By-products of Acrylonitrile Synthesis from Acetylene and Hydrocyanic Acid. II. Amines Obtained by Hydrogenation of Nitriles

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Introduction

In the previous paper[1], the presence of propionitrile, benzonitrile and naphthalene was confirmed and that of five olefinic nitriles, i. e., 1-cyanobutadiene, 2-cyanobutadiene, 1-cyanohexatriene, 2-cyanohexatriene, 3-cyanohexatriene, was suggested in the neutral by-products of acrylonitrile synthesis from acetylene and hydrocyanic acid.

The present paper deals with the comfirmation of these suggestions by means of the identification of the amines which were produced by the hydrogenation of the above mentioned by-products.

Results and Discussion

The neutral by-products of acrylonitrile synthesis were hydrogenated with Raney nickel. The hydrogenation products were divided into two parts, neutral and basic. The basic part was fractionated by distillation through a Stedman-type column. The results obtained are shown in Figs. 1 and 2. Thus the two constant boiling fractions were obtained, i. e., A–2 (b. p. 77–78.5°C) and A–7 (b. p. 103–106°C).

A–2 was treated with phenylisothiocyanate, resulting in the formation of crystals which melted at 61–61.5°C and were identified to be N, N′-*n*-butylphenylthiourea after a mixed melting point test. Treatment of A–7 with

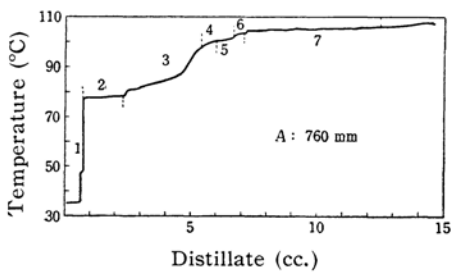


Fig. 1. Distillation curve of A-fractions.

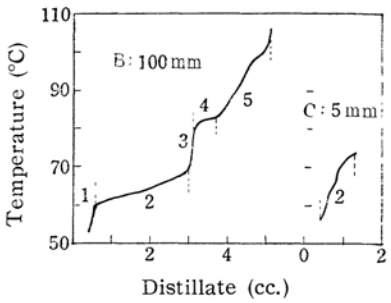


Fig. 2. Distillation curves of B- and C-fractions.

phenylisothiocyanate also gave crystals which melted at 62–63°C. The crystals were identified to be N, N′-*n*-amylphenylthiourea because the mixed melting point showed no depression. So it was confirmed that A–2 and A–7 contained *n*-butylamine and *n*-amylamine, respectively.

The paperchromatograms of hydrochlorides of A–3, A–4, B–2, B–4, B–5 and C–2 showed the presence of butylamines, amylamines, di-propylamine, heptylamines and benzylamine. But this method was not able to separate isomers mutually, i. e., 2-methylbutyl- from *n*-amyl-amine; 2-methylhexyl- and 2-ethylamyl- from *n*-heptyl-amine.

By the chromatography of N-2, 4-dinitrophenylamines (DNP-amines) on the column of cation exchanger the author[2] had already succeeded in separating isomers, i. e., DNP-isopropyl- from DNP-*n*-propyl-amine; DNP-isobutyl- from DNP-*n*-butyl-amine.

By the column-chromatography of DNP-derivatives of A–4, B–4, B–5 and C–2, the presence of *n*-butyl-, 2-methylbutyl-, *n*-amyl-, di-*n*-propyl-, benzyl- and *n*-heptyl-amines and two other primary heptylamines than *n*-heptylamine could be confirmed.

The amines which may be obtained by the hydrogenation of the above mentioned nitriles are as follows:

1) S. Morimoto, This Bulletin, 29, 450 (1956).

2) T. Seki and S. Morimoto, *J. Chm. Soc. Japan (Pure Chem. Sect.)*, 77, 1124 (1956).

$CH_2=CH-CN,\ CH_3-CH_2-CN \longrightarrow CH_3\cdot CH_2\cdot CH_2-NH_2,\ CH_3\cdot CH_2\cdot CH_2-NH-CH_2\cdot CH_2\cdot CH_3$

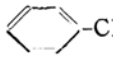
$CH_2=CH-CH=CH-CN \longrightarrow CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2-NH_2$

$CH_2=CH-C(CN)=CH_2 \longrightarrow CH_3\cdot CH_2\cdot CH(CH_3)\cdot CH_2-NH_2$

$CH_2=CH-CH=CH-CH=CH-CN \longrightarrow CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2-NH_2$

$CH_2=CH-CH=CH-C(CN)=CH_2 \longrightarrow CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(CH_3)\cdot CH_2-NH_2$

$CH_2=CH-CH=C(CN)-CH=CH_2 \longrightarrow CH_3\cdot CH_2\cdot CH_2\cdot CH(C_2H_5)\cdot CH_2-NH_2$



The two primary heptylamines other than *n*-heptylamine are possibly 2-methylhexyl- and 2-ethylamyl-amines which may be obtained from 2-cyanohexatriene and 3-cyanohexatriene, respectively.

These facts confirmed the suggestions described in the previous paper. The presence of *n*-butylamine may be explained by the formation of allylcyanide, since the formation of acetonitrile from acetylene and hydrocyanic acid was confirmed in the author's other experiment[3].

Experimental

1. Catalytic Hydrogenation of the Neutral By-products.—The neutral part[1] (109 g.) of by-products which were obtained as the intermediate distillation fraction between acrylonitrile and succinodinitrile was hydrogenated with Raney nickel under the condition shown in Table I.

TABLE I

HYDROGENATION OF THE NEUTRAL BY-PRODUCTS OF ACRYLONITRILE SYNTHESIS

Inhalt of stainless steel autoclave, 330 cc.

Expt. No.	Starting material g.	Catalyst (Alloy) g.	Press. atm.	Temp. °C	Time min.	Hydrogen absorbed mol.	Prod. g.
1	29	5	80–20	130	220	0.90	27
2	80	5	86–18	120	326	1.95	79

TABLE II

FRACTIONAL DISTILLATION OF BASIC HYDROGENATION PRODUCTS

No.	Temp. °C	Distillate cc.	No.	Temp. °C	Distillate cc.
A-Fractions (760 mmHg)			B-Fractions (100 mmHg)		
1	35–47.5	0.7	1	45–59.8	0.6
2	77–78.5	1.6	2	59.9–69.0	2.4
3	79–97.2	3.1	3	69–69.5	0.1
4	97.2–100	0.6	4	77–82.8	0.6
5	100–102	0.7	5	83.4–104.7	1.4
6	102–103	0.4			
7	103–106	5.4	C-Fractions (5 mmHg)		
8	106–107	2.2	1	–56.7	0.4
			2	58–73.5	0.9
			3	74	

The hydrogenation products (106 g.) were dissolved in the same amount of ether and treated with aq. hydrochloric acid solution, resulting in the separation of 11.2 cc. (containing ether and water) of the neutral part and 51 cc. (containing ether and water) of the basic part.

This basic part (51 cc.) was fractionated by distillation through a Stedman-type column (with stainless steel net; plate number 14–18) under different pressures successively: A, 760 mmHg; B, 100 mmHg; C, 5 mmHg: and the results are shown in Table II.

2. N,N′-Alkylphenylthiourea.—To 0.5 cc. of the constant boiling fraction A-2 (b. p. 77–78.5°C), 1 cc. of phenylisothiocyanate was added (exothermic) to form a very viscous liquid. After an addition of petroleum ether, the mixture was allowed to stand for several days to form crystals. These crystals were filtered and melted at 61–61.5°C, after recrystallization from benzene and petroleum ether. Yield 0.1 g. These crystals mixed with N,N′-*n*-butylphenylthiourea (m. p. 65 °C[4]) melted at 62.5–63°C, showing no melting point depression.

Anal. Found: C, 63.71; H, 7.46; N, 13.21. Calcd. for $C_{11}H_{16}N_2S$: C, 63.42; H, 7.74; N, 13.44%.

From the mixture of 0.5 cc. of the constant boiling fraction A-7 (b. p. 103–106°C) and 1 cc. of phenylisothiocyanate, 0.1 g. of crystals were obtained, and melted at 62–63°C. These crystals mixed with N,N′-*n*-amylphenylthiourea (m. p. 68–69°C[4]) melted at 65–68°C, showing no melting point depression.

Anal. Found: C, 65.04; H, 8.13; N, 12.53. Calcd. for $C_{12}H_{18}N_2S$: C, 64.81; H, 8.16; N, 12.60%.

3. Paperchromatography of Amine Hydrochlorides.—The paperchromatograms of hydrochlorides of A-3, A-4, B-2, B-4, B-5 and C-2 are shown in Fig. 3.

4. Chromatographic Separation of DNP-Amines on the Column of Cation Exchange Resin.—The aqueous solution of hydrochloride of A-4, B-4, B-5 or C-2 (5–10 cc., containing 0.3–4.0 mg.), the same amount of acetone, 1 cc. of acetone solution of 1-fluoro-2,4-dinitrobenzene

3) S. Morimoto, To be published.

4) Otterbacher and Whitmore, *J. Am. Chem. Soc.*, **51**, 1909 (1929).

TABLE III

MELTING POINTS AND ANALYTICAL RESULTS OF DNP-AMINES

DNP-Amine	Melting point Found °C	Literat. °C	Analytical results (%) Found C	H	N	Calcd. C	H	N
-benzyl-	115–6	115–6[5] 126[5'])	57.30	4.78	15.75	57.14	4.06	15.38
-*n*-heptyl-	22–3	20[5])	55.64	6.61	15.33	55.50	6.81	14.94

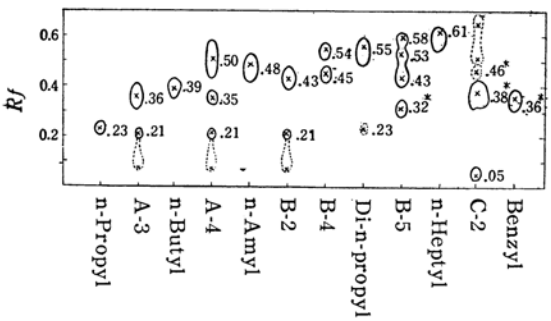


Fig. 3. Paperchromatograms of hydrochlorides of amines.
Developer, Butanol satuarated with water.
*yellow→purple

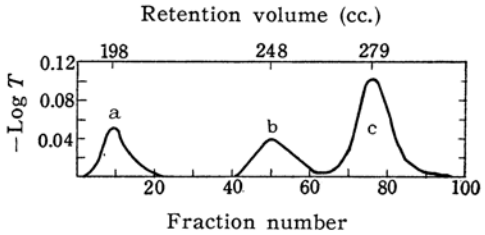


Fig. 4. Elution curve of DNP-A-4
one fraction=1.2 cc.

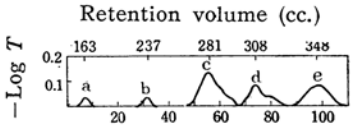


Fig. 5. Elution curve of DNP-B-4
one fraction=1.7 cc.

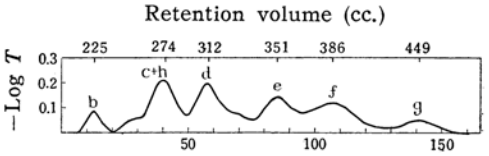


Fig. 6. Elution curve of DNP-B-5
one fraction=1.75 cc.

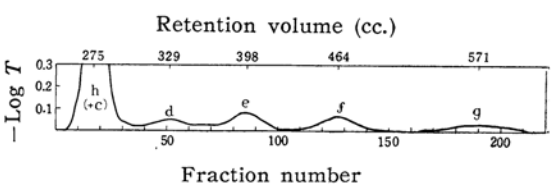


Fig. 7. Elution curve of DNP-C-2
one fraction=1.7 cc.

(FDNB) containing 0.02 g./cc.) and 1 cc. of 2% aqueous sodium bicarbonate solution were mixed and shaken for four hours. Then 1 cc. of aqueous solution of glycine and sodium carbonate (containing 0.008 g. glycine and 0.02 g. sodium carbonate per cc.) was added to the mixture and the resulting mixture was shaken for two more hours. After acetone was evaporated off under reduced pressure, the reaction mixture was extracted with ether three times. From the ether solution, ether was evaporated off under reduced pressure. The residue was dissolved in ten cc. of the mixed solvent (tetrahydrofuran, methylethylketone and water, 4:3:13). Two cc. of the solution was charged on the column (9×400 mm.) of cation exchanger, Amberlite IRC 50 (H-type), and developed with the same solvent.

An ultraviolet spectrophotometer was used to detect and estimate DNP-amines in effluents, taking advantage of the characteristic ultraviolet absorption at 360 mμ. The elution curves are shown in Figs. 4–7. The peaks a, b, c, d, g and h in these figures were identified to be those of DNP-*n*-butyl-, DNP-2-methylbutyl-, DNP-*n*-amyl-, DNP-di-*n*-propyl, DNP-*n*-heptyl- and DNP-benzylamines, by compareing with those of the standard samples, respectively. The peaks e and f are considered to be those of DNP-derivatives of two other primary heptylamines than *n*-heptylamine on the basis of their retention volumes.

5. Preparations of the Standard Samples of DNP-Amines.—N-2, 4-Dinitrophenyl-2-methylbutylamine.—To 30 cc. of aqueous solution containing 0.3 g. of 2-methylbutylamine hydrochloride and 0.6 g. of sodium bicarbonate, 35 cc. of alcoholic (or acetone) solution containing 0.5 g. of FDNB was added and allowed to stand over night in a refrigerator. The oil separated by decantation from the supernatant was dissolved in 30 cc. of alcohol (or acetone). To the solution, 16 cc. of water was added and allowed to stand over night to form 0.35 g. of crystals. The crystals were recrystallized from 25 cc. of alcohol (or acetone) and 11 cc. of water to form 0.3 g. of crystals which melted at 47.3–48°C.

Anal. Found: C, 52.10; H, 5.87; N, 16.87. Calcd. for $C_{11}H_{15}N_3O_4$: C, 52.17; H, 5.97; N, 16.59%. This substance has not been reported in literature up to this time.

5) A. Mulder, *Rec. trav. chim. Pay-Bas*, **25**, 111 (1906); H. J. Backer, ibid., **70**, 92 (1951).
5') G. T. Morgan, *J. Chem. Soc.*, **1915**, **107**, 1307.
6) E. J. Van der Kam, *Rec. trav. chim. Pay-Bas*, **45**, 722 (1926).

By the same way, DNP-benzylamine and DNP-*n*-heptylamine were prepared. Their melting points and analytical results are shown in Table III.

The reaction products of di-*n*-propylamine with FDNB did not solidify by the same way. But the sample showed an unique chromatographic band on the column except for DNP-*n*-propylamine. Thus the sample was employed as a qualitative standard.

The preparations of DNP-derivatives of *n*-propyl-, *n*-butyl- and *n*-amyl-amine were reported in the author's other paper[2].

Summary

The basic substances were obtained from the hydrogenation products of the neutral by-products of acrylonitrile synthesis from acetylene and hydrocyanic acid. They were fractionated by distillation through a Stedman-type column. *n*-Butylamine and *n*-amylamine were isolated and identified as derivatives of phenylthiourea. On the basis of chromatograms, i.e., the paperchromatograms of hydrochlorides of amines and chromatograms of N-2,4-dinitrophenyl-derivatives on the column of cation exchanger, the presence of seven amines, i.e., *n*-propyl-, *n*-butyl-, 2-methylbutyl-, *n*-amyl-, di-*n*-propyl-, *n*-heptyl- and benzyl-amines was confirmed and that of two primary heptylamines other than *n*-heptylamine, i.e., 2-methylhexyl- and 2-ethylamyl-amines, was suggested.

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