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

Alkoxy- and Aryloxystyrenes[1]

BY ROBERT L. FRANK, CLARK E. ADAMS, ROBERT E. ALLEN, ROBERT GANDER AND PAUL V. SMITH

The present paper discusses the methods of preparation of a number of substituted styrenes containing methyl and phenyl ether groups.

The chloroethylation reaction discovered by Quelet and Ducasse,[2] followed by dehydrohalogenation of the resulting 1-chloroethyl derivative, is a feasible method for a limited number of styrenes, although yields are reduced by a secondary reaction during chloroethylation, represented as follows in the case of anisole

$$CH_3OC_6H_5 + CH_3OC_6H_4CHClCH_3 \longrightarrow (CH_3OC_6H_4)_2CHCH_3 + HCl$$

It seemed that an optimum period of reaction might minimize the formation of this by-product, and experiments with anisole (Table I) have shown this to be true. Extending the reaction time past one hour under the conditions used greatly increased the yield of 1,1-di-(4-methoxyphenyl)-ethane, although the yield *in grams* of 4-methoxystyrene was substantially the same in all runs of greater than one hour duration.

TABLE I

CHLOROETHYLATION OF ANISOLE

Reaction time at 5°, hr.	Yield of 4-Methoxystyrene[a] g.	%	Yield of 1,1-di-(methoxyphenyl)-ethane,[b] %
1.25	62.0	32.8	43.4
1.75	65.5	32.1	50.2
3.5	61.0	23.8	72.9
4.0	63.5	26.3	69.7

[a] Yields were based on anisole which was not recovered. Fractions boiling lower than 4-methoxystyrene and having $n^{20}D$ 1.517-1.544 were assumed to be recovered anisole. These fractions contained some 4-methoxystyrene which was recoverable by fractional distillation. [b] All of the high-boiling material remaining after distillation of 4-methoxystyrene was assumed to be 1,1-di-(4-methoxyphenyl)-ethane, in accordance with the findings of Quelet (ref. 2b).

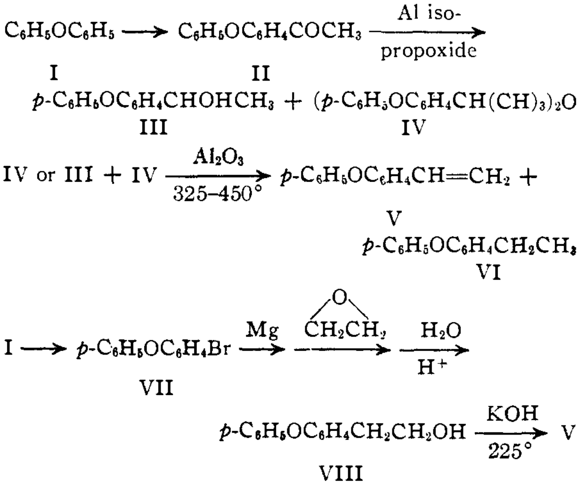
Other styrenes prepared by chloroethylation in yields of 34–49% were 4-methoxy-3-methylstyrene, 2-methoxy-5-methylstyrene and 5-isopropyl-4-methoxy-2-methylstyrene. In all cases the recovery of unchanged starting material was seriously diminished by the formation of diarylethane by-products.

Chloroethylation appears to be more limited in scope than chloromethylation. A single halogen atom on the aromatic nucleus caused sufficient deactivation to prevent reaction. Attempts to chloroethylate *o*-, *m*- and *p*-chloroanisole, *m*- and *p*-bromoanisole, dimethylaniline, N-methylacetanilide and 1,4-dimethoxybenzene were unsuccessful.

The preparation of 3,4-dimethoxystyrene, attempted by chloroethylation of veratrole, gave yields of only 6%, and a more suitable synthesis was sought in the addition of methylmagnesium iodide to veratraldehyde, followed by dehydration of the resulting 1-(3,4-dimethoxyphenyl)-ethanol. The latter compound was best dehydrated by slow distillation under reduced pressure, which gave much better results than heating in the presence of iodine, activated alumina, potassium acid sulfate, sulfuric acid or phosphorus trichloride.

3-Methoxystyrene, an isomer not obtainable by chloroethylation of anisole, was prepared in 37–41% yield by reaction of the Grignard reagent of 3-bromoanisole with ethylene oxide and subsequent catalytic dehydration by means of potassium hydroxide of the resulting 2-(3-methoxyphenyl)-ethanol.

An additional styrene, the 4-phenoxy derivative, was prepared by two routes



$$\underset{\text{I}}{C_6H_5OC_6H_5} \longrightarrow \underset{\text{II}}{C_6H_5OC_6H_4COCH_3} \xrightarrow[\text{propoxide}]{\text{Al iso-}}$$

$$\underset{\text{III}}{p\text{-}C_6H_5OC_6H_4CHOHCH_3} + \underset{\text{IV}}{(p\text{-}C_6H_5OC_6H_4CH(CH)_3)_2O}$$

$$\text{IV or III} + \text{IV} \xrightarrow[325\text{–}450^\circ]{Al_2O_3} \underset{\text{V}}{p\text{-}C_6H_5OC_6H_4CH{=}CH_2} + \underset{\text{VI}}{p\text{-}C_6H_5OC_6H_4CH_2CH_3}$$

$$\text{I} \longrightarrow \underset{\text{VII}}{p\text{-}C_6H_5OC_6H_4Br} \xrightarrow{Mg} \xrightarrow{\overset{O}{CH_2CH_2}} \xrightarrow[H^+]{H_2O}$$

$$\underset{\text{VIII}}{p\text{-}C_6H_5OC_6H_4CH_2CH_2OH} \xrightarrow[225^\circ]{KOH} \text{V}$$

The first of these syntheses (I–III–V) was complicated by the formation in the Meerwein–Ponndorf reduction of 4-phenoxyacetophenone (II) of a mixture of the desired alcohol (III) and its ether (IV), from which only the ether could be isolated in a pure state.

A further complication was the occurrence of an unusual side reaction when either the mixture (III + IV) or the ether (IV) was subjected to dehydration over activated alumina. Reduction as well as dehydration occurred, and the product was a mixture of 4-phenoxystyrene (V) and 4-phenoxyphenylethane (VI), as evidenced by refractive indices, bromine titrations, and the

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(1) The work described in this manuscript was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

(2) (a) Quelet and Ducasse, *Compt. rend.*, **208**, 1317 (1939); (b) Quelet. *Bull. soc. chim.*, (5) **7**, 196, 205 (1940).

preparation and comparison by mixed melting point of the tetrabromide of 4-phenoxyphenylethane (VI) with the tetrabromide of an authentic sample prepared by catalytic hydrogenation of 4-phenoxystyrene. This interesting type of side reaction has recently been encountered in the similar dehydration of 1-(3-N-methylaminophenyl)-ethanol.[3]

Indirect dehydration of the mixture (III + IV) by treatment with hydrogen chloride followed by dehydrochlorination gave 4-phenoxystyrene (V) in 17% yield.

The second synthesis (I–VIII–V) was more suitable, giving an over-all yield of 24.4%.

All the styrenes were polymerizable, giving white powders, briefly described in Table III.

Experimental

General Chloroethylation Procedure.—The procedure was that of Quelet,[2b] except that reaction times were held to one hour instead of two and one-half hours. Reaction temperatures, yields and physical constants were as follows: 4-methoxystyrene: 0–5°, 33%, b. p. 92–93° (13 mm.), n^{20}D 1.5608; 4-methoxy-3-methylstyrene: 0–10°, 38%, b. p. 96–100° (10 mm.), n^{20}D 1.5584; 2-methoxy-5-methylstyrene: 15–20°, 34%, b. p. 96–100° (10 mm.), n^{20}D 1.5521; 5-isopropyl-4-methoxy-2-methylstyrene: 5–10°, 49%, b. p. 105–106° (4 mm.), n^{20}D 1.5400; 3,4-dimethoxystyrene: 0–10°, 6%, b. p. 116° (8 mm.), n^{20}D 1.5693.

o- and *p*-methylanisoles and methyl thymyl ether were prepared by methylation of the corresponding phenols according to the method of Hiers and Hager.[4]

The yields and physical constants of these ethers were as follows: *o*-methylanisole, 87%, b. p. 77° (29 mm.), n^{20}D 1.5170; *p*-methylanisole, 89%, b. p. 85° (35 mm.), n^{20}D 1.5122; methyl thymyl ether, 78%, b. p. 99–101° (14 mm.), n^{20}D 1.5062.

3,4-Dimethoxystyrene (from Veratraldehyde).—In a 5-liter, three-necked, round-bottomed flask fitted with a stirrer, a condenser and a dropping funnel were placed 58.5 g. (2.41 gram atoms) of magnesium turnings and 400 ml. of dry ether. To this was added with stirring 344 g. (2.42 moles) of methyl iodide in 500 ml. of dry ether at such a rate that gentle refluxing occurred. After the addition was complete, 400 g. (2.41 moles) of freshly distilled veratraldehyde in 400 ml. of dry ether was added, again with gentle refluxing of the ether solution. The Grignard complex was decomposed with a solution of 240 g. of ammonium chloride in 720 ml. of water, the solution being added dropwise with stirring. The ether layer was decanted and the residue extracted with three 150-ml. portions of ether. The extracts were combined with the original ether layer, and the whole was dried over calcium sulfate (Drierite). Four runs of this size were combined, and the ether was removed by distillation. Careful fractionation through a two-foot Fenske-type column gave 281 g. (18%) of 3,4-dimethoxystyrene, b. p 113–115° (6–7 mm.); n^{20}D 1.5701; sp. gr. $^{20}_{20}$ 1.087 (Fromm[5] has reported d_{15} 1.049); *MR* calcd.: 49.84 (taking into account an exaltation of 2.24 due to the *m*- and *p*-methoxyl groups in conjunction with the styrene nucleus[6]; *MR* found: 49.65. *Anal.*[7] Calcd. for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.09; H, 7.17. A higher fraction (450 g.), judged to be a mixture of veratraldehyde and 1-(3,4-dimethoxyphenyl)-ethanol, was also obtained, b. p. 115–140° (7 mm.). A fraction boiling at 140° (7 mm.), n^{20}D 1.5784, had a combustion analysis close to that of veratraldehyde, and crystals appeared in the mixture on standing.

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 65.31, 65.01; H, 5.91, 6.02.

A dibromo derivative of 3,4-dimethoxystyrene was prepared by adding bromine in glacial acetic acid to 1.0 g. of the compound. Two recrystallizations from petroleum ether gave colorless crystals, m. p. 97.5–98° (reported[8] 102°).

2-(3-Methoxyphenyl)-ethanol.—The method of Natelson and Gottfried[9] was used with 460 g. (2.45 moles) of *m*-bromoanisole, 65.6 g. (2.7 gram atoms) of magnesium turnings, 1500 ml. of dry ether and 190 g. (4.32 moles) of ethylene oxide. The product, b. p. 104–108° (1–2 mm.); n^{20}D 1.5390, weighed 200 g. (54%).

3-Methoxystyrene.—The dehydration of 2-(3-methoxyphenyl)-ethanol was carried out by the catalytic action of potassium hydroxide. The apparatus[10] consisted of a cylindrical stainless steel (or copper) vessel six inches long and two inches in diameter, fitted with a dropping funnel attached to a copper tube leading to the bottom of the cylinder and an outlet tube attached to a condenser and receiver. The receiver was connected to a water pump so that the whole system could be evacuated. The reactor was one-half filled with potassium hydroxide pellets (*ca.* 250 g.) and heated in an electrically controlled oil-bath at 160°. The pressure was reduced to 15–16 mm. and 2-(3-methoxyphenyl)-ethanol was added through the dropping funnel at such a rate that approximately ten drops of crude product were collected per minute. From 45 g. (0.30 mole) of the alcohol was obtained 36.5 g. of crude 3-methoxystyrene. This was dissolved in chloroform, dried over calcium chloride, and fractionally distilled through a six-inch, Fenske-type column to yield 27.4 g. (69%) of pure product, b. p. 89° (14 mm.), n^{20}D 1.5540 (reported[6b] n^{20} 1.554).

A 1-ml. sample of 3-methoxystyrene was brominated by the slow addition of a dilute solution of bromine in glacial acetic acid until a permanent color of excess bromine was obtained. The product was isolated by the addition of water and twice recrystallized from ethanol to give shiny white platelets, m. p. 66–67°. *Anal.* Calcd. for $C_9H_{10}OBr_2$: C, 36.77; H, 3.43. Found: C, 37.07; H, 3.44.

4-Phenoxyacetophenone (II).—The general directions of Noller and Adams,[11] used also by Ingersoll, Brown, Kim, Beauchamp and Jennings,[12] were followed. From 170 g. (1.00 mole) of phenyl ether, 295 g. (2.21 moles) of aluminum chloride and 100 ml. (108 g., 1.06 moles) of acetic anhydride in 400 ml. of dry carbon disulfide was obtained 173 g. (78.5%, based on acetic anhydride) of 4-phenoxyacetophenone, b. p. 149–154° (1–2 mm.) (mainly 152–154°).

1-(4-Phenoxyphenyl)-ethanol (III) and Its Ether (IV).—In a 3-liter, round-bottomed flask were placed 155 g. (0.73 mole) of 4-phenoxyacetophenone, 200 g. (0.98) mole of aluminum isopropoxide, and 1 liter of dry isopropanol. The flask was heated at 100° while a mixture of isopropanol and acetone was slowly distilled through a six-inch Vigreux column equipped with a total reflux-partial takeoff head. After thirty hours no acetone could be detected in the distillate (by test with 2,4-dinitrophenylhydrazine). Excess isopropanol was then removed by distillation under reduced pressure, and the residue hydrolyzed by the addition of 1 liter of ice water and 300 ml. of concentrated hydrochloric acid. The resulting oil, which showed no tendency to solidify, was extracted from the water by three 200-ml.

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[3] Marvel and Overberger, This Journal, **68**, 185 (1946).

[4] Hiers and Hager, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1941, p. 58.

[5] Fromm, *Ann.*, **456**, 168 (1927).

[6] (a) Cohen, "Organic Chemistry," Vol. II, Longmans, Green and Company, New York, N. Y., 1923, pp. 17–40; (b) Klages, *Ber.*, **36**, 3584 (1903).

[7] Microanalyses were carried out by Mr. Howard S. Clark of the Illinois State Geological Survey.

[8] Barger and Jowett, *J. Chem. Soc.*, **87**, 967 (1905).

[9] Natelson and Gottfried, This Journal, **61**, 1001 (1939).

[10] This apparatus was suggested by Dr. C. A. Weisgerber of Pennsylvania State College; *cf.* Sabetay, *Bull. soc. chim.*, (4) **45**, 69 (1929).

[11] Noller and Adams, This Journal, **46**, 1889 (1924).

[12] Ingersoll, Brown, Kim, Beauchamp and Jennings, *ibid.*, **58**, 1808 (1936).

portions of ether. The ether solutions was dried over calcium sulfate (Drierite) and the ether removed by distillation to give 179 g. of impure 1-(4-phenoxyphenyl)-ethanol. Attempts to purify this by distillation resulted in loss of water. After heating and cooling the oily carbinol, granular crystals slowly formed and were purified by crystallization from warm isopropanol, m. p. 111–113°, or from ether cooled to 0°, m. p. 113.5–114°. Analysis and molecular weight determination indicate that this compound is 1-(4-phenoxyphenyl)-ethyl ether (IV).

Anal. Calcd. for $C_{28}H_{26}O_3$: C, 81.92; H, 6.39; mol. wt., 410. Found: C, 82.04, 82.07; H, 6.49, 6.53; mol. wt. (Rast camphor method), 385.

Catalytic Dehydration of 1-(4-Phenoxyphenyl)-ethanol (III) and its Ether (IV).—The above-described mixture of 1-(4-phenoxyphenyl)-ethanol and its ether, as well as the ether alone, was passed through a Pyrex tube packed with activated alumina (Hydralo) in several experiments using amounts of 25–164 g. with temperatures ranging from 325 to 450°. The products were fractionally distilled under reduced pressure to give yields of 20–49% of the weight of the starting material of liquid fractions boiling in the range 110–120° (1–2 mm.). A correlation of the refractive indices of the various fractions and of the pure styrene (V), obtained as described below, with their degree of unsaturation, determined by bromine titration[13,14] showed by extrapolation that a completely saturated product should have an index ($n^{20}D$) of approximately 1.568.

TABLE II

% Unsaturation	$n^{20}D$
96.4	1.6026
55.4	1.5863
13.8	1.5733

From 2.0 ml. of the fraction of $n^{20}D$ 1.5733 was obtained by treatment with bromine in carbon disulfide, a white crystalline tetrabromo derivative melting at 92–93° after three crystallizations from ethanol. A mixed melting point with the tetrabromo derivative of 4-phenoxyphenylethane, described in the sequel, showed no depression.

Pure *p*-phenoxystyrene, free from the ethane, was not obtained in this experiment.

4-Phenoxystyrene (V) (*via* 1-(4-Phenoxyphenyl)-chloroethane).—Dry gaseous hydrogen chloride was passed for four hours with stirring into 50 g. (0.23 mole calculated on the carbinol) of a mixture of 1-(4-phenoxyphenyl)-ethanol (III) and its ether (IV) dissolved in 300 ml. of ethyl ether in a 1-liter, three-necked, round-bottomed flask equipped with a condenser and gas absorption trap, a stirrer, and an inlet tube extending below the surface of the liquid. Heat was evolved at first. The mixture became dark brown as the reaction proceeded. Most of the ether was then removed by distillation, 175 ml. of pyridine was added, and the pyridine solution heated at 115° for six hours, after which it was poured into 750 g. of ice and 250 ml. of concentrated hydrochloric acid. This mixture was extracted with one 200-ml. and two 100-ml. portions of chloroform, and the chloroform extracts were washed with three 100-ml. portions of water. The chloroform solution, after drying overnight with magnesium sulfate, was fractionally distilled through a six-inch, Fenske-type column to give 8.2 g. (17%) of 4-phenoxystyrene, b. p. 111–113° (1–2 mm.); $n^{20}D$ 1.6031; sp. gr. $^{20}{}_4$ 1.060; *MR* calcd. (employing exaltations of 1.40 for styrene and 1.00 for diphenyl ether): 63.23; *MR* found: 63.58.

Anal. Calcd. for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.56; H, 6.18.

A 20-g. glassy residue remained in the flask.

To 0.4 g. of 4-phenoxystyrene was added a dilute solution of bromine in glacial acetic acid until the color of excess bromine did not fade. Long needles formed on standing. Recrystallization from glacial acetic acid gave colorless needles of 4-phenoxyphenylethylene bromide, m. p. 96–98° (dec.). *Anal.* Calcd. for $C_{14}H_{12}OBr_2$: C, 47.22; H, 3.40. Found: C, 47.30; H, 3.55.

4-Phenoxyphenylethane (VI).—Catalytic hydrogenation of 20.0 g. (0.102 mole) of 4-phenoxystyrene over Raney nickel at 50° and 100 atmospheres pressure gave on distillation 17.0 g. (84%) of 4-phenoxyphenylethane boiling at 112–114° (2–3 mm.), $n^{20}D$ 1.5658; sp. gr. $^{20}{}_4$ 1.037; *MR* calcd. (using exaltation of 1.00 for diphenyl ether): 62.30; *MR* found, 62.34. *Anal.* Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.61; H, 6.95.

Two milliliters (0.01 mole) of 4-phenoxyphenylethane dissolved in 20 ml. of carbon disulfide containing a trace of iodine was brominated by the slow addition of 2.6 ml. (0.05 mole) of bromine. The mixture was allowed to stand overnight, after which the carbon disulfide and excess bromine were removed by warming on a steam cone. The residue crystallized on cooling and was recrystallized three times from ethanol to form clusters of feathery needles of the tetrabromo derivative, m. p. 92–93°. *Anal.* Calcd. for $C_{14}H_{10}OBr_4$: C, 32.72; H, 1.96. Found: C, 32.68; H, 2.05.

4-Phenoxybromobenzene (VII).—The method of Suter[15] was employed to prepare 1232 g. (66%) of 4-phenoxybromobenzene, b. p. 124–128° (3–4 mm.); $n^{20}D$ 1.6088, by the bromination of 1275 g. (7.5 moles) of diphenyl ether dissolved in carbon tetrachloride.

2-(4-Phenoxyphenyl)-ethanol (VIII).—A solution of 100 g. (2.28 moles) of ethylene oxide in 100 ml. of cold dry ether was added slowly to the Grignard reagent prepared from 294 g. (1.18 moles) of 4-phenoxybromobenzene, 28.7 g. (1.18 gram atoms) of magnesium turnings and 450 ml. of absolute ether. Toward the end of the addition the reaction mixture set to a gray jelly. The product was obtained and purified by removal of ether by distillation, decomposition of the complex with ice and sulfuric acid, extraction with two 150-ml. portions of benzene, washing the benzene solution with 10% sulfuric acid and water, and fractional distillation. The product weighed 132.4 g. (52%), b. p. 160–162° (3 mm.); m. p. 14–15°; $n^{20}D$ 1.5861; sp. gr. $^{20}{}_4$ 1.1378; *MR* calcd. (accounting for 1.00 exaltation shown by diphenyl ether), 63.82; *MR* found, 63.45. *Anal.* Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.04; H, 6.42.

The phenylurethan, recrystallized once from chloroform, twice from carbon tetrachloride, and once from ethanol, melted at 80°. *Anal.* Calcd. for $C_{21}H_{19}O_3N$: C, 75.65; H, 5.74. Found: C, 75.65; H, 5.61.

4-Phenoxystyrene (V) (from 2-(4-Phenoxyphenyl)-ethanol (VIII).—Dehydration of 121 g. (0.565 mole) of 2-(4-phenoxyphenyl)-ethanol by means of potassium hydroxide using the technique described above for 3-methoxystyrene gave 98.4 g. of crude 4-phenoxystyrene. The reaction was carried out at 225 ± 5° and 3–4 mm. pressure. Redistillation of the product under nitrogen gave 80.5 g. (77%) of pure material, b. p. 115–117° (3 mm.); $n^{20}D$ 1.6037.

For the distillation and storage of 4-phenoxystyrene it was found necessary to add an efficient polymerization inhibiter such as picric acid (0.001 parts was sufficient).

Polystyrenes.—Poly-3-methoxystyrene was prepared by the method of Strain.[16] The remainder were prepared by the ultraviolet irradiation for twenty-four hours of 2.0 g. of each monomer in a Pyrex tube. They were purified by dissolving in 50 ml. of benzene or chloroform and reprecipitating by pouring the solutions into 300 ml. of methanol or ethanol.

Softening points were determined in sealed capillary tubes.

Intrinsic viscosities were calculated from the observed viscosities of benzene solutions containing 0.066 g. of polymer per 100 ml. of benzene

$$[\eta] = \ln (t/t_0)/c$$

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[13] Uhrig and Levin, *Ind. Eng. Chem., Anal. Ed.*, **13**, 90 (1941).

[14] Bromine titrations were carried out by Mr. W. P. Jennings.

[15] Suter, THIS JOURNAL, **51**, 2581 (1929).

[16] Strain, U. S. Patent 2,121,839 (June 28, 1938), *C. A.*, **32**, 6366 (1938).

in which [η] 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	%H	Found %C	%H	Softening point, °C.	[η]
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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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).