in which $[\eta]$ is intrinsic viscosity; t_0 is flow time for benzene; t is flow time for polymer solution; c is concentration of polymer in grams per 100 ml. of benzene.

TABLE III

POLYMERS FROM SUBSTITUTED STYRENES

Monomer	Analyses of polymer Calcd. %C	Analyses of polymer Calcd. %H	Analyses of polymer Found %C	Analyses of polymer Found %H	Softening point, °C.	$[\eta]$
3-Methoxystyrene	80.56	7.51	80.19	7.53	235–240	0.69
4-Methoxystyrene	80.56	7.51	80.08	7.42	124–129	0.41
4-Methoxy-3-methylstyrene	81.05	8.14	80.22	8.02	137–145	1.46
5-Isopropyl-4-methoxy-2-methylstyrene	82.06	9.54	82.06	9.38	153–157	0.15
3,4-Dimethoxystyrene	73.17	7.32	72.31	7.31	185–188	0.41
4-Phenoxystyrene	85.68	6.16	85.74	6.17	140–145	1.11

Summary

1. Syntheses are described for 3-methoxystyrene, 4-methoxystyrene, 4-methoxy-3-methylstyrene, 6-methoxy-3-methylstyrene, 5-isopropyl-4-methoxy-2-methylstyrene, 3,4-dimethoxystyrene and 4-phenoxystyrene.

2. The formation of substituted styrenes by chloroethylation is discussed.

3. An unusual reduction occurs in the catalytic dehydration of 1-(4-phenoxyphenyl)-ethanol by means of alumina to give 4-phenoxyphenylethane as a by-product.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Pyridines. I. Aldehyde-collidine and 5-Ethyl-2-vinylpyridine[1]

BY ROBERT L. FRANK, JAMES R. BLEGEN, ROBERT J. DEARBORN, ROBERT L. MYERS AND FRED E. WOODWARD

The condensation of acetaldehyde or paraldehyde with ammonia to form 5-ethyl-2-methylpyridine (aldehyde-collidine) has been described by a number of investigators[2] but low yields have been generally obtained due to the formation of higher-boiling pyridines and large amounts of tar. On the assumption that the tarry by-products are most likely the result of polymerization of acetaldehyde with itself or with the substituted pyridines formed, it was thought that the use of a large excess of ammonia might increase the ratio of aldehyde-collidine to higher-boiling pyridines and tar, and this has now been investigated.

Procedure.—Mixtures containing from 0.87 to 8.0 moles of ammonia (1.17 to 10.7 times the theoretical amount) as 28% ammonium hydroxide and 0.044 mole of ammonium acetate per mole of paraldehyde (U. S. P.) were heated in a steel autoclave to a temperature of about 200°, whereupon stirring was begun and the temperature further raised to 250° over a period of an hour. (The reaction is exothermic.) The autoclave was then cooled by means of its internal cooling coil and the two layers of the reaction mixture were separated. To the non-aqueous layer chloroform was added (500 ml. per 24 moles of paraldehyde), causing separation of water which was combined with the main aqueous portion. The aqueous layer was then extracted with three portions of chloroform (400 ml. per 24 moles of paraldehyde), and the extracts were combined with the main organic solution. Fractional distillation through a 30-cm. Fenske-type column[3] gave nearly pure aldehyde-collidine, b. p. 68–75° (20 mm.). Redistillation gave pure material, b. p. 68° (18 mm.), $n^{20}D$ 1.4971. Its picrate melted at 164° (reported ref. 4, 164°).

Results

The yields of aldehyde-collidine increased from 31% when 1.17 times the theoretical amount of ammonia (1.00 mole of ammonia is equivalent to 1.33 moles of paraldehyde) to about 70% when 10.7 times the theoretical amount was used, but it was found convenient to sacrifice some yield to reduce the volume of the reaction mixture; therefore a ratio of 3.7 was adopted. This ratio, using 24 moles of paraldehyde, gave yields in several runs of 52 to 57% of nearly pure aldehyde-collidine.

Refractionation of the fore-run from the distillation gave 45.6 g. of α-picoline, b. p. 127–128°, $n^{20}D$ 1.4882, identified by its picrate, m. p. 163–164° (reported,[5] 164°), and its derivative with mercuric chloride and hydrogen chloride, m. p. 151–152° (reported,[6] 154°). No other pyridines were found in the fore-run.

Reaction of Aldehyde-collidine with Formaldehyde.—The condensation of aldehyde-collidine with formaldehyde or paraformaldehyde to form a mixture of 5-ethyl-2-(2-hydroxyethyl)-pyridine and 5-ethyl-2-vinylpyridine, originally reported by Prausnitz,[7] was then studied.

5-Ethyl-2-(2-hydroxyethyl)-pyridine.—Using the same autoclave as above, a mixture of 2700 g. (22.3 moles) of aldehyde-collidine, 670 g. (22.1 moles) of paraldehyde, 27.0 g. of potassium persulfate, 215 g. of ethanol as solvent and 0.25 g. of *t*-butylcatechol was heated as quickly as possible (three hours) to 220° and then cooled as above so that the time of heating above 150° was only one hour, thus avoiding polymerization of the 5-ethyl-2-vinylpyridine formed during the reaction. The *t*-butylcatechol also helped in this respect.

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[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

[2] For instance, Durkopf, *Ber.*, **20**, 444 (1887); Chichibabin, *Bull. soc. chim.*, [5] **4**, 1831 (1937); Graf, *J. prakt. Chem.*, **150**, 153 (1938).

[3] Fenske, Tongberg and Quiggle, *Ind. Eng. Chem.*, **26**, 1169 (1934).

[4] Auerbach, *Ber.*, **25**, 3485 (1892).

[5] Constam and White, *Am. Chem. J.*, **29**, 38 (1903).

[6] Ladenburg, *Ann.*, **247**, 6 (1888).

[7] (a) Prausnitz, *Ber.*, **23**, 2725 (1890); (b) Prausnitz, *ibid.*, **25**, 2394 (1892).

The contents were rinsed from the bomb with chloroform and fractionally distilled under reduced pressure through a 30-cm. Fenske-type column[3] using a trace of trinitrobenzene to inhibit polymerization. Products were 1137 g. of aldehyde-collidine, b. p. 73–75° (20 mm.), n^{20}_{D} 1.4970, 314 g. of 5-ethyl-2-vinylpyridine, b. p. 64–65° (3 mm.), n^{20}_{D} 1.5383, and 712 g. of 5-ethyl-2-(2-hydroxyethyl)-pyridine, b. p. 103° (1 mm.), 125° (3 mm.), n^{20}_{D} 1.5370. Combined yield, accounting for the recovered aldehyde-collidine, was 73%.

The picrate of 5-ethyl-2-(2-hydroxyethyl)-pyridine, crystallized from ethanol, melted at 101–102°.

Anal.[8] Calcd. for $C_{15}H_{16}N_4O_8$: C, 47.37; H, 4.24. Found: C, 47.55; H, 4.18.

The chloroplatinate was prepared by adding aqueous platinum chloride solution to an alcoholic solution of the product. Pink crystals were obtained, m. p. 165–167° (dec.). Prausnitz[7a] reported the chloroplatinate to be a red crystalline compound, m. p. 159° (dec.).

In the preparation paraformaldehyde (1 mole per mole of aldehyde-collidine is optimal) gives better results than formalin. The use of ethanol as a solvent improves the yields, and it is most interesting that the addition of a trace of potassium persulfate (1% of the aldehyde-collidine) does so materially. Ammonium acetate, zinc chloride, sodium hydroxide, silver and potassium ferricyanide showed no such catalytic effect.

5-Ethyl-2-vinylpyridine.—The conversion of 5-ethyl-2-(2-hydroxyethyl)-pyridine to 5-ethyl-2-vinylpyridine was achieved in good yield by catalytic dehydration, either using alumina at 400–420° or, preferably, molten potassium hydroxide at 175°.

A. By Dehydration over Alumina.—A vertical 19-mm. Pyrex tube heated by an electric furnace for a length of twelve inches was packed with 6-mesh activated alumina (Hydralo) and preheated at 450° to drive off moisture. From a separatory funnel attached directly to the top of the tube was passed 170 g. (1.12 moles) of 5-ethyl-2-(2-hydroxyethyl)-pyridine at a rate of one drop per second. The temperature during this time was maintained at 400–420°. An equal volume of chloroform was then added to the product, the water layer separated, and the organic layer dried over potassium carbonate. Fractional distillation, after the addition of a trace of trinitrobenzene as a polymerization inhibitor, gave 88 g. (66%, or 71% accounting for recovery of 12.6 g. of starting material) of 5-ethyl-2-vinylpyridine, b. p. 95–97° (18 mm.); n^{20}_{D} 1.5380.

B. By Dehydration with Potassium Hydroxide.—The apparatus and procedure was that described previously for the preparation of 3-methoxystyrene.[9] From 160 g. (1.32 moles) of 5-ethyl-2-(2-hydroxyethyl)-pyridine at 175° and 17–18 mm. pressure was obtained 116.3 g. of crude distillate. Redistillation through a 30-cm. Fenske-type column,[3] using a small amount (1:1000) of trinitrobenzene as a polymerization inhibitor, gave 88.8 g. (63%) of 5-ethyl-2-vinylpyridine, b. p. 95–97° (18 mm.); n^{20}_{D} 1.5383.

The picrate of the product, crystallized from water, melted at 129.5–130.5°.

Anal. Calcd. for $C_{15}H_{14}N_4O_7$: C, 49.72; H, 3.90. Found: C, 49.73; H, 3.90.

Summary

In the condensation of ammonia with paraldehyde the use of a large excess of ammonia leads to 50–70% yields of aldehyde-collidine.

The presence of a trace of potassium persulfate improves the yields of 5-ethyl-2-(2-hydroxyethyl)-pyridine in the condensation of aldehyde-collidine with paraformaldehyde.

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(8) Microanalyses were carried out by Mr. Howard Clark.

(9) Frank, Adams, Allen, Gander and Smith, THIS JOURNAL, **68**, 1365 (1946).

[CONTRIBUTION FROM THE STERLING-WINTHROP RESEARCH INSTITUTE]

Studies on the Willgerodt Reaction. III. The Use of Simple Aliphatic Compounds

BY JOHN A. KING AND FREEMAN H. MCMILLAN

Previous communications from these laboratories have shown that the Willgerodt reaction is by no means restricted to aryl alkyl ketones[1] and have suggested a mechanism[2] for the reaction. Although Willgerodt[3] reported, in 1888, that if oenanthol were heated "a long time" at 300° with yellow ammonium sulfide the product was oenanthylamide, no other successful application of the reaction to an aliphatic compound had been published prior to last October. At that time it was demonstrated by Cavalieri, Pattison and Carmack[4] that the reaction can be carried out successfully on purely aliphatic ketones. Experiments conducted in these laboratories similarly have shown that the reaction is applicable to aliphatic ketones, alcohols, thiols and olefins. The present paper describes some of our results and indicates how all data thus far obtained are in accord with our previously proposed reaction mechanism.

It seemed desirable to select as a typical aliphatic ketone one which contained no tertiary alkyl group, in order that the similarity to an aromatic aliphatic ketone would be lessened. Methyl isobutyl ketone, to which we first applied the reaction, gave an 88% yield of isocaproamide.

In order to determine whether the reaction would proceed satisfactorily when neither of the alkyl groups of the ketone contained a branched chain, the reaction was applied to methyl nonyl ketone. The product was undecanoamide.

Willgerodt,[5] in his initial paper on the treatment of carbonyl compounds with yellow ammonium sulfide, found that at room temperature acetone and ammonium polysulfide formed "duplodithioacetone," of unknown constitution. It was easily verified that when acetone and ammonium polysulfide were sealed in a pressure tube the separation of a heavy red oil occurred;

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(1) King and McMillan, THIS JOURNAL, **68**, 525 (1946).

(2) King and McMillan, *ibid.*, **68**, 632 (1946).

(3) Willgerodt, *Ber.*, **21**, 534 (1888).

(4) Cavalieri, Pattison and Carmack, THIS JOURNAL, **67**, 1783 (1945).

(5) Willgerodt, *Ber.*, **20**, 2467 (1887).