found that comparable yields could be obtained in a much shorter time if ethanol or water was used as the solvent.

A mixture of O,O-diethyl chlorothiophosphate (37.7 g.), anhydrous sodium *p*-nitrophenoxide (32.2 g.), and ethanol (200 cc.) was refluxed for one hour, cooled to 20°, filtered, and the filtrate concentrated *in vacuo*. The residue was heated (oil-bath at 100–110°) with stirring at 0.5 mm. for a short period to remove any unreacted O,O-diethyl chlorothiophosphate. The crude parathion was dissolved in toluene (100 cc.) and washed with 5% sodium carbonate, then with water. After drying over Drierite and removal of the toluene at reduced pressure, the product weighed 43.5 g. (75% yield), $n^{25}D$ 1.5361. Distillation of a 200-g. sample prepared in another experiment gave 182 g. of pale yellow oil, b. p. 157–162° (0.6 mm.), $n^{25}D$ 1.5370.

Anal. Calcd. for $C_{10}H_{14}NO_5PS$: C, 41.23; H, 4.84; N, 4.81; P, 10.65; S, 11.01. Found: C, 41.38; H, 4.93; N, 4.60; P, 10.66; S, 11.06.

O,O-Diethyl chlorothiophosphate (41.6 g.) was added during one-half hour to sodium *p*-nitrophenoxide (32.2 g.) in water (100 cc.) at 95–100°, and stirring was continued at this temperature for two hours. After cooling to 20° the lower layer was separated, washed three times with water, and dried over sodium sulfate to give 37 g. (64% yield) of brown oil, $n^{25}D$ 1.5374.

STAMFORD RESEARCH LABORATORIES
AMERICAN CYANAMID COMPANY
STAMFORD, CONNECTICUT RECEIVED OCTOBER 20, 1948

Streptomyces Antibiotics. XX. Conversion of Streptamine into Streptidine

BY FREDERICK W. HOLLY, RALPH MOZINGO AND KARL FOLKERS

Conversion of streptamine into streptidine with S-methyl isothiourea has been reported.[1] Another of the general methods for the preparation of guanidines from amines is also applicable for this conversion. Streptidine is formed when streptamine hydrochloride is heated with aqueous cyanamide. A 6% yield of streptidine, as the sulfate, was obtained by heating the mixture at 100° for forty-eight hours and a 17% yield by heating at 155° for two hours under hydrogen pressure.

Experimental

Streptidine Sulfate.—A solution prepared from 753 mg. of streptamine hydrochloride and 252 mg. of cyanamide in 2.5 ml. of water was heated for two hours at 155° under hydrogen pressure. The reaction mixture was cooled and a dark amorphous solid was removed. To the clear solution 1.0 ml. of concentrated sulfuric acid was added, and the solution was adjusted to *p*H 9 with ammonium hydroxide. The solution was concentrated under reduced pressure to a mixture of oil and crystals, and 4 ml. of 6 *N* ammonium hydroxide was added. The mixture was cooled, the crystals were collected on a filter, washed successively with water, alcohol and ether, and dried to give 180 mg. (17%) of streptidine sulfate.

Anal. Calcd. for $C_8H_{18}N_6O_4 \cdot H_2SO_4 \cdot H_2O$: C, 25.39; H, 5.86; N, 22.21. Found: C, 25.41; H, 5.60; N, 21.68.

A picrate prepared from the sulfate melted at 280–282°; when mixed with streptidine picrate, m. p. 280–282° (dec., microblock), the melting point was unchanged.

A solution containing 200 mg. of streptamine hydrochloride and 400 mg. of cyanamide in 10 ml. of water was refluxed for forty-eight hours. From the reaction mixture 14 mg. (6%) of streptidine sulfate was isolated by the procedure described above.

Concentration of the filtrate after removal of streptidine sulfate gave crystalline streptamine sulfate.

RESEARCH LABORATORIES
MERCK & CO., INC.
RAHWAY, NEW JERSEY RECEIVED JUNE 30, 1948

The Ultraviolet Absorption Spectrum of Gossypol[1]

BY VERNON L. FRAMPTON, JOSEPH D. EDWARDS, JR., AND HENRY R. HENZE

In the formulation of a structure for gossypol, significance was attached to the absorption maximum at approximately 250 millimicrons.[2] We find no evidence for the existence of this maximum in the absorption spectrum of gossypol.

A preparation of gossypol[3] was repeatedly recrystallized from diethyl ether–petroleum ether (30–40°) and finally from chloroform, m. p. sharp at 199°. The absorption spectrum (triangles, Fig. 1) in 95% ethyl alcohol was then determined with a Beckman quartz spectrophotometer. After additional recrystallization from diethyl ether–petroleum ether, from petroleum ether (45–90°) and finally from chloroform, m. p. sharp at 199°, the absorption spectrum (dots, Fig. 1) was again determined.

Nine different gossypol preparations,[4] each from

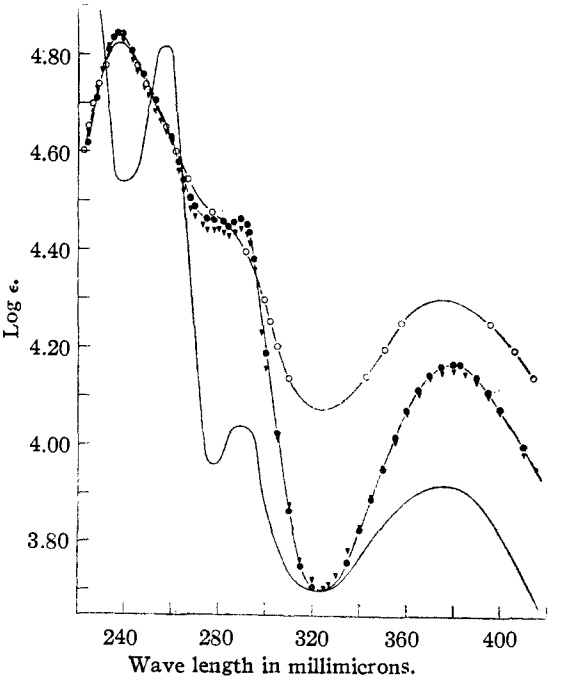

Fig. 1.—● ● ● and ▼ ▼ ▼, gossypol, authors; O O O, gossypol-acetic acid, Grunbaumowna and Marchlewski ref. 4; ——, gossypol, Adams and Kirkpatrick, ref. 1.

(1) Wolfrom and Polglase, THIS JOURNAL, **70**, 1672 (1948).

(1) These several data were drawn from a thesis presented by Joseph Daniel Edwards, Jr. to the Faculty of the Graduate School of the University of Texas in partial fulfillment of the requirements for the Master of Arts degree, January, 1948.

(2) Adams and Kirkpatrick, THIS JOURNAL, **60**, 2180 (1938).

(3) Campbell, Morris and Adams, *ibid.*, **59**, 1723 (1937).

(4) Dr. Boatner kindly supplied two preparations.

a different cottonseed specimen, yielded this same absorption spectrum. This spectrum is in good agreement with that reported[5] for two gossypol-acetic acid preparations (circles, Fig. 1), one of which was supplied by Karrer. We agree with Boatner[6] that gossypol and gossypol-acetic acid have essentially identical absorption spectra.

The absorption spectrum reported herewith is not modified through recrystallization of gossypol from cyclohexane, petroleum ether (45–90°) or diethyl ether–petroleum ether (30–40°).[6]

NOTE ADDED IN PROOF:—The positions of the absorption maxima with three preparations of gossypol, each in a different crystalline form, kindly supplied by Professor Adams after the manuscript was submitted, are in excellent agreement with those reported herewith. In addition these maxima are in agreement with those reported more recently in another journal.[7]

(5) Grunbaumowna and Marchelwski, *Biochem. Z.*, **286**, 295 (1936).

(6) Boatner, *Oil and Soap*, **21**, 11 (1944).

(7) Pons, Murray, O'Connor and Guthrie, *J. Am. Oil Chemists' Soc.*, **25**, 308 (1948).

THE COTTON RESEARCH COMMITTEE OF TEXAS
AUSTIN, TEXAS, AND
THE DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TEXAS
AUSTIN, TEXAS
VERNON L. FRAMPTON
JOSEPH D. EDWARDS, JR.
HENRY R. HENZE
RECEIVED APRIL 9, 1948

Nicotinamide from Nicotinonitrile by Catalytic Hydration

BY ALEXANDER GALAT

The conversion of nicotinonitrile into nicotinamide has been reported in several recent publications. In acid medium, by the conventional sulfuric acid procedure, the yield of nicotinamide was negligible.[1] In alkaline medium in the presence of hydrogen peroxide a yield of 19% has been obtained.[1] A good yield was reported by the use of ammonia under pressure, 73% of the nitrile being converted into nicotinamide and the rest into nicotinic acid.[2] Similarly, high yields were obtained by the use of small amounts of sodium hydroxide or salts producing alkaline solutions.[3]

The fact that the hydration of nitriles into amides is catalyzed by alkalies has been reported by several investigators.[2,4] The disadvantage inherent in the use of alkalies is the formation of acids as by-products with the corresponding decrease in yield and the necessity of separating the products formed. It appeared to us that by the use of a water-insoluble catalyst of basic nature it should be possible to avoid or to minimize the hydrolytic action, while maintaining the catalytic effect due to hydroxyl ions present on the surface of the catalyst. The synthetic resin IRA-400, which has recently become commercially available,[5] seemed well suited for this purpose. It is a high-molecular, water-insoluble quaternary ammonium chloride which on treatment with alkalies is converted into a water-insoluble quaternary ammonium hydroxide. When nicotinonitrile was boiled in aqueous solution in the presence of IRA-400 (base), a rapid conversion into nicotinamide took place in high yield (86–90%). The evaporation of the solution to dryness gave a fairly pure product, m. p. 127–128°, indicating that the amount of by-products was insignificant. On recrystallization from alcohol followed by the concentration of the mother liquors, practically the entire amount was recovered as pure nicotinamide, m. p. 128.5–129.5°.

Procedure.—Twenty grams of moist IRA-400 (the resin, as supplied, contains about 50% of water) was stirred with 100 ml. of a 5% sodium hydroxide solution for ten minutes. The resin was then washed repeatedly with carbon dioxide-free distilled water to remove the salt and the excess alkali. The wet IRA-400 base was added to a warm solution of 10.4 g. (0.1 mole) of nicotinonitrile in 75 ml. of water and the mixture boiled for one hour under reflux. It was then filtered and the resin washed on the filter with hot distilled water. The filtrate was evaporated to dryness and yielded 10.5–11 g. (86–90%) of crude nicotinamide, m. p. 127–128°. The recrystallization from 50 ml. of alcohol with the addition of activated charcoal and the concentration of the mother liquors to a small volume yielded 10–10.5 g. of a white amide m. p. 128.5–129.5°. The remainder, obtained by evaporation to dryness, was somewhat colored and melted unsharply at about 120°.

(1) A. Georg and P. Bachmann, *Helv. Chim. Acta*, **26**, 361 (1943).

(2) C. F. Krewson and J. F. Couch, THIS JOURNAL, **65**, 2256 (1943).

(3) British Patent 563,184 (1944).

(4) *J. Ind. Chem. Soc.*, **12**, 652 (1935); *C. A.*, **30**, 1736 (1936).

(5) A sample was kindly supplied by The Resinous Products and Chemical Co.

61 So. BROADWAY
YONKERS, N. Y.
RECEIVED AUGUST 18, 1948

Meta Rearrangement in the Reaction of *p*-Bromoanisole with Lithium Diethylamide

BY HENRY GILMAN AND ROBERT H. KYLE

Recent studies[1] have shown that *o*-halogenoanisoles and related types undergo rearrangement condensations with alkali amides in liquid ammonia and with lithium dialkylamides in ether to give the *m*-amino- and *m*-dialkylamino ethers, respectively. We have observed that the rearrangement with lithium diethylamide also occurs with *p*-bromoanisole.

$$p\text{-}CH_3OC_6H_4Br + LiN(C_2H_5)_2 \longrightarrow m\text{-}CH_3OC_6H_4N(C_2H_5)_2 + LiBr$$

In addition, there is also formed some of the normal condensation product: *p*-methoxydiethylaniline.

In view of the marked similarity of rearrangements with alkali amides in liquid ammonia and with lithium dialkylamides in ether, it seems likely that there might have been contained in the reaction product of 2-bromodibenzofuran and sodamide[1a] some 3-aminodibenzofuran. Also, it appears that a reaction of *p*-bromodimethylaniline

(1) (a) Gilman and Avakian, THIS JOURNAL, **67**, 349 (1945); (b) Gilman and Nobis, *ibid.*, **67**, 1479 (1945); Gilman, Crounse, Massie, Benkeser and Spatz, *ibid.*, **67**, 2106 (1945).