

duces a detectable amount of a volatile material giving the xanthate test for carbon disulfide. Mere oxygen concentration does not seem to govern the amount produced, for the test with air was very faint. The results also strongly suggest that ethylene alone is without effect.

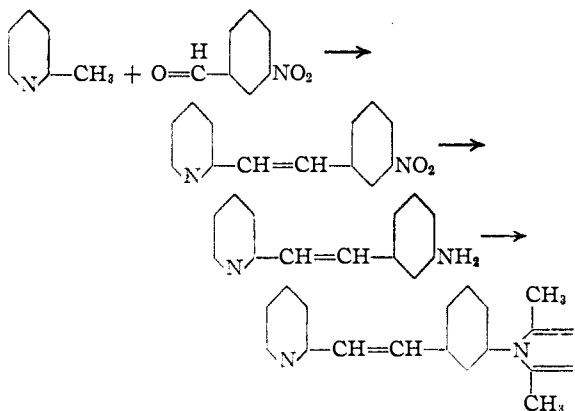
The poisoning effect of carbon disulfide on nickel catalysts is well known and may account for the erratic results obtained using Fieser's solution.

CHEMICAL LABORATORY
THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND RECEIVED NOVEMBER 24, 1944

Some Styrylpyridines and -Quinolines

BY H. GILMAN AND GEORGE KARMAS

Incidental to a study of anils, several substituted styrylpyridines and -quinolines have been prepared. Some of the nitrostyryl types were reduced to the corresponding aminostyryls, and these in turn were condensed with acetylacetone to give the corresponding 2,5-dimethylpyrrylstyryl compounds. The following is an illustrative sequence of transformations:



Experimental

The condensations of aldehydes with the picolines, quinaldine, and lepidine were effected by conventional procedures.^{1,2} In a few comparative preparations it was observed that the method using acetic anhydride was better than the one in which anhydrous zinc chloride was used. The general results are given in Table I. Tests on the following compounds will also be reported later: α -(*p*-dimethylaminostyryl)-quinoline³; α -(*m*-aminostyryl)-quinoline⁴; α, α' -(*di-m*-nitrostyryl)-pyridine⁵; α - and γ -(*m*-nitrostyryl)-pyridine^{2,5}; α -(*m*-nitrostyryl)-quinoline⁶; α -(*p*-nitrostyryl)-quinoline⁷; α -(*m*-2,5-dimethylpyrrylstyryl)-quinoline; α - and γ -(*p*-nitrostyryl)-pyridine^{2,5}; and α - and γ -(*m*-aminostyryl)-pyridines.⁸

The authors are grateful to Parke, Davis and Company for arranging the tests.

- (1) Kaplan and Lindwall, *THIS JOURNAL*, **65**, 927 (1943).
- (2) Shaw and Wagstaff, *J. Chem. Soc.*, 77 (1933).
- (3) Noelting and Witte, *Ber.*, **39**, 2750 (1906). Our m. p. for this compound was 181–182°, and they reported 177°.
- (4) Wartanian, *Ber.*, **23**, 3648 (1890). Our m. p. for this compound was 160–161°, and he reported 158–159°.
- (5) Wagstaff, *J. Chem. Soc.*, 277 (1934).
- (6) Taylor and Woodhouse, *ibid.*, 2971 (1926).
- (7) Bulach, *Ber.*, **20**, 2047 (1887).
- (8) See footnotes *f* and *g* in Table I.

TABLE I
STYRYL DERIVATIVES

Product	M. p. (cor.), °C.	Anal., % N Calcd.	Found
α, γ -(C ₆ H ₅ N)(CH=CHC ₆ H ₄ NO ₂ - <i>m</i>) ₂ ^a	242–243	10.80	11.02
γ -(C ₆ H ₅ N)CH=CHC ₆ H ₄ N(CH ₃) ₂ - <i>p</i> ^b	240–241	12.50	12.37
γ -(C ₆ H ₅ N)CH=CHC ₆ H ₄ N(CH ₃) ₂ - <i>p</i> ^c	141–142	10.23	10.36
γ -(C ₆ H ₅ N)CH=CHC ₆ H ₄ O- α (picrate) ^d	212–214	14.00	14.25
α -(C ₆ H ₅ N)CH=CHC ₆ H ₄ CF ₃ - <i>m</i> ^e	104–105	4.68	4.18
α -(C ₆ H ₅ N)CH=CHC ₆ H ₄ NH ₂ - <i>m</i> ^f	103–104	14.30	14.32
γ -(C ₆ H ₅ N)CH=CHC ₆ H ₄ NH ₂ - <i>m</i> ^g	189–190	14.30	14.45
α -(C ₆ H ₅ N)CH=CHC ₆ H ₄ NC ₆ H ₅ - <i>m</i> ^h	87–88	10.20	10.40
α -(C ₆ H ₅ N)CH=CHC ₆ H ₄ NC ₆ H ₅ - <i>m</i> ⁱ	132–133	8.63	8.70

^a This condensation product of α, γ -lutidine and *m*-nitrobenzaldehyde was crystallized from tetrachloroethane. The yield was 34%. ^b Crystallization of the condensation product from *p*-dimethylaminobenzaldehyde was from methanol. ^c Crystallization was from petroleum ether (b. p. 80–110°). ^d The condensation product with furfural distilled at about 200° (18 mm.), and because of its instability in air was converted to the picrate which was crystallized from ethanol. ^e This compound was synthesized in 65% yield by condensation with *m*-trifluoromethylbenzaldehyde (prepared by F. Yeoman), and was crystallized from dilute ethanol. ^f The nitrostyrenes were reduced to the corresponding amines by refluxing an ethanol solution with a saturated aqueous solution of sodium sulfide. The hemi-hydrate of this *m*-aminostyryl derivative of α -picoline was reported to melt at 85° [Schufftan, *Ber.*, **23**, 2717 (1890)]. Our product, obtained in 49% yield, was crystallized from dilute ethanol. ^g No m. p. was given for this compound. See Deutsche Hydrierwerke Akt.-Ges., French Patent 775,101 (June 27, 1934) [*Chem. Zentr.*, **106**, I, 3853 (1935)]. Our product, obtained in 47% yield, was crystallized from ethanol. ^h The *m*-2,5-dimethylpyrrylstyryl compound, obtained by condensation of the *m*-aminostyryl product with acetylacetone, distilled as a viscous light yellow oil at 180–190° (0.001 mm.). This solidified after a short time, and crystallization from dilute methanol gave small, colorless flakes. ⁱ The reduction of α -(*m*-nitrostyryl)-quinoline by sodium sulfide gave the corresponding amine in a 57% yield and melting at 160–161°. The m. p. reported by Wartanian, *Ber.*, **23**, 3648 (1890), is 158–159°. In addition to the amine we isolated a small quantity of an orange colored compound which was insoluble in hot ethanol, but crystallized from dioxane as fine, orange needles melting at 226–227°. This may be the azo compound, C₉H₈NCH=CHC₆H₄N=NC₆H₄CH=CHC₆H₅N. *Anal.* Calcd. for C₃₄H₂₁N₄: N, 11.46. Found: N, 11.21. The *m*-(3,5-dimethylpyrrylstyryl) product, obtained in 72% yield by condensation of the amine with acetylacetone, distilled at 200–210° (0.001 mm.). Crystallization from ethanol gave fine, buff platelets.

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

RECEIVED OCTOBER 21, 1944

Fluorescence Chromatography of the Methyl Glucoses¹

BY ETHELDA J. NORBERG, IRVING AUERBACH² AND R. M. HIXON

Several investigators have attempted, by chromatographic techniques, the quantitative separation of the ultimate hydrolysis products of methylated starch: *i. e.*, 2,3-dimethyl glucose,

(1) Journal Paper No. J. 1244 of the Iowa Agricultural Experiment Station, Ames, Iowa. Project 817. Supported in part by a grant from the Corn Industries Research Foundation.

(2) Present address, Chemistry Department, Ohio State University, Columbus, Ohio.

2,3,6-trimethyl glucose, and 2,3,4,6-tetramethyl glucose. Mertzweiller, Carney and Farley³ separated a synthetic mixture of the pure sugars by conversion to their colored azoyl esters and adsorption on a silica column. Jones⁴ hydrolyzed methylated starch with methyl-alcoholic hydrogen chloride to give the tri- and tetramethyl methyl glucosides, which were adsorbed on an alumina column. By analysis of successive portions of the eluate, he showed that these glucosides could be quantitatively eluted in separate fractions.

This laboratory has applied the chromatographic method directly to the methyl glucoses. It was found that ultraviolet light can be used to facilitate the development of such chromatograms, since it permits following visually the separation of the fluorescent glucoses.

When a solution of tri- and tetramethyl glucose in benzene is passed through an alumina column, a single fluorescent band is formed which, upon further development with benzene separates into two bands, the lower being tetramethyl glucose. After forcing the adsorbent out of the tube, the respective bands may be cut from the column and the sugars extracted with methanol. Evaporation of the methanol solution has given a quantitative recovery (95-105%) of the tri- and tetramethyl glucoses.

Since dimethyl glucose is not soluble in benzene, it was separated as follows: A solution of di-, tri- and tetramethyl glucose in acetone-benzene (1:1) was passed through an alumina column and developed with benzene. The dimethyl glucose was adsorbed as a fluorescent band, while the other two sugars passed through unadsorbed. They were recovered by evaporation of the solvent, redissolved in benzene, and separated as described above. The separation of dimethyl glucose from the tri- and tetramethyl glucoses has as yet been carried out only on a qualitative basis, since it was necessary to discontinue the work temporarily.

Experimental

Fibrous alumina was prepared and activated according to the Wislicenus method.⁵ It is only faintly fluorescent, while all available commercial alumina preparations proved to be highly fluorescent. The adsorption tubes were 7-inch lengths of 8-mm. Pyrex tubing. A mercury vapor lamp with suitable filter provided a source of ultraviolet light. Since the columns were packed and developed under a constant air pressure (25 cm.), a convenient apparatus for adding the solutions without interrupting the pressure was devised.

In most cases, the following procedure was found satisfactory. The fibrous alumina was made into a thick slurry with benzene and poured into the adsorption tube containing a cotton plug at the bottom. The column was packed by application of pressure to give a 10-cm. length of adsorbent, care being taken not to let it become free of solvent at any time. About 20-50 mg. of the mixed tri- and tetramethyl glucoses, dissolved in 5-10 ml. of warm

benzene and cooled, was passed through the column. Development with benzene was then begun and continued until the desired separation of bands was obtained. The tube was occasionally moved to a dark box for observation of the fluorescent bands under ultraviolet light. The recovered methyl glucoses were identified by their methoxyl contents and melting points.

The 2,3-dimethyl glucose used in these experiments was obtained through the courtesy of Drs. Coleman and McCloskey at the State University of Iowa.

PLANT CHEMISTRY SUBSECTION

IOWA AGRICULTURAL EXPERIMENT STATION

AMES, IOWA

RECEIVED NOVEMBER 13, 1944

Aryl Sulfides and Sulfones Containing the Diethylaminoethyl Group

BY B. PUETZER¹ AND A. R. SURREY

Several aryl sulfides and sulfones containing the 4- β -diethylaminoethylamino group have been prepared for the purpose of testing their activity against certain organisms. It has been found that they have only a slight bacteriostatic action *in vitro* against *Staph. aureus*. Similar tests against various intestinal bacilli demonstrated that 4-(β -diethylaminoethylamino)-phenyl 4-nitrophenyl sulfone has definite antibacterial activity toward several members of this group.² However, *in vivo* tests showed the compound to be quite toxic to mice.

Experimental

4-(β -Diethylaminoethylamino)-phenyl 4-Nitrophenyl Sulfide (I).—Forty-six grams of β -diethylaminoethyl chloride and 75 g. of 4-nitrophenyl 4-aminophenyl sulfide³ were heated with stirring in 150 ml. of nitrobenzene at 120-130° for six hours. The nitrobenzene was removed by steam distillation and the residue was treated with a small amount of ether. On stirring, a solid separated which was filtered off; the yield was 32 g. (30%). Several recrystallizations from alcohol gave yellow plates melting at 89°.

Anal. Calcd. for C₁₃H₂₂N₃O₂S: N, 12.17. Found: N, 12.28.

4-(β -Diethylaminoethylamino)-phenyl 4-Nitrophenyl Sulfide Dihydrochloride.—Alcoholic hydrogen chloride was added to a solution of the base (I) in acetone. Addition of dry ether caused precipitation of the dihydrochloride. It was recrystallized several times from acetone-ether. A light yellow powder was obtained melting at 140-142°.

Anal. Calcd. for C₁₃H₂₂N₃O₂Cl₂S: N, 10.05; Cl, 17.0. Found: N, 10.18; Cl, 16.6.

4-(β -Diethylaminoethylamino)-phenyl 4-Aminophenyl Sulfide.—Thirty-two grams of the base (I) was refluxed for three hours in a well-stirred suspension of 120 g. of iron filings in 540 ml. of 50% alcohol containing 3 ml. of acetic acid. The hot reaction mixture was made alkaline with sodium carbonate and filtered. The alcohol was distilled from the colorless filtrate under reduced pressure and the residue was extracted with ether. After removing the ether, the amine was distilled; yield, 7.5 g.; b. p. 234° (1 mm.).

Anal. Calcd. C₁₃H₂₁N₃S: N, 13.33. Found: N, 13.33.

(1) Present address: Vick Chemical Co., New York, N. Y.

(2) Our thanks are due to Dr. C. A. Lawrence and G. R. Goetchius for this report.

(3) Gabel and Grinberg, *C. A.*, **34**, 6244 (1940).

(3) Mertzweiller, Carney and Farley, *THIS JOURNAL*, **65**, 2367 (1943).

(4) Jones, *J. Chem. Soc.*, 333 (1944).

(5) As described in Strain's "Chromatographic Adsorption Analysis," Interscience Publishers, New York, N. Y., 1942, p. 54.