evaporated to an oily residue (0.46 g.) which was distilled at 100° and 30 mm. to give a white, crystalline solid (0.19 g., 17% yield), m.p. 54–57°. The infrared spectrum had a carbonyl band at 5.86 microns. This material stained the skin dark green.

Anal. Calcd. for $C_6H_4N_2O_3$: C, 47.38; H, 2.65; N, 18.42. Found: C, 47.31; H, 2.78; N, 18.36.

The oxime was white, m.p. 190–191°; the 2,4-dinitrophenylhydrazone was chrome yellow, m.p. 250–252° with sintering at 228–232°; the thiosemicarbazide was yellow, m.p. 177–179°.

2-Nitropyridine-5-carboxylic acid. 2-Nitro-5-methylpyridine, m.p. 93–95°, (average yield 66%) was prepared from 2-amino-5-methyl pyridine,[16] and oxidized by permanganate[17] to 2-nitropyridine-5-carboxylic acid, m.p. 178–180°, yield 41–89% (average 66%) based on unrecovered starting material.

Methyl 2-nitropyridine-5-carboxylate. 2-Nitropyridine-5-carboxylic acid (8.3 g., 0.0494 mole) was dissolved in refluxing absolute ether (1000 ml.), cooled to 25°, and treated with diazomethane in ether. Evaporation left a residue of white crystalline methyl 2-nitropyridine-5-carboxylate (8.3 g., 92% yield) m.p. 130–131°, strong carbonyl band at 5.85 μ.

Anal. Calcd. for $C_7H_6N_2O_4$: C, 46.16; H, 3.32; N, 15.38. Found: C, 46.27; H, 3.45; N, 15.15.

Ethyl 2-hydroxypyridine-5-carboxylate. Concentrated sulfuric acid (25 ml.) was added with cooling to a solution of 2-nitropyridine-5-carboxylic acid (20.0 g., 0.119 mole) in absolute ethanol (50 ml.). The solution was heated on a steam bath for 3 hr., cooled, poured on ice (about 300 g.), made basic with ammonium hydroxide (70 ml.), and chilled. The solid which precipitated was collected by filtration, combined with the residue from chloroform extraction of the filtrate, and recrystallized from ethyl acetate to give white crystalline ethyl 2-hydroxypyridine-5-carboxylate (14.4 g., 72%) m.p. 149–151° (lit.[18] m.p. 149–150°), strong hydroxyl band at 2.90 μ and carbonyl band at 5.89 μ.

Anal. Calcd. for $C_8H_9NO_3$: C, 57.48; H, 5.43; N, 8.38. Found: C, 57.58; H, 5.54; N, 8.48.

2-Hydroxypyridine-5-carboxylic acid. 2-Nitropyridine-5-carboxylic acid (0.75 g.) was refluxed 1 hr. in a solution of 6*N* sulfuric acid (10 ml.) and ethanol (5 ml.); crystalline 2-hydroxypyridine-5-carboxylic acid, m.p. 300° *dec.* (lit.[16] m.p. 301–302° *dec.*), precipitated on cooling.

Methyl 2-chloropyridine-5-carboxylate. 2-Nitropyridine-5-carboxylic acid (26.5 g., 0.158 mole) was dissolved in absolute methanol (265 ml.), and a slow stream of hydrogen chloride was introduced with stirring and chilling during 90 min. and then kept at 0° for 12 hr. The solution became golden yellow after 1 hr., indicating the formation of nitric oxide. The reaction mixture was evaporated under reduced pressure, neutralized with sodium carbonate at 0° and the white precipitate which formed was collected by filtration and combined with the residue from the chloroform extract of the filtrate. The product was recrystallized from benzene-petroleum ether to give a white crystalline chlorine containing compound shown to be methyl 2-chloropyridine-5-carboxylate (17.5 g., 65% yield) m.p. 86–87° (lit.[19] m.p. 86–89°). The infrared spectrum indicated the absence of nitro or hydroxyl functions.

2-Chloropyridine-5-carboxylic acid. A mixture of 2-nitropyridine-5-carboxylic acid (0.75 g.) and concentrated hydrochloric acid (5 ml.) was boiled for 5 min.; nitric oxide was evolved. Evaporation to dryness gave white crystalline 2-chloropyridine-5-carboxylic acid (0.70 g.) m.p. 195–200° (lit.[20] m.p. 199° *dec.*). Esterification according to the previous experiment gave the methyl ester, m.p. 86–87°; a mixture melting point with sample prepared in the previous experiment was undepressed.

Methyl 2-methoxypyridine-5-carboxylate. Methyl 2-nitropyridine-5-carboxylate (0.14 g.) and methanol (0.10 ml.) were dissolved in benzene (10 ml.). Sodium hydride (0.14 g.) was added, and the mixture was refluxed 4 hr. A solid was collected by filtration which gave brown fumes on acidification, and a positive "brown ring test" with ferrous sulfate and concentrated sulfuric acid, indicating the presence of nitrite ion. The filtrate residue was sublimed to long white needles of methyl 2-methoxypyridine-5-carboxylate (0.09 g.) m.p. 48–49° (lit.[21] m.p. 42°).

Anal. Calcd. for $C_8H_{10}O_3N$: OCH_3 37.1. Found: 36.5.

Under the same conditions, but without the addition of methanol, sodium hydride was recovered by filtration and methyl 2-nitropyridine-5-carboxylate by evaporation of the filtrate. With sodium methylate in methanol the same product was obtained on sublimation but the yield was lower.

2-Aminopyridine-5-carboxylic acid. Methyl 2-nitropyridine-5-carboxylate (0.60 g.) was added to a sodium amide suspension prepared by the addition of sodium (0.08 g.) to liquid ammonia (50 ml.). The mixture immediately became deep purple, then slowly faded to brown. Evaporation of the ammonia left an amorphous gray water-soluble powder, which evolved nitric oxide upon acidification with 3*N* hydrochloric acid. From the acid solution, a small amount (10 mg.) of crystalline 2-aminopyridine-5-carboxylic acid was obtained, m.p. 290–310° dec. (lit.[22] 312° dec.).

Attempted condensations with ethyl acetate using sodium hydride, sodium amide or sodium triphenylmethyl in inert solvents were unsuccessful.

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(21) H. Meyer, *Monatsh.*, **26**, 1320 (1905); **28**, 60 (1907).

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The Synthesis of 5-Azaindole[1]

SHIGENOBU OKUDA AND MICHAEL M. ROBISON[2]

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Since 7-azaindole and 7-azatryptophan[3] have exhibited interesting biological activity in a number of systems,[4] a synthesis of 5-azaindole and deriva-

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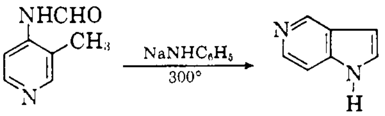
(2) To whom inquiries should be addressed at CIBA Pharmaceutical Products, Inc., Summit, N. J.

(3) M. M. Robison and B. L. Robison, *J. Am. Chem. Soc.*, **77**, 457 (1955).

(4) *Cf.* G. W. Kidder and V. C. Dewey, *Biochim. et Biophys. Acta*, **17**, 288 (1955); A. B. Pardee, V. G. Shore, and L. S. Prestidge, *Biochim. et Biophys. Acta*, **21**, 406 (1956); A. B. Pardee and L. S. Prestidge, *Biochim. et Biophys. Acta*, **27**, 330 (1958); E. R. B. Sundaram and P. S. Sarma, *Current Sci.* (India), **26**, 13 (1957); *Chem. Abstr.*, **51**, 9799 (1957).

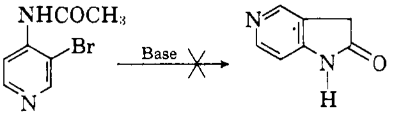
tives seemed desirable. 5-Azaindole itself was first prepared by Möller and Süs[5] by a photochemical ring contraction of 3-diazo-1,6-naphthyridin-4-(3*H*)-one and decarboxylation of the resulting 5-azaindole-3-carboxylic acid. Earlier unsuccessful attempts to prepare the heterocycle included application of the Madelung cyclization of 4-formamido-3-picoline,[6] as well as a Bischler-Napieralski-type reaction of 2-(2-formamidoethyl)-pyrrole.[7] Since 7-azaindole could be prepared in greatly improved yield by use of sodium anilide[3] in the Madelung reaction, rather than sodium ethoxide,[8] it was thought that a reinvestigation of the cyclization using the former reagent might be fruitful. A further inducement to this study stemmed from the fact that Clemo and Swan[6] attempted the synthesis employing an impure, noncrystalline preparation of 4-formamido-3-picoline. Preliminary studies on the formylation of 4-aminopyridine produced the hitherto unreported 4-formamidopyridine and made possible the selection of reaction conditions which led to 4-formamido-3-picoline in good yield and in crystalline form. Cyclization of the latter by the procedure employed for 7-azaindole[3,9] afforded 5-azaindole in 21% yield. The product was identical with the compound prepared by Möller and Süs.[10]



Several attempts were made to convert 5-azaindole to 5-azatryptophan. The substance, however, differs appreciably in its reactivities from 7-azaindole and the reaction sequence employed with the latter was unsuccessful. Thus attempted conversion to "5-azagramine" by several modifications of the Mannich reaction led to materials which could not be crystallized or purified. Further, no well characterized compounds could be isolated on treatment of the crude Mannich reaction product with acetamidomalonic ester, nor was it possible to isolate any crystalline substance from the direct treatment of 5-azaindole with diethyl piperidinomethylformamidomalonate.[11]

5-Azaindole differs in other respects from its 7-aza analog. Thus, attempted atmospheric-pressure hydrogenation in acidic medium over Adams' catalyst did not take place.[12] A considerably lower absorption value for the longer wave-length ultraviolet absorption maximum compared to the 7-azaindole[3] and 4-methyl-5-azaindole[7] maxima was also noted. The identity of the products prepared by the two different syntheses, however, together with the analytical data, molecular weight determinations and characteristic color reactions (*vide infra*) allow no other expression for the product.

Another possible approach to the synthesis of the 5-azaindole ring system involves the creation of an intermediate "pyridyne" species, so substituted that an adjacent nucleophilic center might add intramolecularly. This method of synthesis of heterocyclic compounds was first elucidated by Hrutfiord and Bunnett.[13,14] Experiments were first carried out with 4-acetamido-3-bromopyridine, a derivative which is relatively easily available. It may be noted, however, that attempts to prepare the compound by bromination of 4-acetamidopyridine were unsuccessful, starting material being recovered. The substance was obtained *via* 3-bromopyridine-*N*-oxide by nitration, reduction and acetylation. Treatment of the product with a wide variety of basic reagents did not result in the desired cyclization to 5-azaindole. In all cases starting material was recovered or dehalogenation or hydrolysis was observed. It was thought that salt formation involving the active hydrogen of the amide group might be interfering with the cyclization, and accordingly attempts were made to prepare the acetyl derivative of 4-benzylamino-3-bromopyridine. It was found that 4-benzylaminopyridine can be prepared in good yield by treatment of 4-aminopyridine with benzaldehyde and subsequent reduction with formic acid.



No well characterized products were obtained on bromination of the amine, however. The desired combination of halogen and benzylamino groups was finally attained by treatment of 4-amino-3-bromopyridine with benzyl alcohol and potassium hydroxide.[15] The resulting 4-benzylamino-3-bromopyridine, which was isolated as the picrate was not investigated further because of the termination of the project.

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(10) The authors wish to express their sincere appreciation to Drs. Möller and Süs, who kindly provided a generous sample of their preparation for comparison.

(11) A. Butenandt, H. Hellmann, and E. Renz, *Z. Physiol. Chem.*, **284**, 175 (1949).

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(14) The authors wish to express their sincere appreciation to Dr. Bunnett, who provided a copy of the above manuscript before publication and suggested applications to the synthesis of azaindoles.

(15) *Cf.* I. Hirao and M. Hayashi, *J. Pharm. Soc. Japan*, **74**, 853 (1954), *Chem. Abstr.*, **49**, 10308 (1955).

EXPERIMENTAL[16,17]

4-Formamidopyridine. A formylating mixture, prepared by heating 2.5 ml. of 98% formic acid and 6.3 ml. of acetic anhydride at 50° for 2 hr., was cooled to ice-bath temperature and a solution of 1.88 g. of 4-aminopyridine in 40 ml. of dry tetrahydrofuran was added slowly with cooling. The mixture was allowed to stand at room temperature for 2 days, another anhydride solution prepared by heating 1.7 ml. of formic acid and 4.2 ml. of acetic anhydride was added and the reaction was allowed to stand one more day. It was then evaporated to dryness *in vacuo* and the residue was washed with ether and recrystallized from acetone. The 1.98 g. (80%) of white sand melted at 160–162°. The analytical sample, prepared by two more recrystallizations from acetone, melted at 162–163°.

Anal. Calcd. for $C_6H_6N_2O$: N, 22.92. Found: N, 22.94.

4-Formamido-3-picoline. The 4-amino-3-picoline was prepared on a large scale by a modification of the two-step reduction of 4-nitro-3-picoline-N-oxide.[18] It was found that the intermediate 4-nitro-3-picoline could be hydrogenated on a 22-g. scale in 90% yield at 1–3 atmospheres pressure, provided that the shaker bottle was cooled continuously during the early, exothermic stage of the hydrogenation by a stream of running water. In the absence of such cooling some undesired side reaction took place and almost none of the desired product was obtained. A solution of 32.2 g. of the amine in 200 ml. of dry tetrahydrofuran was added slowly to a formylating mixture prepared, as in the 4-formamidopyridine preparation, from 38 ml. of formic acid and 95 ml. of acetic anhydride. After standing and treatment with a second portion of anhydride solution, prepare from one half the above quantities of reagents, the reaction mixture was worked up as in the previous case. The residue from the evaporation was triturated with 200 ml. of dry ether and the resulting 33 g. of white solid was purified by chromatography on 300 g. of alumina.[19] Elution with about 1000 ml. of 2:1 benzene-acetone afforded, after recrystallization from benzene, 22.9 g. of white needles, m.p. 141°. About 10 g. of crude material, obtained from the mother liquors, from the earlier ether washings and from later chromatogram fractions was chromatographed again on 125 g. of alumina. By this procedure an additional 5.13 g. of white needles, m.p. 140–141°, was obtained. Thus, the total yield was 69%. The analytical sample, m.p. 142–143°, was prepared by sublimation at 140° (0.2 mm.).

Anal. Calcd. for $C_7H_8N_2O$: C, 61.75; H, 5.92; N, 20.58. Found: C, 61.75; H, 5.71; N, 20.53.

The picrate formed yellow needles from ethanol, m.p. 199–200° (reported[6] m.p. 199–200°).

5-Azaindole. The cyclization of the amide was effected by the procedure used for 7-azaindole.[3,9] In the single large scale reaction carried out, 42.4 g. of amide was cyclized using appropriate quantities of sodium hydride and aniline,[9] the only variation in procedure being the use of 44.5 g. of dry *sodium* formate, instead of the potassium salt. It has been found that the sodium salt is more satisfactory for 7-azaindole preparations, as well. The usual reaction workup afforded, in the final distillation, 14.1 g. of red oil, b.p. 163–166° (0.5 mm.). After the oil had partially crystallized the solid was separated by filtration and recrystallized from ether-petroleum ether. The 2.48 g. of white solid melted at 105–107°. Chilling of the oil yielded more solid, which after two recrystallizations weighed 1.32 g. and melted at 110–111°. The combined oils and materials from the mother liquors were purified by chromatography on 150 g. of alumina.[19] Elution with about 800 ml. of 4:1 ether-acetone afforded, after recrystallization, 2.96 g. of additional product. Rechromatography of the crude fractions through another 100-g. alumina column produced a final fraction of 1.03 g. of 5-azaindole. The total yield was 7.79 g. or 21%. The analytical sample was prepared by recrystallizations from benzene-cyclohexane, from chloroform-hexane and from water and by sublimation at 105° (0.3 mm.). The white solid melted at 111.5–112.5° and the melting point was undepressed on admixture with a sample prepared by Möller and Süs. 5-Azaindole gives a negative Ehrlich test, but a dark blue-green color on treatment with sodium nitroprusside and alkali, as does 7-azaindole.[3] The ultraviolet spectrum shows a minimum at 238 mμ (log ϵ 3.13) and a maximun at 265 mμ (log ϵ 3.62). The corresponding values determined from the sample provided by Möller and Süs were λ_{min} 237 mμ (3.16) and λ_{max} 265 mμ (3.63). The equivalent weight of the substance was determined by perchloric acid titration of an acetic acid solution using crystal violet indicator, while the molecular weight was approximated by a crude semimicro Rast procedure.[20]

Anal. Calcd. for $C_7H_6N_2$: C, 71.19; H, 5.09; N, 23.73; mol. wt. 118. Found: C, 71.41; H, 5.16; N, 23.86; neut. equiv., 118; mol. wt., 141.

4-Amino-3-bromopyridine. This known material was prepared from 3-bromopyridine by nitration of the N-oxide and reduction. A number of improvements were made in the steps. Räth[21] reported the preparation of 3-bromopyridine in 56% yield by diazotization of 3-aminopyridine in sulfuric acid–hydrobromic acid and treatment with copper powder. Since, in our hands, this method gave a yield of only 28%, the reaction was run in a mixture of 3 volumes of 48% hydrobromic acid and 1 volume of water. By this modification the yield was increased to 41–53%. Den Hertog[22] prepared 4-amino-3-bromopyridine in approximately 23% yield from the 3-bromo compound. This over-all yield was approximately doubled by: (1) Use of peracetic acid, rather than perphthalic acid in the oxidation, and isolation of 3-bromopyridine-N-oxide as the hydrochloride. (2) Nitration of the hydrochloride salt. (3) Prolonged extraction of the iron-acetic acid reduction product into ether in a continuous extraction apparatus.

4-Benzylamino-3-bromopyridine picrate. A mixture of 0.43 g. of 4-amino-3-bromopyridine, 0.30 g. of benzyl alcohol, 0.30 g. of potassium hydroxide, and 5 ml. of xylene was refluxed 7 hr., cooled, and added to 30 ml. of ether. Insoluble material was separated by filtration and the organic layer was evaporated *in vacuo.* Since the residual oil afforded no crystalline material on chromatography, a picrate was formed in ethanol. The 0.61 g. of yellow needles melted at 160–165°. After recrystallizations from absolute ethanol the compound had m.p. 163–165°.

Anal. Calcd. for $C_{18}H_{14}N_5O_7Br$: N, 14.23. Found: N, 14.30.

4-Acetamido-3-bromopyridine. A mixture of 3.1 g. of the amine and 30 ml. of acetic anhydride was refluxed 6 hr. and evaporated *in vacuo.* The residue was dissolved in 150 ml. of ether and extracted with three 150 ml. portions of cold 3% aqueous sodium hydroxide.[23] The sodium hydroxide solution was saturated with carbon dioxide and the resulting precipitate was washed with cold water and dried. The 2.88 g. (75%) of 4-acetamido-3-bromopyridine had m.p. 96–100°. Recrystallization from ether-petroleum ether afforded white needles, m.p. 86–87°. Thorough drying of

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[16] Melting points are corrected, boiling points uncorrected.

[17] Analyses by Weiler and Strauss, Oxford, England, except for some nitrogen analyses which were carried out by a semimicro Kjeldahl technique in this laboratory.

[18] W. Herz and L. Tsai, *J. Am. Chem. Soc.*, **76**, 4184 (1954).

[19] Fisher adsorption alumina was used.

[20] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 55.

[21] C. Räth, *Ann.*, **486**, 100 (1931).

[22] H. J. Den Hertog and J. Overhoff, *Rec. trav. chim.*, **69**, 468 (1950).

[23] The solubility of amides of 2- and 4-aminopyridine in strong aqueous base is general when the amide nitrogen is unsubstituted.

these crystals at 70° caused a change to prisms, m.p. 102.5–103.5°. The analytical sample, prepared by further recrystallizations from the same solvent pair, had m.p. 86–87°, which changed to 101–102.5° after storage of the product for one month at room temperature.

Anal. Calcd. for $C_7H_7N_2OBr$: N, 13.03. Found: N, 12.96.

No cyclization products were obtained from reactions in which the substance was treated with potassium amide in liquid ammonia, with sodium ethoxide in ethanol at 150–160°, with sodium hydride in refluxing xylene or with sodium amide in refluxing cumene.

4-Benzylaminopyridine. A mixture of 3 g. of 4-aminopyridine, 4.5 g. of benzaldehyde and 10 ml. of cumene was refluxed for 2 hr., during which period water was removed periodically by co-distillation with cumene. The mixture was cooled, then after addition of 6 ml. of 98% formic acid it was refluxed again for 17 hr. Fifty ml. of water was added to the two-phase system after cooling and the aqueous layer was separated, washed with three 25-ml. portions of ether, then made alkaline with saturated aqueous sodium carbonate. The precipitated white solid weighed 4.19 g. and melted at 107.5–109.5°. Recrystallizations from ether-petroleum ether afforded 3.99 g. (69%) of white prisms, m.p. 110.5–111°. The picrate was formed in methanol and recrystallized from the same solvent, m.p. 138.5–139.5°.[24]

Absorption spectra. The ultraviolet spectra of the 5-azaindole samples were determined from $10^{-4}M$ solutions in 95% ethanol. Measurements were carried out with either a Beckman model DU spectrophotometer or a Beckman model DK-1 instrument.

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[24] T. Kahto and M. Ohta, *J. Pharm. Soc. Japan*, **71**, 217 (1951) report m.p. 108–109.5° for the amine and m.p. 140–142° for the picrate.

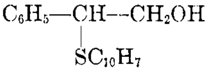
Reaction of Styrene Oxide with 2-Naphthalenethiol

Cyrus O. Guss and Herbert S. Wilgus III[1]

Received December 31, 1958

Styrene oxide has been shown by Gilman and Fullhart[2] to react with potassium methyl mercaptide and form the secondary alcohol, $C_6H_5CHOHCH_2SCH_3$. More recently Rondestvedt[3] reported that the reaction of styrene oxide with potassium benzyl mercaptide in dioxane gave the corresponding secondary alcohol. This direction of ring opening was considered normal by these investigators.

Since styrene oxide had been found to react with sodium 2-naphthoxide in water predominantly by nuclear attack, forming 2-(2-hydroxy-1-naphthyl)-2-phenylethanol,[4] and since the analogous compound that would result from a comparable reaction between styrene oxide and 2-naphthalenethiol was now sought, the latter compounds were subjected to appropriate reaction conditions. This was undertaken in spite of the known lack of nucleophilic reactivity of the ring in such thiophenols.[5] The substance that was isolated, in 80% yield, was shown to have structure I. The reaction in aqueous medium with excess sodium hydroxide present was relatively rapid at 0–5°. Little, if any, of the secondary alcohol could have been formed. Both of the possible isomeric alcohols were synthesized by reliable methods for structure proof as reported in the experimental portion.



$$C_6H_5-\underset{\underset{\displaystyle SC_{10}H_7}{|}}{CH}-CH_2OH$$

I

The direction of ring opening of styrene oxide in aqueous alkali is thus the same with 2-naphthol and 2-naphthalenethiol. For these two compounds differences in the rate of reaction and structure of products seem to result, in part, from the nature of the nucleophilic species.[5,6] It is our conjecture that solvent effects are partially responsible for the difference in the direction of ring opening of styrene oxide observed by us and the aforementioned investigators.[7] In an experiment not reported here the reaction of styrene oxide with the sodium salt of 2-naphthalenethiol in dioxane evidently formed the secondary alcohol predominantly.

EXPERIMENTAL[8]

Reaction of styrene oxide with 2-naphthalenethiol in aqueous sodium hydroxide. A mixture of 2-naphthalenethiol (11.0 g., 0.069 mole, Eastman product recrystallized to m.p. 80–82°) in sodium hydroxide (5.0 g., 0.125 mole) and water (75 ml.) was stirred under nitrogen with warming to aid dissolution of the thiol. This was then cooled in an ice bath to below 5° prior to the addition of styrene oxide (4.0 g., 0.033 mole, b.p. 45° (2 mm.), n_D^{20} 1.5345) in portions in 5 min. A reaction occurred almost immediately as evidenced by the appearance of a fine precipitate. After 2 hr. the mixture was allowed to warm to room temperature, filtered, washed by

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[1] Taken in part from the M.S. thesis of Herbert S. Wilgus III, December 1955.

[2] H. Gilman and L. Fullhart, *J. Am. Chem. Soc.*, **71**, 1478 (1949).

[3] C. S. Rondestvedt, Jr., *J. Org. Chem.*, **21**, 911 (1956).

[4] C. O. Guss and L. H. Jules, *J. Am. Chem. Soc.*, **72**, 3878 (1950).

[5] *Eg.*, D. S. Tarbell, and A. H. Herz, *J. Am. Chem. Soc.*, **75**, 1668 (1953) and references mentioned there.

[6] O. R. Quale and E. E. Royals, *J. Am. Chem. Soc.*, **64**, 226 (1942); J. F. Bunnett and G. T. Davis, *J. Am. Chem. Soc.*, **76**, 3011 (1954).

[7] C. O. Guss and H. R. Williams, *J. Org. Chem.*, **16**, 1809 (1951).

[8] Temperature measurements are uncorrected.