The Cleavage of β-Oxypropionitriles with Lithium Aluminum Hydride[1]

By Louis M. Soffer and Elizabeth W. Parrotta

The reduction of β-oxypropionitriles with excess lithium aluminum hydride in diethyl ether solution results in significant amounts of cleavage at the ether linkage. The products, exclusive of the expected primary amine, are the parent alcohol, hydrogen, n-propylamine, and traces of ammonia. Cleavage is least with the alkoxypropionitriles (5–10%) and most with the aryloxypropionitriles (20–25%). When the reduction is performed in tetrahydrofuran solution the cleavage reaction predominates and in some cases is practically quantitative. It is shown that the greatly different degrees of cleavage exhibited in the two solvents are due to the solvents themselves, and not to different reaction temperatures. A mechanism for the cleavage reaction is discussed in terms of the possible elimination of acrylonitrile by lithium aluminum hydride:

$$ROCH_2CH_2CN \xrightarrow{\text{LiAlH}_4} \underset{\ominus}{ROCH_2CHCN} + AlH_3 + H_2; \quad \underset{\ominus}{ROCH_2CHCN} \longrightarrow RO\ominus + CH_2{=}CH{-}CN.$$ The experimental evidence, however, indicates that the actual mechanism is probably more complex and that elimination of acrylonitrile, as such, is not the principal process.
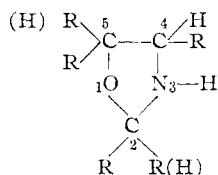
Introduction

During the hydrolysis of the reaction mixture of a β-alkoxypropionitrile and lithium aluminum hydride, the formation of a volatile amine was observed. The compound was n-propylamine, and the other products were the parent alcohol and the desired γ-alkoxypropylamine. It was later observed that trace amounts of ammonia were also produced. Investigation of a number of β-oxy-

$$RO(CH_2)_2CN \xrightarrow{\text{LiAlH}_4}$$
$$ROH + RO(CH_2)_3NH_2 + CH_3CH_2CH_2NH_2$$

propionitriles has shown that the cleavage is general and occurs with an evolution of hydrogen.

The general instability of β-alkoxypropionitriles to heat and aqueous base is well known.[2] Moe, Miller and Buckley[3] have reported that cleavage at the ether linkage resulted when the hydrolysis of the β-cyanoethyl ethers of certain polysaccharides was attempted in alkaline solution. Wright and Minsk[4] observed the cleavage of polyvinyl β-cyanoethyl ether by sodium hydroxide in a water–methyl cellosolve system and reported that the principal reaction was direct decyanoethylation. The fate of the nitrile fragment was not investigated.

Two instances in which cleavage has been observed with somewhat related materials may be noted. Reduction of substituted oxazolidines of the type

with lithium aluminum hydride resulted in scission between the 1- and 2-positions producing substituted 2-aminoalkanols.[5] Hatch and Cram have reported recently that the reduction of 2,3-diphenyl-2-ethoxyethylenimine with lithium alu-

(1) Presented, in part, at the 124th Meeting of the American Chemical Society, Chicago, Ill., September, 1953.

(2) H. A. Bruson in "Organic Reactions," Roger Adams, Ed., Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 90.

(3) O. A. Moe, S. E. Miller and M. I. Buckley, This Journal, 74, 1325 (1952).

(4) J. F. Wright and L. M. Minsk, ibid., 75, 100 (1953).

(5) E. D. Bergman, D. Lavie and S. Pinchas, ibid., 73, 5662 (1951).

minum hydride resulted in scission of the ethoxy fragment to form cis-2,3-diphenylethylenimine.[6]
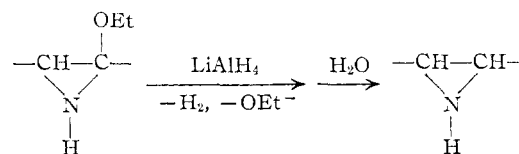
Discussion and Results

The results of the cleavage reactions are summarized in Table I. The data have been calculated on two bases: (1) the quantity of unsplit amine, $ROCH_2CH_2CH_2NH_2$, isolated and (2) the amount of product alcohol found. The true percentage cleavage, because of normal isolation losses, is somewhere between the two. The total percentage recovery, the summation of the amounts of unsplit amine and product alcohol, was in all cases in excess of 90%. It can be seen in Table I that the relative cleavages were least for the alkyl analogs and most for the aryl, with the benzyl in an intermediate position. The practically quantitative cleavage experienced with β-2-naphthoxypropionitrile is the result of the reaction being carried out in refluxing tetrahydrofuran. This matter will be discussed further below.

Table I

LiAlH₄ Cleavage of β-Propionitriles in Ether (35°)

β-Propionitrile	Cleavage, %, based on unsplit amine	Cleavage, %, based on product alcohol	Recovery, %
Isopropoxy	7.4	1.9	94.5
n-Butoxy	9.8	5.4	95.6
n-Octyloxy	9.4	3.2	93.8
Benzyloxy	11.5	11.0	99.5
Phenoxy	25.3	16.1	90.8
2-Naphthoxy	..	92.6[a]	92.6

[a] The reaction was run in tetrahydrofuran (65°) because of the insolubility of the nitrile in ether.

It seemed of interest to determine whether cleavage would occur if, instead of the nitrile, the unsplit amine was subjected to the identical reaction procedure. From such experiments one could determine (1) the amounts of cleavage resulting from the reaction of the nitrile with lithium aluminum hydride, and (2) the amount, if any, occurring

(6) M. J. Hatch and D. J. Cram, ibid., 75, 40 (1953).

unavoidably during the hydrolysis of the complex and unreacted hydride (Table II).

TABLE II

ACTION OF LiAlH₄ ON γ-PROPYLAMINES (ETHER, 35°)

γ-Propylamine	Cleavage, %, based on unsplit amine	Cleavage, %, based on alcohol	Recovery, %
Isopropoxy	14.5	Trace	85.5
n-Butoxy	3.4	Trace	96.6
n-Octyloxy	9.7	2.4	92.7
Benzyloxy	6.9	Trace	93.1
Phenoxy	8.6	Trace	91.4

These data suggest the following conclusions: One, with the possible exception of β-n-octyloxy-propylamine, no significant amount of cleavage occurred through any action of hydride on γ-propyl-amines or during the hydrolysis of complex and unreacted hydride. Therefore, the observed cleavages with the propionitriles were real and did occur on the nitrile. Two, without the isolation of the alcohol in question, "cleavages" of approximately 10% or less would be best regarded as no cleavage at all, since normal isolation losses may indicate such values.

As noted in Table I the reaction of β-2-naphth-oxypropionitrile was performed in tetrahydrofuran (65°) because of the material's insolubility in ether. From the failure to isolate any γ-2-naphthoxypro-pylamine and from the excellent recovery of β-naphthol it was concluded that cleavage was probably complete. In order to determine whether this result was due to the higher temperature, the different solvent or, less likely, was peculiar to β-2-naph-thoxypropionitrile, the phenoxy analog was run in tetrahydrofuran at 34° and at 65°. In contrast with the 25% maximum value found for cleavage in ether, scission in both runs was practically complete, thus demonstrating the importance of the role of the solvent (see Table III). In addition, high cleavages also were obtained with the benzyl-oxy and n-octyloxy derivatives. This "solvent effect" is being studied further.
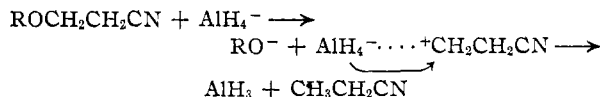
TABLE III

LiAlH₄ CLEAVAGE OF β-PROPIONITRILES IN TETRAHYDRO-FURAN

β-Propionitrile	Temp., °C.	Cleavage, %, based on unsplit amine	Cleavage, %, based on alcohol	Recovery, %
2-Naphthoxy	65	. . . .	92.6	92.6
Phenoxy	65	Very high[a]	99.3	99.3
Phenoxy	34	Very high[a]	94.7	94.7
Benzyloxy	34	86.2	77.4	91.2
n-Octyloxy	34	92.6	91.3	98.7
Isopropoxy	65	88.7	. .	88.7

[a] Sufficient amount of γ-phenoxypropylamine was isolated to obtain the infrared spectrum.

Since it was evident that scission did not occur on the propylamino ether it must have taken place on the nitrile or some intermediate reduction species. The simplest possible mechanism would involve the nucleophilic displacement of the alkoxy (or aryloxy) fragment by the aluminohydride ion.[7]

(7) The equation is intended to merely express the scission in the broadest sense and should not be taken literally. Undoubtedly, neither the alkoxy fragment nor the nitrile function are present in the reaction mixture in the forms shown.

$$ROCH_2CH_2CN + AlH_4^- \longrightarrow$$
$$RO^- + AlH_4^- \cdots{}^+CH_2CH_2CN \longrightarrow$$
$$AlH_3 + CH_3CH_2CN$$

The most serious objection to such a mechanism is that it is incompatible with the fact that hydrogen is evolved during the reaction. It can be seen in Table IV that the amounts of gas produced (on a mole per cent. basis) are in good agreement, for the runs in ether, with the degree of cleavage observed.[8,9]
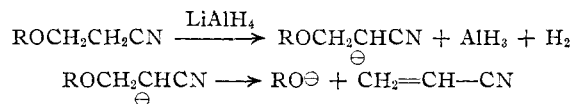
TABLE IV

EVOLUTION OF HYDROGEN DURING β-PROPIONITRILE RE-DUCTION

β-Propionitrile	Mole % cleavage, on basis of un-split amine recd.	Mole % H₂ evolved, on basis of propionitrile used
	In ether solution	
n-Butoxy	10.4	7.9
n-Octyloxy	9.4	9.1
Isopropoxy	7.4	13.2
Phenoxy	25.3	24.3
Benzyloxy	11.5	13.8
	In tetrahydrofuran solution	
n-Octyloxy	92.6	102.1
Isopropoxy	88.7	99.5
Benzyloxy	86.2	101.9

A second and more attractive mechanism would involve the elimination of acrylonitrile, as suggested by Wright and Minsk[4] for the decyanoethylation of polyvinyl β-cyanoethyl ether by sodium hydroxide in a water–methyl cellosolve system. Presumably, the acrylonitrile would be further reduced to n-pro-pylamine. It is possible, of course, that elimination and reduction of acrylonitrile would occur simultaneously. In either event the reaction would be an example of an elimination effected by lithium aluminum hydride. It is well known that elimination reactions occur with organometallic reagents such as butyllithium and phenyllithium[10,11] as well as with the Grignard reagent.[12] Similarities in chemical behavior between the latter reagent and lithium aluminum hydride have been pointed out by several workers.[5,13,14]

Crudely expressed, this mechanism would be

$$ROCH_2CH_2CN \xrightarrow{\text{LiAlH}_4} ROCH_2\overset{\ominus}{C}HCN + AlH_3 + H_2$$
$$ROCH_2\overset{\ominus}{C}HCN \longrightarrow RO^\ominus + CH_2{=}CH{-}CN$$

(8) Although it does not appear to be stated explicitly it may be inferred from the literature (see ref. 13, 14 and 24) that hydrogen is not evolved during the hydride reduction of an aliphatic nitrile in ether solution, especially where an excess of hydride is used. In our experiments it was observed that very little gas (0.01–0.02 mole per mole of nitrile) was evolved during the reductions of n-butyronitrile and of n-valeronitrile.

(9) The amounts of hydrogen evolved during reductions of β-propionitriles in tetrahydrofuran were always in excess of the observed degree of cleavage. Furthermore, it was found, in contrast to the case in ether, that the reductions of n-butyronitrile and n-valeronitrile resulted in a considerable evolution of hydrogen. This difference in the course of the reduction in the two solvents is undergoing further study.

(10) R. L. Letsinger and E. Bobko, THIS JOURNAL, 75, 2649 (1953).

(11) R. L. Letsinger, A. W. Schnizer and E. Bobko, ibid., 73, 5708 (1951); ref. 3.

(12) V. Grignard, Compt. rend., 138, 1048 (1904).

(13) R. F. Nystrom and W. G. Brown, THIS JOURNAL, 70, 3738 (1949).

(14) W. G. Brown, in "Organic Reactions," Roger Adams, ed., Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 470.

Some support for this mechanism would be had if acrylonitrile were reduced by lithium aluminum hydride, under the conditions of our experiments, to n-propylamine. A search of the literature failed to indicate the reaction had been performed. When attempted[15] it was found that the addition of acrylonitrile to hydride in ether yielded at contact, as the principal product of the reaction, a yellow solid which appeared to be a polymeric, and partially reduced, acrylonitrile.[16]

The realization that there was a gross difference between (1) a possible slow elimination of acrylonitrile from the β-propionitriles and (2) the sudden introduction of relatively large amounts of acrylonitrile in this latter experiment led to the repetition of the reduction with diluted acrylonitrile (1 part nitrile to 25 parts of ether by weight). The product was again a yellow polymer and, as before, difficult to separate from the inorganic material present. A third attempt was made in which the nitrile was further diluted (1 part to 175 parts of ether by weight). This time there was no formation of the yellow polymer; instead, the principal product was a viscous material regarded as a polymeric amine.

It is concluded from these experiments that the major process by which scission occurs in ether is not the elimination of acrylonitrile as such. However, this latter process may well account for a small amount of cleavage, since small amounts of n-propylamine were obtained when acrylonitrile was reduced with hydride. It is possible that the actual mechanism by which the large portion of the cleavage occurs involves a prior partial reduction of the propionitrile moiety, followed by its elimination, or a simultaneous partial reduction and elimination. Whether or not the cleavage is actually an elimination (in the strict sense of the term) might be decided by studying the reduction of the analogous -oxyacetonitriles ($ROCH_2CN$) and -oxybutyronitriles ($ROCH_2CH_2CH_2CN$). Another approach, based on the fact that one of a pair of geometrical isomers usually undergoes preferential elimination, would be to study the reactions with the *cis–trans* isomers of the 1-cyano-2-alkoxycyclohexanes.[17]

Experimental[18,19]

Materials.—Lithium aluminum hydride was obtained from Metal Hydrides, Inc., Beverly, Massachusetts. Anhydrous ether, Baker Analyzed reagent grade, was used throughout the experiments. Commercial tetrahydrofuran was purified by distillation from lithium aluminum hydride and used promptly (b.p. 65–66°).

β-Oxypropionitriles.—The following nitriles were used: β-n-butoxypropionitrile, b.p. 83–89° at 8 mm., n^{24}D 1.4164; lit.[20] b.p. 98° at 20 mm., n^{20}D 1.4180; β-isopropoxypropionitrile, b.p. 83° at 25 mm., n^{24}D 1.4067; lit.[20] b.p. 82.5° at 25 mm., n^{20}D 1.4089; β-benzyloxypropionitrile, b.p. 113–115° at 0.5 mm., n^{24}D 1.5110; lit.[20] b.p. 114–116° at 0.5 mm., n^{20}D 1.5111; β-n-octyloxypropionitrile, b.p. 152–153° at 20 mm., n^{24}D 1.4324; lit.[21] b.p. 150° at 20 mm.; β-phen-

oxypropionitrile, m.p. 62°; lit.[22] m.p. 61–62°; and β-2-napthoxypropionitrile, m.p. 107°; lit[23] m.p. 105.5–107.0°. The infrared spectra served as a check on the absence of moisture and parent alcohol.

Reduction of the Various Oxynitriles.—Experiments were made with 0.15–0.20 mole of nitrile. The ratio of hydride to nitrile in all runs was 2 to 1 in order to ensure the reduction of the nitrile function.[24] Essentially identical procedures were used for reactions in ether and in tetrahydrofuran, with exceptions as noted. In some of the ether runs a very small amount of high-boiling, viscous, basic material remained as pot residue after stripping out the unsplit amine. In no case was unreacted nitrile recovered. The reduction of β-n-butoxypropionitrile in ether illustrates the procedure.

In a 1-liter, 3-necked flask equipped with a mercury-sealed paddle stirrer, efficient reflux condenser and dropping funnel were placed 15.2 g. (0.4 mole) of crushed lithium aluminum hydride and 400 ml. of anhydrous ether. All outlets were protected with Ascarite drying tubes. After several hours refluxing, 26.0 g. (0.204 mole) of β-n-butoxypropionitrile was added dropwise over the period of one hour.[25] Refluxing was continued for an additional 1.5 hours. The reaction mixture was cooled to 10°, and maintained at this temperature while water was carefully added dropwise, until the excess hydride and complex were hydrolyzed. The mixture was made slightly acidic by the dropwise addition of concentrated hydrochloric acid (5–10°). The ether layer was separated and the solid residue extracted five times with ether. The combined ether extracts were dried over anhydrous sodium sulfate and the ether distilled through an efficient fractionating column. The last 10–20 ml. of solution were transferred to a micro distilling apparatus and the last of the ether removed. The residue (1 ml., 0.011 mole) was a slightly colored liquid whose infrared spectrum was identical with that of n-butyl alcohol (n^{25}D 1.3987, lit.[26] n^{25}D 1.3974; m.p. of 3,5-dinitrobenzoate, 61–62.5°, lit.[26] 64°, 62.5°, no depression on admixture with authentic sample).

After the addition of 200 ml. of ether to the solid residue from the above extraction, the mixture was carefully made slightly alkaline (10°) and extracted five times with ether. The extracts were combined, dried over sodium sulfate, and the ether (and n-propylamine) distilled at 34°. The distillate was dried over potassium hydroxide pellets. Passage of dry hydrogen chloride gas into the cold solution precipitated 20–40 mg. of n-propylamine hydrochloride (m.p. of chloroplatinate 214–215° dec.; lit.[27] 214°, mixed m.p. with authentic sample showed no depression; m.p. picrate 135°; lit.[27] 135°, mixed m.p. with authentic sample showed no depression.

Distillation of the pot liquid at the water-pump yielded 24.1 g. (0.184 mole) of γ-n-butoxypropylamine (b.p. 78° at 23 mm., n^{24}D 1.4251); lit.[20] 75–76° at 21 mm., n^{20}D 1.4273).

The recovery was 0.195 mole or 95.6%. The degree of cleavage was 5.4% based on n-butyl alcohol and 9.8% based on β-n-butoxypropylamine.

The gases evolved during hydrolysis of the reaction mixture were passed through dilute hydrochloric acid. The presence of trace amounts of ammonia in these gases was demonstrated by taking the solution to dryness and identifying the minute amount of white salt as ammonium chloride by its m.p. behavior, infrared spectrum in perfluorokerosene, and chloroplatinate derivative.

The volume of gas evolved during the reduction process was determined by passing the gases through a Dry Ice–acetone trap to remove solvent and collecting them over water. Gas samples for infrared analysis were collected over mercury. *In all cases the gas was shown to be hydrogen.*

(15) See Experimental for details.

(16) The polymerization of acrylonitrile in butane at low temperatures by means of lithium diphenylamide has been reported by O. H. Bullitt, Jr., U. S. Patent 2,608,554, Aug. 26, 1952; C. A., 47, 1430 (1953).

(17) Suggested by George S. Hammond, Iowa State College.

(18) All m.p.'s and b.p.'s are uncorrected.

(19) Initial experiments were performed by George S. Melville, Jr.

(20) W. P. Utermohlen, Jr., This Journal, 67, 1506 (1945).

(21) J. H. MacGregor and C. Pugh, J. Chem. Soc., 535 (1945).

(22) A. H. Cook and K. J. Reed, ibid., 920 (1945).

(23) G. B. Bachman and H. A. Levine, This Journal, 69, 2343 (1947).

(24) L. H. Amundsen and L. S. Nelson, ibid., 73, 243 (1951).

(25) The solids, β-phenoxypropionitrile and β-2-naphthoxypropionitrile were added in ether and in tetrahydrofuran solution, respectively.

(26) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds, Order 1," John Wiley and Sons, Inc., New York, N. Y., 1941.

(27) F. Wild, "Characterization of Organic Compounds," Cambridge University Press, 1947, p. 237.

In the reduction of the alkoxy nitriles in tetrahydrofuran, including the benzyl analog, hydrolysis was followed by removal of most of the solvent (water-pump). After the addition of 200 ml. of ether the isolation was performed as described.

In the case of the phenoxy and naphthoxy analogs, removal of the tetrahydrofuran was followed by extraction of the unsplit amine (where present) with ether. Acidification of the solid residue, followed by extraction with ether, yielded the respective alcohol. Phenol was assayed in ether solution by the measurement of its absorption band in the 14.4 μ region.[28] Control experiments indicated the ether was a satisfactory substitute for acetone, the latter being used by Smith and co-workers.

Characterization of Reaction Products. (a) From β-n-Butoxypropionitrile.—n-Butyl alcohol (n^{25}D 1.3987; lit.[26] n^{25}D 1.3974; 3,5-dinitrobenzoate, m.p. 61–62.5°; lit.[26] 64°, 62.5°, mixed m.p. with authentic sample no depression). γ-n-Butoxypropylamine (b.p. 78° at 23 mm., n^{24}D 1.4251; lit.[20] b.p. 75–76° at 21 mm., n^{20}D 1.4273). n-Propylamine (m.p. of chloroplatinate[29] 214–215° dec.; lit.[27] 214°, mixed m.p. with authentic sample no depression; m.p. of picrate 135°; lit.[27] 135°, mixed m.p. with authentic sample no depression).

(b) From β-Isopropoxypropionitrile.—Isopropyl alcohol (n^{24}D 1.3785; lit.[26] 1.3781; m.p. of p-nitrobenzoate 110°; lit.[26] 110.5°, 111°). γ-Isopropoxypropylamine (b.p. 78–79° at 85 mm., n^{20}D 1.4190; lit.[20] b.p. 85–86° at 102 mm., n^{20}D 1.4195; neut. equiv. found 118.3, theor. 117.2; m.p. chloroplatinate 203°, lit. none). n-Propylamine (constants given above).

(c) From β-n-Octyloxypropionitrile.—n-Octyl alcohol (m.p. of 3,5-dinitrobenzoate 60–61°; lit.[26] 60.8°; mixed m.p. with authentic sample no depression). γ-n-Octyloxypropylamine (b.p. 101° at 1 mm., n^{24}D 1.4383; lit. none; neutral equivalent found 188.3, theor. 187.3; m.p. of chloroplatinate 197–198° dec.).

(d) From β-Benzyloxypropionitrile.—Benzyl alcohol (b.p. 109–110° at 25 mm., n^{25}D 1.5367; lit.[26] b.p. 205.5° at 760 mm., n^{20}D 1.53955; m.p. of p-nitrophenylurethan 154–156°; lit.[26] 157°, mixed m.p. with authentic sample no depression). γ-Benzyloxypropylamine (b.p. 103° at 2 mm., n^{24}D 1.5138; lit.[20] b.p. 93.5° at 0.75 mm., n^{20}D 1.5170; neut. equiv. found 167.3, theor. 165.2; chloroplatinate m.p. 194–195°). n-Propylamine (constants are given above).

Anal. Calcd. for C₂₀H₃₂O₂N₂PtCl₆: Pt, 26.37. Found: Pt, 26.38.

(e) From β-Phenoxypropionitrile.—Phenol (m.p. of 3,5-dinitrobenzoate 145–146°; lit.[26] 145.8°, mixed m.p. with authentic sample no depression); γ-phenoxypropylamine (b.p. 110–112° at 3 mm., n^{24}D 1.5224; lit. none); m.p. of benzamide 120.5°; m.p. of p-nitrobenzamide 135–136°; m.p. of chloroplatinate 210–211°. n-Propylamine (constants are given above).

(28) J. J. Smith, F. M. Rugg and H. M. Bowman, *Anal. Chem.*, **24**, 497 (1952).

(29) M.p. of chloroplatinates were obtained by inserting the capillary in the bath at 190° and raising the temperature at the rate of 2° per minute.

Anal. Calcd. for C₁₆H₁₇O₂N: N, 5.49. Found: N, 5.54.

Anal. Calcd. for C₁₈H₂₈O₂N₂PtCl₆: Pt, 27.3 Found: Pt, 27.4.

(f) From β-2-Naphthoxypropionitrile.—2-Naphthol (m.p. 123°; lit.[26] same, no depression upon admixture with authentic sample; m.p. of 3,5-dinitrobenzoate 210°; lit.[26] 210.2°, no depression upon admixture with authentic sample).

Reaction of Acrylonitrile with Lithium Aluminum Hydride. (a) Undiluted.—In the usual apparatus were placed 22.8 g. (0.60 mole) of hydride and 600 ml. of anhydrous ether. After two hours refluxing, the heat was removed and 15.9 g. (0.30 mole) of acrylonitrile was added dropwise. A vigorous reaction occurred at contact with the hydride solution, evolving a yellow smoke and splattering a yellow solid on the walls of the flask and condenser. The mixture was refluxed for 1.5 hours after the completion of the addition, cooled to 10°, and carefully hydrolyzed by the dropwise addition of water. The evolved gases were passed through dilute hydrochloric acid. Ammonium chloride, 0.62 g., was later isolated from this solution. The hydrolyzed mixture was repeatedly extracted with ether, and the extract dried and distilled at 34°. Passage of dry hydrogen chloride into the distillate yielded 2.3 g. of n-propylamine hydrochloride. The high boiling residue from the ether distillation was a viscous, yellow material (3 ml.). It was concluded from the infrared spectrum that this material was a partially reduced, polymerized acrylonitrile.

The ether-insoluble solids were extracted with water and the aqueous extract distilled (water-pump) into a receiver packed in Dry Ice. Acidification of the distillate and removal of the water produced 1.8 g. of ammonium chloride.

Extraction of the ether-insoluble, water-insoluble residue with benzene yielded 1.5–2 g. of basic, viscous material apparently similar to that isolated earlier. Extraction of the solid residue with concentrated hydrochloric acid, followed by concentration of the acid solution to a small volume, resulted in a few grams of viscous material which could not be separated from the salts present. The insoluble residue from these operations was 1.7 g. of a yellow powder whose infrared spectrum indicated the presence of amine, nitrile and, possibly, imine functions.

(b) Diluted.—In the usual apparatus were placed 3.8 g. (0.1 mole) of hydride and 100 ml. of anhydrous ether. After two hours refluxing, a solution of 2.65 g. (0.05 mole) of acrylonitrile dissolved in 660 ml. of ether was added dropwise. The vigorous reaction obtained with undiluted acrylonitrile and the formation of a yellow solid were not observed. The products of the reaction were 0.25 g. of n-propylamine hydrochloride and 0.5 g. of a yellow, viscous, high-boiling material which could not be solidified. The material lacked nitrile absorption in the infrared and was possibly a polymeric amine.

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