[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE ACTION OF HEAT ON ETHYLAMINE AND BENZYLAMINE

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RECEIVED AUGUST 11, 1930 PUBLISHED OCTOBER 6, 1930

The only primary aliphatic amines whose pyrolysis has been studied are ethylamine and propylamine. The former has been investigated at 500, 700 and 1000° over kaolin by Upson and Sands.[2] At the lower temperatures the major primary reaction is the formation of acetonitrile and hydrogen, along with the not inappreciable production of ethylene and ammonia. The products at 1000° are stated to be hydrogen, nitrogen and butane. Müller[3] found that at 1240° the products are hydrogen cyanide and methane. From *n*-propylamine at 700°, Upson and Sands obtained propionitrile, hydrogen cyanide, ammonia, ethylene, propylene, hydrogen and nitrogen.

In the present investigation, an experiment with ethylamine at 600° was carried out but our major interest was at higher temperatures. Several runs were made at 890–900° (furnace temperature of 980°), and in these the contact time was varied from one second to 300 seconds.

Acetonitrile was found at 600° but not at 900°. Hydrogen cyanide was always present at the higher temperature, but only a small amount of ammonium cyanide was noticed when the contact time was in excess of one minute. No cyanogen was formed whatsoever. The effect of contact time on the yield of ethylene at 900° is marked. With a contact time of one second the ethylene content of the gases was 10.3%; with 15.5 seconds, 5.0%; with eighty seconds, 0.5%; and with longer durations, no ethylene at all. This agrees with Bone and Coward's[4] statement that ethylene is nine-tenths decomposed in one minute at 950°, chiefly into methane and hydrogen.

In experiments with a kaolin-packed tube (as in Upson and Sands' experiments), the formation of appreciable volumes of carbon monoxide was observed. This is not a new type of observation for Bone and Coward[5] noticed carbon monoxide formation in the high-temperature pyrolysis of methane in a porcelain tube. These authors mention that it is impossible to avoid reduction of the porcelain by carbon at temperatures above a red glow.

In the theoretical treatment of Upson and Sands' paper it is stated that the primary dissociation of ethylamine yields the ethylidene radical and ammonia: $CH_3CH_2NH_2 \longrightarrow CH_3CH{=} + NH_3$. The ethylidene was regarded as the precursor of ethylene (by rearrangement), of ethane (by

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[1] Du Pont Fellow during 1929–1930.

[2] Upson and Sands, THIS JOURNAL, **44**, 2306 (1922).

[3] Müller, *Bull. soc. chim.*, [2] **45**, 439 (1886).

[4] Bone and Coward, *J. Chem. Soc.*, **93**, 1216 (1908).

[5] Ref. 4, p. 1206.

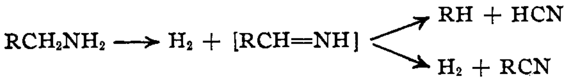
hydrogenation) and of butane. Regarding the latter it is stated: "Butane was the chief hydrocarbon formed at 1000°. This must have been formed by the union of 2 ethylidene radicals and 2 atoms of hydrogen as in the Wurtz reaction: $2CH_3CH{=} + 2H \longrightarrow C_4H_{10}$."

The data of Upson and Sands appear to show that at 1000° 32.9 g. (26.9 g. C and 6.0 g. H) of butane was formed per 100 g. of ethylamine decomposed. To be sure, the stated ratio of 26.9 g. C to 6.0 g. H, or 4.48 to 1, corresponds fairly well to the value for butane which is 4.8 to 1. However, it agrees even more closely to the C–H ratio in propane, which is 4.5 to 1. Because of subsequent work wherein it has been demonstrated that both *n*- and *i*-butane are rapidly decomposed[6] at temperatures far below 1000°, namely, at 650–700°, it seemed to us that this recorded synthesis of butane from ethylamine at 1000° was of sufficient theoretical importance to merit further study.

In our work butane was searched for under a wide variety of conditions at 900–1000° but none was ever found. Attempts to condense it at −78° from the gaseous products were fruitless, though butane had been shown to condense in this manner even if highly diluted. Furthermore, in our analyses of the paraffin gases of the reaction, methane rather than butane was indicated. The value of n in the hydrocarbon formula, C_nH_{2n+2}, was only slightly greater than unity (1.02–1.15).

Benzylamine.—Benzylamine was subjected to different temperatures for various lengths of time. Its stability is evidenced by the fact that heating at 275–300° for several hours produced no change. It was also found to be stable at 545° with a contact time of about one minute. With the use of a temperature of 630° and a contact time of 160 seconds, pyrolysis into benzene, toluene, benzonitrile, hydrogen cyanide and ammonia was effected. Much unchanged benzylamine was apparent when a contact time of forty-nine seconds at 700° was chosen. The other products were benzene, toluene, gas and only a trace of benzonitrile.

Mechanism of the Pyrolysis.—In certain respects the behavior of ethylamine and benzylamine at high temperatures is strictly comparable. The formation of acetonitrile and hydrogen from the former is analogous to the production of benzonitrile and hydrogen from the latter. So also, the formation of methane, hydrogen cyanide and hydrogen from ethylamine has its parallel (in benzylamine) in the production of benzene, hydrogen cyanide and hydrogen. Both of these processes may be considered to proceed through an intermediate aldimide, RCH=NH, wherein R represents methyl or phenyl.



$$\begin{tikzcd}
 & & RH + HCN \\
RCH_2NH_2 \arrow[r] & H_2 + [RCH{=}NH] \arrow[ur] \arrow[dr] & \\
 & & H_2 + RCN
\end{tikzcd}$$

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[6] Pease, THIS JOURNAL, **50**, 1779 (1928); Hurd and Spence, *ibid.*, **51**, 3353 (1929).

Hydrogen escapes in part but presumably only in part. Reaction with unused amine would give rise to ammonia and either ethane or toluene

$$RCH_2NH_2 + 2H \longrightarrow RCH_3 + NH_3$$

both of which were observed. Further reduction[7] of the RCH_3 into RH (methane or benzene) and CH_4 would also follow in part.

Ethylamine is "ammono-ethyl alcohol." The analogies in the water and the ammonia system of compounds may be extended to the field of pyrolysis. Alcohol, on pyrolysis, undergoes reactions[8] of dehydration and of dehydrogenation

$$CH_3CH_2OH \begin{array}{l} \nearrow H_2 + CH_3CHO \\ \searrow H_2O + CH_2{=}CH_2 \end{array}$$

Ammono-ethyl alcohol may be expected to undergo similar reactions of deammonation and of dehydrogenation

$$CH_3CH_2NH_2 \begin{array}{l} \nearrow H_2 + [CH_3CH{=}NH] \\ \searrow NH_3 + CH_2{=}CH_2 \end{array}$$

The dehydrogenation reaction, leading to the aldimide and eventually to cyanides, has already been discussed. Equally representative of fact is the deammonation reaction, of which ethylene is an important reaction product.

Benzyl alcohol and benzylamine are analogous compounds in the two systems. The former cannot lose water unimolecularly without changing into the phenylmethylene radical. This it evidently does not do since stilbene is not formed. Bimolecular dehydration into dibenzyl ether or its pyrolytic products (toluene and benzaldehyde) is the reaction which has been recorded.[9] Similarly, no test for stilbene could be obtained in the pyrolysis of benzylamine. With no evidence for the phenylmethylene radical from this source, it seems equally unnecessary to postulate the ethylidene radical from the ethylamine pyrolysis. For a bimolecular deammonation of benzylamine, dibenzylamine or its decomposition products (toluene and iminobenzaldehyde) would be anticipated. Traces of a secondary amine were realized but the high temperature of the reaction practically excluded the possibility of the synthesis of dibenzylamine. The decomposition of the aldimide, which may thus be formed from dibenzylamine or directly from benzylamine, into benzene and hydrogen cyanide is evidently more rapid than the alternative decomposition into benzonitrile and hydrogen, since only traces of benzonitrile were among the decomposition products from a run at 700° with a contact time of forty-nine seconds. At 630° and

[7] Cobb and Dufton, *Gas World*, **69**, 127 (1918); Fischer and Schrader, *Brennstoff Chem.*, **1**, 22 (1920); Hurd and Spence, THIS JOURNAL, **51**, 3569 (1929).

[8] Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., New York, **1929**, p. 150.

[9] Lachman, THIS JOURNAL, **45**, 2358 (1923).

TABLE I

PYROLYSIS OF ETHYLAMINE

Run number	2	3	4	5	6	7	8	9	10	11
Size of sample, g.	7.0	3.5	7.0[d]	5.6	10.5[h]	10.5	10.5	10.5	10.5	9.8
Tube filling	None[f]	None[a]	[k]	[k]	[k]	[k]	Kaolin cubes	Kaolin cubes	Kaolin cubes	None
Inside temp., °C.	600[b]	890	890	895	890	890	900	900	900	900
Contact time, sec.	300	122	130	162	23.2	15.5	77	81	84	1.08
CH_3CN and NH_4CN formed, g.	2.25[i]	..	..	0.25[j]	..	3.4[e]	0.16	0.34	0.21	3.35[e]
Gas collected (S. T. P.), cc.	1760	2060	5870	2940	7540	4950	8640	10,200	10,800	7640
Gas analysis, % by volume										
Hydrogen	52.1	51.2	76.2	72.4	70.1	51.6	60.9	73.2	74.4	50.2
Unsatd. hydrocarbons	None	None	None	None	0.6	5.0	0.5	None	0.7	10.3
Paraffins	4.9	16.8	11.2	3.7	2.8	3.2	12.8	9.4	6.6	33.0
							$n = 1.15$	$n = 1.02$	$n = 1.15$	$n = 1.02$
Carbon monoxide	None	None	None	None	None	None	5.0	5.9	5.9	1.0
Nitrogen	39.3[g]	30.0[g]	9.6	22.3	26.3	39.2	17.3	9.3	11.2	3.7
Gases liquefied at −80°, g.	0.2[l]	1.0[l]	Not used	0.0	0.0	0.0	0.0	...	0.0	0.0
Calcd. weight of products from 100 g. of ethylamine, g.										
Unsatd. hydrocarbons (as C_2H_4)	..	..	..	..	0.54	2.94	0.52	None	0.90	10.0
Hydrogen	1.17	2.71	5.74	3.51	4.52	2.18	4.50	6.37	6.85	3.52
Nitrogen	..	..	10.00	14.7	23.6	23.1	17.8	11.3	14.4	3.43
Satd. hydrocarbons (as CH_4)	0.88[c]	7.07[c]	6.69[c]	1.39[c]	1.43[c]	1.08[c]	8.52	6.65	5.50	18.78
Carbon monoxide	..	..	..	..	..	..	5.14	7.15	7.60	0.97

[a] An iron thermocouple sheath was used in this run. It seemed to cause considerable carbonization, and was accordingly omitted in later runs. [b] Indicates outside temperature. [c] Calculated as methane. [d] A negative search was made for cyanogen in this run. The off-gas was passed through concentrated hydrochloric acid. No precipitate was formed as is the case with even traces of cyanogen. [e] Mostly ammonium cyanide. [f] A small amount of tar was formed in the reaction tube. [g] Not freed from the nitrogen used before the run. [h] In this and in the following runs considerable carbonization was noted. [i] This consisted of 2.0 g. CH_3CN and 4.25 g. NH_4CN. [j] This is all NH_4CN. [k] The filling here consisted of porcelain chips coated with kaolin. [l] This condensate boiled above room temperature and thus was not butane.

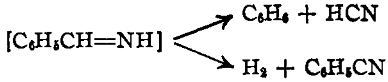
160 seconds, however, benzonitrile was an important product. With ethylamine, a similar phenomenon was noticed, for the proportionate yield of methane was far greater in a run of 900° and one second than at 900° and fifteen seconds.

Thus, the primary equations for the pyrolysis of benzylamine may be summarized as follows

$$C_6H_5CH_2NH_2 \longrightarrow H_2 + [C_6H_5CH{=}NH]$$

$$2C_6H_5CH_2NH_2 \longrightarrow NH_3 + C_6H_5CH_3 + [C_6H_5CH{=}NH]$$

These reactions are followed by reduction and by decomposition of the aldimide



$$[C_6H_5CH{=}NH] \begin{cases} \nearrow C_6H_6 + HCN \\ \searrow H_2 + C_6H_5CN \end{cases}$$

Experimental Part

Ethylamine.—The data obtained from pyrolysis of ethylamine are shown in Table I. One experiment at an "outside temperature" of 500° is not listed, since no pyrolysis occurred. A brief summary of experimental details will serve to make clear the means of arriving at these results.

Apparatus.—An empty pyrex tube was used for the decomposition of ethylamine at 500 and at 600°. For the 890–900° temperatures a quartz tube of 2 cm. diameter was employed. In Run 11 a quartz tube with a diameter of 0.55 cm. was used in order to obtain a short time of contact. The temperatures were obtained by the use of a potentiometer and a calibrated chromel–alumel thermocouple. In one instance an iron thermocouple sheath was present, but it was omitted in later runs on account of its tendency to increase carbonization. In four runs a filling of porcelain chips coated with kaolin was present; in three runs small cubes of kaolin were used. An ordinary gas combustion furnace was suitable for the lower temperatures but a Hoskins electric furnace with an effective heating length of 25 cm. was used in the vicinity of 900°.

Liquid ethylamine was pushed into the reaction tube from a 25-cc. graduated capsule in an ice–salt bath by displacement with mercury. In this manner the rate of feed could be easily controlled. The off gas first passed through a U-tube cooled in an ice–salt bath to about −10°. This served to collect ammonium cyanide, acetonitrile and the greater part of any unchanged amine. Next in the train was a gas washing bottle containing 200 cc. of hydrochloric acid of such concentration as to be equivalent to more than the total base used. The gases were then dried by passing them through a 15-cm. calcium chloride drying tower and a U-tube containing dehydrite. To condense any butane in the previously dried gases, a spiral condenser held at −78° by a mixture of acetone and solid carbon dioxide in a Dewar flask was used. This condenser was so constructed that any condensate could be volatilized and analyzed as a gas. It is of the type described by H. S. Davis.[10] Under the conditions used, butane could be readily condensed from 2-liter samples containing 10% by volume and detected as a liquid when only 5% was present. Finally, the residual gas was collected over water in 2.5-liter bottles. The connections used were of rubber tubing with extra heavy walls.

Procedure.—The ethylamine was Eastman's anhydrous product. The filling used in Runs 4 to 7, inclusive, was prepared by wetting porcelain chips and rolling them in kaolin. The filling for Runs 8 to 10, inclusive, was made by grinding kaolin into a stiff paste with water, spreading it on a plate and cutting it as it dried into cubes about 5 mm.

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[10] Davis, *Ind. Eng. Chem., Anal. Ed.*, 1, 61 (1929).

on an edge. In order to insure that the filling did not contain moisture, the tube was heated to 500° along the filled length while a stream of dry nitrogen was passed through. The volume of the filling was determined after the run by pouring it into a graduated cylinder partly full of water and noting the volume increase. Before each experiment the whole train was swept out with dry nitrogen.

The furnace used was thrown directly on the line and carried a practically constant current during the run. The temperatures were taken inside the tube at the end of the operation and, as can be seen from the table, varied from 890 to 900°. These correspond to a temperature outside the tube of 980°.

Cyanide was tested for in the usual way by boiling an alkaline solution of the sample with ferrous sulfate and ferric chloride solutions, and then acidifying to obtain Prussian blue.

In Run No. 2, the only one made at 600°, 2 g. of acetonitrile, b. p. 79–80°, was definitely identified.

In Run No. 4 cyanogen was tested for by passing the off gas through concentrated hydrochloric acid. No oxamide was obtained, as is the case when even traces of cyanogen are present.[11]

Benzylamine.—Benzylamine from Eastman Kodak Company was used. In sealed tube experiments this material was recovered practically unchanged after five hours of heating at 275° and eight hours at 300°. In the latter experiment, however, a positive test for secondary amine was obtained by Liebermann's nitroso reaction. Using the flow method through a pyrex tube, benzylamine was also recovered unchanged at 535° with a contact time of fifty-four seconds.

Pyrolysis at 630°.—Fifteen grams of benzylamine was allowed to run very slowly during 8.25 hours from a dropping funnel into a 50-cc. distilling flask heated at 270° in a fused salt bath. The arm of the distilling flask was connected to an unfilled pyrex tube (1.1 × 60 cm.) heated to 630° in a gas combustion furnace. The thermocouple was encased by a small pyrex tube within the main reaction tube. The products were condensed in a 25-cc. distilling flask surrounded by an ice–salt bath. A U-tube, at the same temperature and in series with the first receiver, collected nothing. The system was swept out with nitrogen before the run.

A contact time of 160 seconds was used. From a 15-g. sample were obtained 13.1 g. of liquid product and about 1500 cc. of gas insoluble in water. Hydrogen cyanide and ammonia were also evolved. Distillation of the liquid product gave 20 g. of benzene boiling up to 90°; 2.28 g. at 90–103° (mostly at 102°) identified as toluene; 1.38 g. of a mixture of products at 103–185°. Continuation at 50 mm. gave 2.85 g. at 102°, identified as benzonitrile through evolution of ammonia and formation of benzoic acid on boiling with potassium hydroxide solution; at 102–190°, 0.90 g., one-third of which was identified as benzylamine. A dark mobile residue remained in the flask. Qualitative tests failed to show the presence of lophine or stilbene, which are listed as pyrolytic products[12] of di- and tribenzylamine.

The gas contained 81.5% hydrogen, 2.0% carbon monoxide, 6.0% saturated hydrocarbons (n in C_nH_{2n+2} = 1.22) and 10.5% nitrogen.

Pyrolysis at 700°.—A 30-g. sample of benzylamine was displaced by mercury from a graduated capsule into a vertical pyrex tube heated in a multiple unit electric furnace held at 700° by a Leeds and Northrup recording controller. The time was fifty-eight minutes, the tube 2.1 × 90 cm., giving thus a contact time of 49.4 sec. The bottom of the reaction tube was sealed to a piece of smaller bore. The latter extended into a 100-cc.

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[11] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1916, Vol. II, p. 226.

[12] Limpricht, *Ann.*, **144**, 307 (1867); Brunner, *ibid.*, **151**, 133 (1869).

distilling flask immersed in an ice–salt bath. A U-tube in series with the first receiver and at the same temperature collected nothing. The residual gas was collected over water.

The weight of liquid product was 26.2 g. Distillation gave 4.3 g. of material boiling up to 110° at ordinary pressure. This distillate was evidently a mixture of benzene and toluene as previously encountered. Distillation of the residue at 23 mm. gave a product at 80–85° which weighed 18.1 g. While it possessed the characteristic odor of benzonitrile, it gave practically no benzoic acid on hydrolysis with potassium hydroxide. Treatment of 1.8 g. with 35 cc. of 2 N potassium hydroxide and 5.0 g. of *p*-toluenesulfonyl chloride gave 3.7 g. of *p*-toluenesulfonebenzylamide, corresponding to the yield from a pure sample. The derivative melted at 117° on recrystallization from methyl alcohol, and a mixed melting point with an authentic sample confirmed its identity.

Three liters of gas was collected which, by volume, was 68.8% hydrogen, 10.1% saturated hydrocarbons ($n = 1.09$), 11.3% nitrogen, 2.3% carbon monoxide, 4.4% oxygen and 0.1% carbon dioxide.

Preparation of *p*-Toluenesulfonebenzylamide.—A mixture of 5.4 g. of benzylamine, 18 g. of *p*-toluenesulfonyl chloride and 100 cc. of 2 N potassium hydroxide was allowed to stand overnight. After acidification of the mixture with 3 N hydrochloric acid, the solid material was filtered off. It was then boiled for five minutes with 75 cc. of 2 N potassium hydroxide, cooled and filtered. (A precipitate often forms here even when the hot alkali has given a clear solution; accordingly the separation must be applied with caution in the case of benzylamine mixtures. The treatment of alkali-insoluble material with sodium ethoxide should never be omitted. The solution was made by dissolving 0.4 g. of sodium in 10 cc. of 95% alcohol for each gram of base used. Under the conditions the primary amine derivative is soluble.) The filtrate was acidified with hydrochloric acid and the product filtered off.

The crude weight was 9 g., 69% of the calculated amount. Purification was effected by one or two crystallizations from methyl alcohol, using bone black. The pure product melted at 117.8° (119°, corr.).

Anal. Subs., 0.4478, 0.4101: 0.1311 N HCl, 13.06, 11.88. Calcd. for $C_{14}H_{15}O_2NS$: N, 5.36. Found: N, 5.34, 5.33.

Preparation of *p*-Toluenesulfonedibenzylamide.—*p*-Toluenesulfonedibenzylamide was also prepared for purposes of comparison. A mixture of 2 g. of benzylamine and 3 g. of benzyl bromide was allowed to stand for three hours. A crystalline hydrobromide separated. Without any preliminary separation, 40 cc. of 2 N potassium hydroxide solution and 6 g. of *p*-toluenesulfonyl chloride were added. The mixture was allowed to stand overnight and was worked up in the usual way. The alkali-insoluble material was treated with sodium ethoxide. The residue from this operation was crystallized from methyl alcohol accompanied by treatment with charocoal. It formed small white needles, melting at 80.8° (81.3°, corr.).

Anal. Subs., 0.5526: 0.1311 N HCl, 12.06 cc. Calcd. for $C_{21}H_{21}O_2NS$: N, 3.99. Found: N, 4.01.

Summary

The subjection of ethylamine to a temperature of 600° has been found to produce largely acetonitrile and hydrogen. Some ethylene, ammonia, hydrogen cyanide and methane were also produced.

A number of pyrolyses of ethylamine at 890–900°, inside temperature, or 980° outside temperature, have been carried out with various tube

fillings and contact times. No butane was found in any instance although especial search was made for it because its presence has been inferred by other investigators. With a contact time of one second, the gas produced carried 10.3% ethylene; 15.5 seconds, 5.0%; eighty seconds, 0.5 per cent; with longer contact time, none at all. Hydrogen cyanide was always present at 890–900°, but only traces of ammonium cyanide or acetonitrile were noted except in a run made with a contact time of one second. In this particular run the saturated hydrocarbon content was also unusually high. Cyanogen is not a product of the pyrolysis.

Benzylamine was unchanged on being heated for several hours at 275–300° in a sealed tube. It was, furthermore, almost unchanged at 535° with a contact time of fifty-four seconds.

Benzylamine decomposed in 160 seconds at 630° to give benzonitrile, benzene, toluene, saturated hydrocarbons, hydrogen, hydrogen cyanide and traces of secondary amine. A mechanism for the reaction has been proposed.

p-Toluenesulfonebenzylamide and *p*-toluenesulfonedibenzylamide have been synthesized and characterized.

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RESEARCHES ON CHLORIMINES. II. SOME NEGATIVELY SUBSTITUTED AROMATIC ALD-CHLORIMINES

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RECEIVED AUGUST 11, 1930 PUBLISHED OCTOBER 6, 1930

A recent communication[2] from this Laboratory has described the preparation and properties of *o*-chlorobenzalchlorimine and anisalchlorimine. It has been shown that the latter compound undergoes spontaneous decomposition more rapidly than does the former, according to the general equation $RCH{=}NCl = RCN + HCl$. This difference in rate of decomposition of these compounds suggests that the nature of a substituent group in an aromatic ald-chlorimine may be an important factor in its stability.

In the present investigation a number of aromatic ald-chlorimines have been prepared with the purpose of studying the effect of the presence of substituent groups on the stability of these compounds as well as extending the list of readily available ald-chlorimines to be used in subse-

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[1] This paper is in part constructed from portions of a thesis presented by A. Gillaspie in partial fulfilment of the requirements for the degree of Master of Arts in the Graduate School of Arts and Sciences, Duke University.

[2] Hauser and Hauser, THIS JOURNAL, 52, 2050 (1930). It should be mentioned that Raschig seems to have condensed anisaldehyde with monochloramine but no details are given; Raschig, "Schwefel und Stickstoff-Studien," 1924, p. 80.