[Contribution from the Noyes Chemical Laboratory, University of Illinois]

THE ADDITION OF 1,3-BUTADIENE TO PROPIONITRILE[1]

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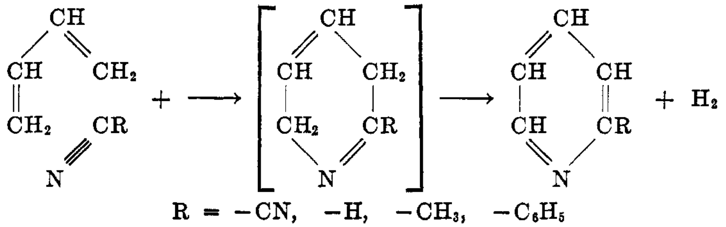
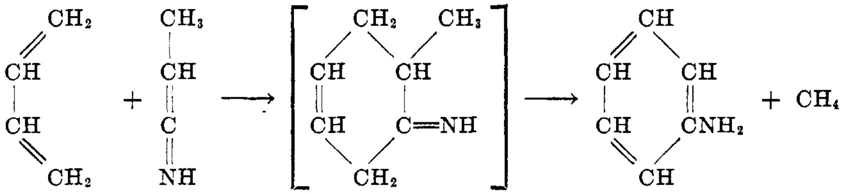
The addition of butadiene to cyanogen, hydrogen cyanide, acetonitrile, and benzonitrile at relatively high temperatures has been reported by Janz and his co-workers (1, 2). The products are α-substituted pyridines which apparently result from a Diels-Alder type addition between the diene and the —C≡N group followed by dehydrogenation.



This reaction seemed suited to the preparation of 2-ethylpyridine by use of propionitrile for the cyanogen derivative. Accordingly the reaction was carried out under the general conditions used before.

In our experiments with butadiene and propionitrile at 600° and atmospheric pressure reaction did occur, but the liquid product proved to be a mixture containing some butadiene dimer (vinylcyclohexene) and a basic fraction which contained a pyridine derivative first identified by the characteristic odor and later characterized as 2-ethylpyridine, and a primary amine which proved to be aniline. The pyridine derivative was formed in only about 0.5% yield and the aniline in 4.0% yield (based on the total butadiene employed) in one pass through the hot tube.

The formation of aniline in the reaction was extremely surprising. Further examination of the reaction products demonstrated that methane was also produced and this accounts for the carbon atom which is lost when butadiene and propionitrile yield aniline. We at first thought some acetonitrile might be formed in our hot tube by cracking propionitrile, but this was shown not to be the case. We have postulated the following probable intermediates to account for the proproduction of aniline.



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Under the same general reaction conditions acetonitrile adds butadiene to give aniline as the principal reaction product and very little, if any, pyridine derivative is formed. Acetyl cyanide at 315°, 400°, or 530° did not add butadiene.

Packing the hot tube with various catalysts such as calcium sulfate, steel wool, silica gel, chromic oxide, and cuprous oxide did not seem to change the course of the reaction. Fresh aluminum-oxide surfaces did suppress the yield of aniline, although the total amount of the basic addition product remained about the same as when no catalytic surface was present.

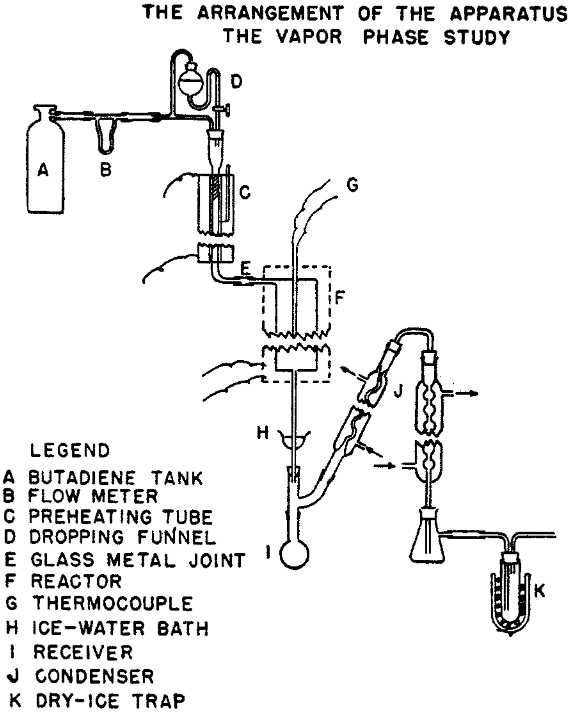

FIGURE 1.

EXPERIMENTAL

All melting points and boiling points reported are uncorrected. All microanalyses were done by the Clark Microanalytical Laboratory. We are indebted to Mrs. J. L. Johnson for the infrared spectra determinations and their interpretation.

Apparatus. The reaction tube was built on the plan outlined by Janz and his co-workers (1, 2) and the apparatus was assembled as in Figure 1.

Procedure. Before each run the whole system was swept out with nitrogen gas and after each run the hydrocarbon-nitrile vapors were again swept out of the apparatus with nitrogen in the interest of safety. When the temperature of the furnace was at the proper point, the flow of butadiene was started and propionitrile in excess was admitted from the dropping-funnel into the preheater which was maintained at 260–280°. Glass beads were placed in the upper part of the preheater to give heat transfer surface.

The dark liquid which gathered in flask I was fractionated in an 11-in. helices-packed column to separate unchanged propionitrile and the residue was extracted with three or four 10–20-ml. portions of 5% hydrochloric acid. The acid extract was washed with benzene and with ether and was heated to remove any dissolved solvent. It was then made alkaline with excess solid potassium hydroxide, the oil was separated, and the aqueous layer was extracted with ether. The combined oil and extract were dried over potassium carbonate and distilled.

TABLE I

REACTION OF BUTADIENE WITH PROPIONITRILE AT ELEVATED TEMPERATURES

RUN NO.	REACTANTS		EXPERIMENTAL CONDITIONS			RECOVERY[d]				YIELD[g]			
	Propionitrile,[a] g.	Butadiene,[b] g.	Temp. of Reactor, °C.	Time of Pass, Sec.[c]	Catalyst	Propionitrile[e]		Butadiene[f]		Aniline[h]		2-Ethylpyridine[h]	
						g.	%	g.	%	g.	%	g.	%
7	338	54	600	109	None	262	78	—	—	4.1	4.4	—	—
8	157	20	600	88	"	110	70	6.5	32	1.5	4.4	—	—
9	188	176	610	29	"	153	81	68	39	1.3	0.4	0.2	0.1
10	156	23	610	101	"	105	67	15.5	67	1.6	4.0	.2	.5
11[i]	141	169	600	99	"	96	68	62.5	37	1.1	0.4	.3	.1
12[i]	141	147	610	60	"	88	62	49.5	34	0.8	.3	.2	.1
15	[j]	[j]	700	100	"	—	—	—	—	Extensive pyrolysis			
16	81	82	300	30	Al_2O_3[k]	64	79	60	73	—	—	.5[l]	.3

[a] B.p. 96.9–97°, n_{D}^{20} 1.3651–1.3661. [b] Special purity grade, Phillips Petroleum Company, Bartlesville, Oklahoma. [c] Calculated assuming both reactants in the gaseous state are ideal gases. [d] The percentage recoveries of propionitrile and butadiene were based on the total amounts of the respective reagents employed in the reaction. [e] B.p. 95–97°, n_{D}^{20} 1.3667–1.3997. [f] The butadiene collected in a Dry-Ice trap during the reaction and during the fractionation of the reaction condensate, constitutes this total recovery. [g] The yields of aniline and 2-ethylpyridine in runs 7–10 were based on the total amount of butadiene employed whereas the yields in runs 11, 12, and 16 were based on the total amount of propionitrile employed in the reaction. [h] Estimated from the infrared absorption spectra and the indices of refraction of the distilled product. [i] The reaction condensate, after removal of unchanged propionitrile, was fractionated directly in an 8-in. helices-packed column. 2-Ethylpyridine and aniline were then isolated from the corresponding fractions. [j] Molar ratio of propionitrile to butadiene was 7.0:1. [k] Reaction conducted in a 23-in. pyrolysis tube packed with the catalyst (10-mesh Hydralo, 157 g.). The catalyst was heated at the reaction temperature for ½-1 hour before the reaction was started. [l] Picrate, m.p. 102–105.5°.

Table I is a summary of typical experiments.

Other runs were made with tube packings of anhydrous calcium sulfate (Drierite, blue indicator, 8 mesh), steel wool (Beaver grade No. 1), silica gel (6–16 mesh), chromic oxide, and cuprous oxide in an iron tube at 500° and 600°. Aniline and 2-ethylpyridine were found in approximately the same ratio as in the unpacked tube.

Identification of aniline. The crude base separated from run 7 was distilled under reduced pressure; the major portion boiled at 79–81° at 15 mm. This material gave a picrate, m.p. 188–189°, a salt with methyl *p*-toluenesulfonate, m.p. 227–229.5°; a benzenesulfonamide, m.p. 108.5–109.5°; an acetyl derivative, m.p. 113.5–114.5°; and a derivative with phenyl isothiocyanate, m.p. 150.7–151°. Since aniline was unsuspected, the salts with picric acid (A) and methyl *p*-toluenesulfonate (B) were analyzed.

Anal. Calc'd for (A) $C_{12}H_{10}N_4O_7$: C, 44.80; H, 3.13; N, 17.38.

Found: C, 45.27; H, 2.89; N, 17.23.

Anal. Calc'd for (B) $C_{14}H_{17}O_3S$: C, 60.30; H, 6.16; N, 5.02; S, 11.46.
Found: C, 59.01; H, 6.08; N, 4.48; S, 11.48.

With this clue to the composition, the other derivatives were analyzed and compared with the corresponding derivatives of authentic aniline. Benzenesulfonamide of aniline, m.p. 106–107°; mixed m.p. with benzenesulfonamide of unknown, 107–108.5°. Acetanilide, m.p. 113–114°; mixed m.p. with acetyl derivative of unknown, 112.5–114°. Diphenylthiourea, m.p. 150.5–151.5°; mixed m.p. with phenyl isothiocyanate derivative of unknown, 149.5–150.5°.

A micro boiling-point determination of the unknown base gave 184° at 740 mm.; $n_D^{24.2}$ 1.5772. The infrared pattern of the unknown and of aniline were identical showing characteristic bands at 1420, 1435, 1465, 1500, 1520, and 1540 cm.$^{-1}$.

Identification of methane. The gas evolved in run 11 was collected over water. It was then washed with saturated bromine water and 20% potassium hydroxide, and dried over calcium chloride, Ascarite, and Hydralo in sequence. This purified gas gave infrared absorption bands at about 1300 and 3000 cm.$^{-1}$ which are characteristic of methane (3).

Identification of 2-ethylpyridine. The condensate in run 11 was fractionated in an 8-in. helices-packed column and the fraction boiling at 87–95°/100 (n_D^{20} 1.5006) was collected (4.2 g.). The basic material in this fraction was dissolved in 5% hydrochloric acid and separated. Then the basic material was salted out by the additon of excess solid potassium hydroxide. About 0.3 ml. of base was obtained as a liquid. The aqueous alkali was extracted with ether and 2 ml. of the extract obtained. The characteristic pyridine odor was noted in these extracts.

To 1 ml. of the ether extract was added a saturated solution of picric acid in ether. The solid *picrate* which separated was twice recrystallized from water, m.p. 104–106.5°. A sample of authentic picrate of 2-ethylpyridine,[3] m.p. 108–109.5°, was mixed with the above in equal amounts and the mixture melted at 105.5–107.5°.

The remaining 1 ml. of ether extract was treated with 0.25 ml. of 10% hydrochloric acid, the ether layer was separated, and a solution of 0.20 g. of mercuric chloride in 1.5 ml. of hot water was added to the acid solution. The precipitate which formed was recrystallized twice from hot water, m.p. 102.5–106.5°. A mixture of this salt with authentic 2-ethylpyridine mercuric chloride salt (4), m.p. 102.5–106°, melted at 103.5–106°.

Addition of butadiene to acetonitrile. When 22.5 g. of butadiene and 206 g. of acetonitrile were allowed to react in the unpacked reactor at 600° and 60-seconds passage time, the basic condensate (0.4 g., 1% yield found on the total butadiene used) boiled at 186–187° at 740 mm.; n_D^{23} 1.5760; benezenesulfonyl derivative, m.p. 104–107°. These data support the view that this base was nearly all aniline.

Attempted pyrolysis of propionitrile at 600°. Passage of propionitrile through the unpacked reactor at 600° and 87-seconds passage time did not produce an appreciable amount of low-boiling material and no evidence of methane production was found.

Attempted addition of butadiene to acetyl cyanide. Acetyl cyanide prepared by the method of Migrdichian (5) was passed through the reactor with butadiene as described in the acetonitrile experiment at three different temperatures, 315°, 400°, and 530°. The product obtained in each case was the dimer of butadiene and the dimer of acetyl cyanide. No evidence of the formation of 2-acetylpyridine could be obtained.

SUMMARY

Butadiene and excess propionitrile in the vapor phase combine at 600° to give low yields of aniline and 2-ethylpyridine. In the presence of fresh aluminum-

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[3] 2-Ethylpyridine was prepared by the catalytic hydrogenation of 2-vinylpyridine over Raney nickel in alcoholic solution at 25° and 2.5 atm., b.p. 147–148°, n_D^{21} 1.4964. Frank and Phillips, *J. Am. Chem. Soc.*, **71**, 2804 (1949), prepared 2-ethylpyridine from ethyllithium and pyridine; their picrate had m.p. 110–111° (private communication, March 1948). Gregg and Craig, *J. Am. Chem. Soc.*, **70**, 3138 (1948), report m.p. 108.5–110°. Furst, *J. Am. Chem. Soc.*, **71**, 3550 (1949) reports m.p. 107–107.5°.

oxide surfaces the ethylpyridine is formed and aniline is not produced in appreciable quantitites. Butadiene and acetronitrile also react at 600° to give aniline. No evidence of addition of butadiene to acetyl cyanide was found.

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