was added an excess of dilute hydrochloric acid and the mixture was filtered and extracted with toluene. The aqueous layer was made basic with excess sodium hydroxide and the amine was taken up in toluene, dried and distilled to give 69 g. (81%) of 4-phenylpyridine (III), b.p. 99–101° (1.0 mm.). This crystallized and after two recrystallizations from heptane melted at 77–78°.

Anal. Calcd. for $C_{11}H_9N$: C, 85.13; H, 5.84; N, 9.03. Found: C, 85.20; H, 6.00; N, 8.98.

The picrate was prepared and melted at 195–197°.

Anal. Calcd. for $C_{17}H_{12}N_4O_7$: C, 53.13; H, 3.15; N, 14.58. Found: C, 53.36; H, 3.23; N, 14.36.

B. Nitrobenzene Omitted.—A mixture of 40 g. (0.25 mole) of 4-phenyl-1,2,3,6-tetrahydropyridine (II) and 5 g. of 5% palladium-on-alumina was stirred and heated in an atmosphere of nitrogen during 4 hr. while the temperature rose from 135 to 200°. The mixture was maintained at 200° for 2 hr., cooled, diluted with ethanol, filtered and distilled to give 20 g. (52%) of 4-phenylpyridine (III), b.p. 95–105° (1.5 mm.). This crystallized and melted at 68–71°.

Anal. Calcd. for $C_{11}H_9N$: C, 85.13; H, 5.84; N, 9.03. Found: C, 84.72; H, 6.43; N, 8.88.

4-Phenylpyridine (III) (from 1-Methyl-4-phenyl-1,2,3,6-tetrahydropyridine).—A mixture of 96 g. (0.55 mole) of 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine, 4 g. of 5% palladium-on-alumina and 430 g. (3.50 moles) of nitrobenzene was stirred under N_2 at 130–135° for 2 hr. After cooling and filtering there was slowly added excess dilute hydrochloric acid and the mixture was extracted with toluene. The aqueous phase was made basic with excess 50% sodium hydroxide and the amine was taken up in toluene, dried and distilled to give 60 g. (70%) of 4-phenylpyridine (III), b.p. 104–107° (2.2 mm.). This crystallized and melted at 74–76° after two recrystallizations from heptane. A mixed melting point with 4-phenylpyridine (III) prepared by method A from 4-phenyl-1,2,3,6-tetrahydropyridine (II) was 75–77°.

Anal. Calcd. for $C_{11}H_9N$: C, 85.13; H, 5.84; N, 9.03. Found: C, 85.47; H, 5.91; N, 9.04.

4-Phenyl-4-piperidinol (IV) by Hydration of 4-Phenyl-1,2,3,6-tetrahydropyridine (II).—A mixture of 10 g. (0.063 mole) of 4-phenyl-1,2,3,6-tetrahydropyridine (II) and 200 ml. of glacial acetic acid was saturated with anhydrous hydrogen bromide during 2 hr. at 10–20°. After standing overnight at room temperature the acetic acid was distilled off at reduced pressure at a maximum temperature of 45°. The solid residue was dissolved in 300 ml. of water, stirred 0.25 hr. at room temperature and 2 hr. on a steam-bath, cooled and made basic with excess 50% sodium hydroxide. The amine was taken up in ether, dried over potassium carbonate and filtered. The filtrate deposited 5 g. (45%) of 4-phenyl-4-piperidinol (IV) on standing. After recrystallization from toluene the melting point was 158–160°.

Anal. Calcd. for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.78; H, 8.44; N, 7.89.

4-Phenyl-4-piperidinol (IV) by Rearrangement of 6-Methyl-6-phenyltetrahydro-1,3-oxazine (I).—A mixture of 125 g. (0.71 mole) of 6-methyl-6-phenyltetrahydro-1,3-oxazine (I) and 150 g. (0.76 mole) of 18.5% hydrochloric acid was stirred on a steam-bath for 2 hr., allowed to stand overnight, poured into 500 ml. of water and made basic with excess 50% sodium hydroxide. The amine was taken up in warm toluene, dried over potassium carbonate and filtered while warm. The solid which precipitated on cooling was filtered off and recrystallized twice from toluene to give 12 g. (10%) of 4-phenyl-4-piperidinol (IV), m.p. 158–160°.

Anal. Calcd. for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.63; H, 8.59; N, 8.00.

The hydrochloride melted at 215–216° after recrystallization from acetone–isopropyl alcohol.

Anal. Calcd. for $C_{11}H_{16}NOCl$: C, 61.82; H, 7.55; N, 6.56; Cl, 16.6. Found: C, 61.73; H, 7.35; N, 6.60; Cl, 16.5.

4-Phenyl-4-piperidinol (IV) (from α-Methylstyrene, Formaldehyde and Ammonium Chloride).—The procedure of Hartough[6] for the reaction of α-methylstyrene, formaldehyde and ammonium chloride was followed. The material boiling at 140–160° (1.5 mm.) (12%) crystallized and was recrystallized from toluene to 4-phenyl-4-piperidinol (IV), m.p. 158–160°.

Anal. Calcd. for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.54; H, 8.64; N, 8.07.

The hydrochloride melted at 215–217° after recrystallization from acetone containing about 5% isopropyl alcohol.

Anal. Calcd. for $C_{11}H_{16}NOCl$: C, 61.82; H, 7.55; N, 6.56; Cl, 16.6. Found: C, 61.96; H, 7.84; N, 6.23; Cl, 16.6.

This hydrochloride was prepared previously by McElvain and McMahon[11] *via* 1-benzoyl-4-piperidone and phenylmagnesium bromide.

4-Phenyl-1,2,3,6-tetrahydropyridine (II) by Dehydration of 4-Phenyl-4-piperidinol (IV).—A mixture of 50 g. (0.28

(11) S. M. McElvain and R. E. McMahon, THIS JOURNAL, **71**, 901 (1949).

mole) of 4-phenyl-4-piperidinol (IV) and 100 g. (1.0 mole) of concentrated hydrochloric acid was stirred on a steam-bath for 2.5 hr., cooled, poured into 300 ml. of water, and made basic with excess 50% sodium hydroxide solution. The amine was taken up in toluene, dried, and distilled to give 40 g. (89%) of 4-phenyl-1,2,3,6-tetrahydropyridine (II), b.p. 97–106° (1.2 mm.).

Anal. Calcd. for $C_{11}H_{13}N$: C, 82.97; H, 8.23; N, 8.80. Found: C, 82.86; H, 8.40; N, 8.74.

The hydrochloride melted at 200–201° after recrystallization from acetone containing about 5% isopropyl alcohol. A mixed melting point with the hydrochloride of a sample of 4-phenyl-1,2,3,6-tetrahydropyridine (II) prepared directly from α-methylstyrene, formaldehyde and ammonium chloride melted at 200–201°.

Anal. Calcd. for $C_{11}H_{14}NCl$: C, 67.51; H, 7.21; N, 7.16; Cl, 18.1. Found: C, 67.55; H, 7.23; N, 7.18; Cl, 18.0.

4-Phenylpiperidine.—A mixture of 90 g. (0.57 mole) of 4-phenyl-1,2,3,6-tetrahydropyridine (II), 200 ml. of ethanol and 5 g. of 5% palladium on alumina catalyst was shaken for 8 hr. in an autoclave at 65–70° under a pressure of hydrogen of 1500 p.s.i. After cooling, the contents were filtered and the filtrate was distilled to give 50 g. (55%) of 4-phenylpiperidine, b.p. 85–88° (1.2 mm.). This crystallized and after recrystallization from heptane melted at 60–63°.

Anal. Calcd. for $C_{11}H_{15}N$: C, 81.93; H, 9.38; N, 8.69. Found: C, 81.83; H, 9.10; N, 8.65.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM ORGANIC CHEMISTRY SECTION, BALLISTIC RESEARCH LABORATORIES]

Direct and Reverse Addition Reactions of Nitriles with Lithium Aluminum Hydride in Ether and in Tetrahydrofuran

BY LOUIS M. SOFFER AND MANFRED KATZ

RECEIVED AUGUST 8, 1955

The reductions of nitriles in ether and in tetrahydrofuran at various hydride–nitrile ratios have been investigated, using both direct and reverse addition procedures. The various reduction products include primary amines, aldehydes, hydrogen, 1,3-diamines (resulting from dimerization) and other higher products. Reaction sequences are proposed for the major processes in both types of reaction. No evidence was obtained for the presence of a carbon–lithium bond in the final reduction complexes. The presence of a small amount of carbon–aluminum bond, however, was indicated for the final reduction species from phenylacetonitrile. A one-step preparation of aromatic anils, $RCH{=}NCH_2R$, from aromatic nitriles, $RC{\equiv}N$, is described.

It has been reported[1] recently that the direct addition[2] (DA) reductions of *n*-butyronitrile and of *n*-valeronitrile by lithium aluminum hydride in ether occurred with only small amounts of hydrogen evolved, whereas much more gas was evolved when the identical reactions were performed in tetrahydrofuran. We have since observed that RA reductions of these nitriles in both ether and tetrahydrofuran evolve considerable hydrogen.[3] Experiments with various types of nitriles have been performed in order to determine the source of the gas as well as obtain a better understanding of the reduction of nitriles by hydride.[4]

Results and Discussion

DA Reductions of Nitriles in Ether.—Previous studies[4] were essentially concerned with the major product and the over-all stoichiometry. On the latter subject the earlier proposal[3,4a] that 0.5 mole of hydride was sufficient for the reduction of one mole of nitrile has been questioned by Amundsen and Nelson. These authors concluded, from experiments on caprylonitrile and benzonitrile, that at least one mole of hydride was necessary for optimum reduction.

In Table I, runs 1, 2 and 4, are shown typical DA reductions at molar ratios of hydride to nitrile (MRHN) of one or higher in which little or no hydrogen was evolved, and in which high yields of primary amines were obtained. At a MRHN of 0.5, however, the yield of *n*-butylamine was only 39.7%, or about one-half the optimum. For benzonitrile, runs 4–6, lowering the MRHN resulted in the increasing formation of benzaldehyde, which was isolated in the form of the anil, N-benzalbenzylamine.[5] It can be seen from these data that about half of the available hydride hydrogen is found in the identified products, thus supporting Amundsen's view that only half of the hydride hydrogen is available for reduction of nitrile groups at 35°.

In accord with current ideas[4b,6] on the mechanism of hydride reactions the over-all process may be regarded as the formation of a primary aluminohydride ion capable of undergoing further reaction with another molecule of nitrile, producing a new species which is further reduced to the primary amine precursor. It will be noted that partial reduction, such as might result from an insufficient amount of hydride, yields aldehyde.

$$RCH_2C{\equiv}N + AlH_4^- \longrightarrow R{-}CH_2CH{=}NAlH_3^-$$

$$RCH_2C{\equiv}N + R{-}CH_2CH{=}NAlH_3^- \longrightarrow (RCH_2CH{=}N)_2AlH_2^-$$

$$(RCH_2CH{=}N)_2AlH_2^- + AlH_4^- \longrightarrow 2RCH_2CH_2NAlH_2^-$$

Of the nitriles studied at 1.1 MRHN, phenylacetonitrile (run 7) yielded considerably more gas and less primary amine. Concomitantly, there was a larger amount of higher products, among which was identified 2,4-diphenyl-1,3-butanediamine. Ex-

(1) L. M. Soffer and E. W. Parrotta, THIS JOURNAL, **76**, 3580 (1954); R. F. Nystrom, *ibid.*, **77**, 2544 (1955).

(2) Direct addition means that the nitrile was added to the hydride solution; reverse addition (RA) is the opposite procedure.

(3) H. E. Zaugg and B. W. Horrom, *Anal. Chem.*, **20**, 1026 (1948), observed the evolution of hydrogen in RA reactions of diphenylacetonitrile.

(4) For previous studies see the preceding references, and the following: (a) R. F. Nystrom and W. G. Brown, THIS JOURNAL, **70**, 3738 (1949); (b) W. G. Brown, "Organic Reactions," R. Adams, ed., Vol. 6, John Wiley and Sons, Inc., New York, N. Y.; (c) L. H. Amundsen and L. S. Nelson, THIS JOURNAL, **73**, 243 (1951).

(5) The fair yield of N-benzalbenzylamine suggests the possibility of an easy, general preparation of aromatic anils, $RCH{=}NCH_2R$, from aromatic nitriles, $RC{\equiv}N$.

(6) H. R. Snyder and R. E. Putnam, THIS JOURNAL, **76**, 1893 (1954).