acid (m. p. 282°). Caustic fusion of the sulfopicolinic acid gave a hydroxypicolinic acid (m. p. 269–270°), which is not identical with the 3-hydroxypicolinic acid reported by Kirpal,[10] but which corresponds to the 5-hydroxypicolinic acid reported by Bellman[11] and Urbanski.[12] The 5-hydroxypicolinic acid in turn establishes the structure of the picolinesulfonic acid as 6-methyl-3-pyridinesulfonic acid.

Experimental

6-Carboxy-3-pyridinesulfonic Acid.—Commercial grade 2-picoline, obtained from the Barrett Company, was sulfonated in 69% yield by means of the method of McElvain and Goese with the heating time reduced from twenty-four to five hours. The yield of 69% with a loss of 6% α-picoline may be compared with a 45% yield with a 12% loss upon twenty-four hours of heating.

87.5 g. of sodium 6-methylpyridine-3-sulfonate was dissolved in 3 liters of distilled water; 175 g. of potassium permanganate was added in portions over a one and one-half hour period while the mixture was stirred and heated at 70°. The reaction was over in three hours. The manganese dioxide was filtered off, and the filtrate was evaporated to a volume of one liter. Dilute hydrochloric acid was added to *p*H 6.0. A solution of 20% barium chloride was added to maximum precipitation of the barium salt of the carboxypyridinesulfonic acid. The barium salt, filtered and washed with warm water, was suspended in 500 cc. of boiling water and dilute sulfuric acid added to remove the barium. Evaporation of the filtrate gave crystals of 6-carboxy-3-pyridinesulfonic acid m. p. 287° dec. The yield was 64 g. or 70% of the theoretical.

Anal. Calcd. for $C_6H_5NO_5S$: N, 6.89; titration equivalent, 101.5. Found: N, 6.85; titr. equiv., 102; pKa_1, 1.65; pKa_2, 3.46; pKb, 12.68.

5-Hydroxypicolinic Acid.—Five grams of 6-carboxy-3-pyridinesulfonic acid was mixed in a nickel crucible with 20 g. of sodium hydroxide pellets and 4 cc. of water. The mixture was stirred and heated at 220° for one hour. The reaction mass was diluted to 250 cc. with hot water. Addition of dilute hydrochloric acid to *p*H 5 gave 3 g. of fine white needles. Recrystallization from 250 cc. of hot water gave 2.6 g. of a crystalline monohydrate. When dried at 130° overnight, the product changed to a white powder which melted at 269–270° dec. It gave a characteristic red color with ferric chloride solution.

Anal. Calcd. for $C_6H_5NO_3$: N, 10.1. Found: N, 10.1.

On heating *in vacuo* at 280–300°, carbon dioxide was evolved and 3-hydroxypyridine, m. p. 128–129°, was obtained on distillation.

Decarboxylation of 6-Carboxy-3-pyridinesulfonic Acid.—Ten grams of potassium 6-carboxypyridine-3-sulfonate was suspended in 50 cc. of mineral oil. The temperature was adjusted to 240°, and the suspension was stirred for two and one-half hours until the evolution of carbon dioxide ceased. The solid was filtered and washed free of oil with ligroin. The product was dissolved in 50 cc. of water and treated with Norit A. After removing the Norit, the filtrate was concentrated to the point of crystallization when an equal volume of alcohol was added. Potassium 3-pyridinesulfonate was obtained in nearly quantitative yield. Conversion of the salt to the free acid gave 3-pyridinesulfonic acid, m. p. 354° dec.

Anal. Calcd. for $C_5H_5NO_3S$: S, 20.1; titration equivalent, 159.2. Found: S, 20.1; titr. equiv., 159.5.

Potassium 4-carboxypyridine-3-sulfonate can be decarboxylated in the same way.

5-Carboxy-3-pyridinesulfonic Acid.—3-Methyl-5-pyridinesulfonic acid was prepared according to McElvain and Goese,[3] using 3-picoline obtained from Reilly Tar and Chemical Corporation; 13.5 g. of the product was dissolved in 300 cc. of water, and 22 g. of potassium permanganate was added portionwise over a two-hour period with stirring at 100°. On heating another hour, the permanganate color disappeared. The manganese dioxide was removed, and the filtrate was adjusted to *p*H 6.5 with hydrochloric acid. An excess of 20% barium chloride solution was added. The solution was concentrated and filtered. The precipitate weighed 7 g. and proved to be barium oxalate. Concentration of the filtrate to 20 cc. gave a precipitate of the barium salt of 5-carboxy-3-pyridinesulfonic acid. Following treatment with dilute sulfuric acid and recrystallization from an alcohol–water mixture, the acid, melting at 335° dec., was obtained.

Anal. Calcd. for $C_6H_5NO_5S$: N, 6.89; titration equivalent, 101.5. Found: N, 6.86; titr. equiv., 102.

4-Carboxy-3-pyridinesulfonic Acid.—4-Picoline, b. p. 143–145°, obtained from Eastman Kodak Co., was sulfonated according to Webb and Corwin[4]; 39 g. of the sodium-4-methylpyridine-sulfonate was dissolved in 1040 cc. of water, and 78 g. of potassium permanganate was added over a period of six hours at 60°. The excess of permanganate was discharged by addition of alcohol. The manganese dioxide was removed, and the clear filtrate was passed through a column of Amberlite resin IR-100 to remove sodium and potassium ions. The filtrate, which was strongly acid, was evaporated to a volume of 100 cc. and cooled; 7.2 g., or 17.8% of 4-carboxy-3-pyridinesulfonic acid was obtained as white crystals. On recrystallization from alcohol–water, the melting point was 315–316° dec. Sucharda and Troszkiewicz,[9] who prepared this product through an oxidation of 4-carboxy-3-pyridylmercaptan, reported a melting point of 318°.

Anal. Calcd. for $C_6H_5NO_5S$: N, 6.89; titration equivalent, 101.5. Found: N, 6.78; titr. equiv., 102.

Acknowledgment.—The authors gratefully acknowledge the assistance of Messrs. Sidney Gister and Charles Lutomski, who carried out some of the reactions, and Mr. Theodore Fand, who supplied the analytical data.

CONTRIBUTION FROM THE
RESEARCH LABORATORIES OF THE
PYRIDIUM CORPORATION
NEPERA PARK, YONKERS, N. Y.

RECEIVED JANUARY 17, 1949

(10) A. Kirpal, *Monatsh.*, **29**, 227 (1908).
(11) Bellman, *J. prakt. Chem.*, **29**, 7 (1884).
(12) T. Urbanski, *J. Chem. Soc.*, 32 (1947).

Note on Friedel–Crafts Copolymerization

BY R. E. FLORIN

Results similar to those reported by Alfrey and Wechsler[1] have been obtained upon the system styrene (M_1)/2,5-dichlorostyrene (M_2), copolymerized at 0° in ethyl chloride solution, with aluminum chloride as catalyst. Under these conditions, $r_1 = 14.8 \pm 2$ and $r_2 = 0.34 \pm 0.2$. The reactivity ratios were evaluated by the procedure of Mayo and Lewis[2] from basic data shown in Table I.

Under the same general conditions, styrene/vinylidene chloride in all ratios yields only polystyrene, vinyl *n*-butyl ether/vinylidene chloride yields only the polyether, and styrene/vinyl *n*-butyl ether yields liquid products at low styrene ratios and semi-solid products at high styrene ratios, whose refractive indices are always close to that of the polyether.

(1) T. Alfrey, Jr., and H. Wechsler, THIS JOURNAL, **70**, 4266 (1948).
(2) F. R. Mayo and F. M. Lewis, *ibid.*, **66**, 1594 (1944).

Experimental

Materials.[3]—Aluminum chloride, anhydrous, Eastman Kodak Co. practical; ethyl chloride, U. S. P.; styrene, Eastman, stabilized with *t*-butyl catechol, found free from polymer; 2,5-dichlorostyrene, freshly distilled at 7 mm.; vinyl *n*-butyl ether, freshly distilled; vinylidene chloride, freshly distilled; stannic chloride, General Chemical Co.

Polymerizations.—About 2–5 g. of monomer mixture was prepared by weighing components into a stoppered test-tube, and the tube transferred to an ice-bath. An equal volume (±1 ml.) of ethyl chloride was added. A catalyst solution was prepared by dissolving 20–100 mg. of aluminum chloride in 10 ml. of cold ethyl chloride; it was pale yellow in color. Small increments of this solution, 0.1–0.5 ml. at a time, were added to the monomer solution with shaking and stirring until slight coloration and an increase in viscosity were observed. There were no special precautions to exclude moisture. A threshold amount of 1–2 ml. solution was required for reaction, which then took place rapidly to the extent of 5–10% conversion in one to five minutes upon adding a single increment, but would proceed no farther in several hours without adding more catalyst. Mixtures containing much vinylidene chloride reacted much more slowly. The product was diluted with 1 ml. of methanol and 5–10 ml. of chloroform, and precipitated as a powder by stirring into 150–200 ml. methanol. After two reprecipitations, it was filtered in a Selas sintered-glass crucible, dried for two days at 70°, and weighed.

Chlorine Determinations.—A 0.1–0.3-g. sample was fused for three hours with two to four times its weight of sodium in a sealed Pyrex tube at 470°. After destroying sodium with methanol, contents were boiled thirty minutes with 50–100 ml. water, neutralized with nitric acid, and filtered. High chlorines were determined gravimetrically, low chlorines by the Volhard titration.

Errors were estimated by repeating the Mayo and Lewis calculation, assuming conversion 2% higher and chlorine 0.5% lower for no. 4, and chlorine 0.1% lower for no. 1.

TABLE I

COPOLYMERIZATION OF STYRENE (M_1) AND 2,5-DICHLOROSTYRENE (M_2) IN ETHYL CHLORIDE AT 0°

Experiment	Styrene, g.	2,5-Dichlorostyrene, g.	Conversion, %	Cl in polymer %
Sn[a]	6.2567	0.6699	60–70	0.558
1[b]	2.6055	0.6665	4.64	0.739
2[b]	1.9415	1.9675	13.29	3.05
3[b]	0.6672	2.4975	27.19	17.9
4[b]	0.2691	2.5385	48.30	34.0

[a] Catalyst, two drops $SnCl_4$ in 10 ml. of ethyl chloride. [b] Catalyst, $AlCl_3$.

The principal conclusion is obviously identical with that expressed by Alfrey and Wechsler: the form of the copolymerization equation is satisfied, and the relative magnitudes of r_1 and r_2 are in inverse order to those reported for the free-radical catalyzed reaction. It is not certain whether r_1 and r_2 will be invariant for the same monomers with all catalysts of the Friedel–Crafts type; the experiment Sn, Table I, suggests that at least they may not differ widely for $AlCl_3$ and $SnCl_4$.

Results satisfy the mechanism of Alfrey and Wechsler.[1] They can also satisfy a mechanism of the type proposed by Fontana and Kidder,[4] involving rearrangement of a complex. We may write, for example

$$M_1^*C + M_2 \underset{}{\overset{K_{12}}{\rightleftharpoons}} M_1^*CM_2$$

$$M_1^*CM_2 \xrightarrow{k_{12}} M_2C$$

where K_{12} is the equilibrium constant for formation of a complex containing a polymer molecule having end-group M_1, a molecule of M_2, and a molecule of catalyst, and k_{12} is the rate constant for rearrangement of this complex to one containing only a polymer molecule with end-group M_2 and a molecule of catalyst. By using fundamental rate equations of this type in the derivation of the original copolymerization equation,[2] with low catalyst concentration and short-time steady state, one arrives at the same equation, but with $r_1 = k_{11}K_{11}/k_{12}K_{12}$, $r_2 = k_{22}K_{22}/k_{21}K_{21}$. In this case, it is unlikely that the various K's and their ratios would remain equal for all catalysts, and r_1 and r_2 should depend upon the specific catalyst used.

(3) Thanks are due to Professor C. S. Marvel, University of Illinois, for the 2,5-dichlorostyrene used; to Dow Chemical Co., and Professor F. T. Wall, University of Illinois, for the vinylidene chloride; and to General Aniline and Film Corp. for the vinyl *n*-butyl ether.

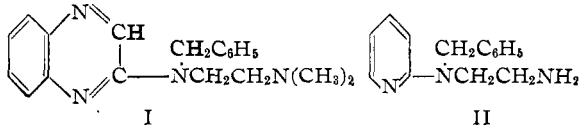
(4) C. M. Fontana and G. A. Kidder, THIS JOURNAL, **70**, 3745 (1948).

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
THE UNIVERSITY OF NEBRASKA
LINCOLN, NEBRASKA
RECEIVED JANUARY 29, 1949

Some Heterocyclic Derivatives of Ethylenediamine

BY JOHN H. GARDNER[1] AND JOSEPH R. STEVENS

In an attempt to obtain compounds exhibiting antihistamine activity, two new heterocyclic derivatives of ethylenediamine have been prepared, 2-N-benzyl-N-(2-dimethylaminoethyl)-aminoquinoxaline (I) and N-benzyl-N-2-pyridylethylenediamine (II). For the preparation of I, dimethylaminoethyl chloride was condensed with N-benzylbenzamide to give N-benzoyl-N-benzyl-N′,N′-dimethylethylenediamine, which was hydrolyzed to N-benzyl-N′,N′-dimethylethylenediamine. This was condensed with 2-chloroquinoxaline to form I. In an effort to develop a more satisfactory synthesis, 2-N-benzylaminoquinoxaline was prepared by condensing benzyl chloride and 2-aminoquinoxaline in the presence of sodium hydride. Further condensation with dimethylaminoethyl chloride failed, 2-N-benzylaminoquinoxaline being recovered unchanged.



I II

II was prepared by condensing β-bromoethylphthalimide with 2-N-benzylaminopyridine and

(1) Present address: Operations Research Office, The Johns Hopkins University, Ft. Lesley J. McNair, Washington 25, D. C.