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]

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(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).

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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°.

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(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.

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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

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(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).

with lithium diethylamide might, like the corresponding reaction with *o*-bromodimethylaniline,[2] give some *m*-N,N-dimethyl-N′,N′-diethylphenylenediamine.

Experimental

Reaction of *p*-Bromoanisole with Lithium Diethylamide.—The lithium diethylamide was prepared in ether by adding, in a nitrogen atmosphere, 0.2 mole of methyllithium to 0.23 mole of diethylamine. To the stirred, pale cream colored mixture which gave a negative color test I[3] was added 0.2 mole of *p*-bromoanisole in 50 cc. of ether. Reaction set in at once and the mixture gradually assumed a red color. After stirring and refluxing for twenty-four hours, the mixture was hydrolyzed by water. Fractionation of the dried ether extracts gave in addition to a recovery of 9.3 g. (25%) of *p*-bromoanisole, 12.2 g. of a mixture of *m*- and *p*-methoxydiethylanilines which is a 34% yield (or 45% based on the *p*-bromoanisole actually used up). The picrate, prepared in 95% ethanol, melted at 142.5–143.5°. An authentic specimen of the picrate of *m*-methoxydiethylaniline melted at 145–146°, and the mixed melting point was 143.5–144.5°.

Anal. Calcd. for $C_{17}H_{20}O_8N_4$: N, 13.7. Found: N, 13.7.

From a second experiment starting with 0.5 mole of *p*-bromoanisole, there were isolated as picrates both the *m*-methoxydiethylaniline, and a lesser amount of *p*-methoxydiethylaniline from the mother liquor of the picrate of *m*-methoxydiethylaniline. The *m*-isomer was again characterized by the picrate, the mixed melting point with an authentic specimen being 143.5–145°. The picrate of *p*-methoxydiethylaniline was obtained as yellow prisms melting at 122–123.5°. The picrate of an authentic specimen melted at 124–125°, and the mixed melting point was 123–124°. The *p*-methoxydiethylaniline[4] was prepared from *p*-anisidine, ethyl iodide and sodium hydroxide.

Anal. Calcd. for $C_{17}H_{20}O_8N_4$: N, 13.7. Found: N, 13.8.

In view of the fact that the critical *m*-methoxydiethylaniline might have formed from *o*- and *m*-bromoanisoles, a special examination of the *p*-bromoanisole was made and the compound was shown to be pure.

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(2) Gilman, Kyle and Benkeser, *ibid.*, **68**, 142 (1946).

(3) Gilman and Schulze, *ibid.*, **47**, 2002 (1925).

(4) Davies, *Bull. soc. chim.*, [5] **2**, 295 (1935).

DEPARTMENT OF CHEMISTRY
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RECEIVED AUGUST 20, 1948

N-Phenacyltetrahydroisoquinoline

BY WILLIAM E. GOODE

During the course of an investigation of certain N-substituted tetrahydroisoquinolines, an apparent error in the melting point of N-phenacyltetrahydroisoquinoline, as reported by Wedekind and Oechslen,[1] was noted. They recorded a melting point of 100–101° for this compound as obtained from the reaction of phenacyl bromide with tetrahydroisoquinoline.

It now appears that when N-phenacylisoquinolinium bromide is reduced catalytically, N-phenacyltetrahydroisoquinoline, m. p. 75°, is obtained. In contrast, the melting point described by Wedekind and Oechslen is suggestive of the isomeric N-phenacyltetrahydroquinoline (needles, m. p. 101–103°,[2] 104°[3]). Indeed, when pure tetrahydroisoquinoline and phenacyl bromide were caused to react under conditions similar to those employed by Wedekind and Oechslen, the product melted at 75–76° and was identical with N-phenacyltetrahydroisoquinoline as obtained by the reduction procedure.

Experimental

N-Phenacylisoquinolinium Bromide.—To 20.0 g. (0.1 mole) of phenacyl bromide in 100 ml. of anhydrous ether was added a solution of 13.0 g. (0.1 mole) of isoquinoline in 50 ml. of anhydrous ether. The solution was allowed to stand at room temperature for twenty-four hours and then filtered. The product was recrystallized from an absolute ethanol–petroleum ether mixture; yield, 28.0 g. (85%); m. p. 201–203°.

Anal. Calcd. for $C_{17}H_{14}BrNO$: Br, 24.35. Found: Br, 24.28.

Reduction of N-Phenacylisoquinolinium Bromide.—Sixteen and four-tenths grams (0.05 mole) of N-phenacylisoquinolinium bromide was hydrogenated at 2 atm. and 60° over 0.2 g. of platinum oxide catalyst during one and one-half hours. After removal of the catalyst, the solution was evaporated to dryness. The residue was dissolved in water and 5% sodium bicarbonate solution was added. The yellow solid which separated was extracted with ether; the ether was evaporated, and the residue was recrystallized from 80% ethanol as faint yellow plates; yield, 7.8 g. (62%); m. p. 75°.

Anal. Calcd. for $C_{17}H_{17}NO$: C, 81.27; H, 6.77. Found: C, 81.30; H, 6.94.

N-Phenacyltetrahydroisoquinoline.—To 9.9 g. (0.05 mole) of phenacyl bromide was added 13.3 g. (0.1 mole) of tetrahydroisoquinoline. The mixture was cooled in running water to keep the temperature in the range 70–80°. The solid residue was extracted with two 100-ml. portions of boiling ether, and the ether was evaporated on the steam-cone. The product recrystallized from 80% ethanol as faint yellow plates; yield, 8.2 g. (66%); m. p. 73–74°. Further recrystallization raised the melting point to 75–76°. This product did not depress the melting point of the N-phenacyltetrahydroisoquinoline as obtained by the reduction procedure.

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(1) Wedekind and Oechslen, *Ber.*, **36**, 1161 (1903).

(2) Meisenheimer, Angerman, Finn and Vieweg, *ibid.*, **57**, 1744 (1924).

(3) Kunckell, *ibid.*, **30**, 576 (1897).

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Derivatives of Nitrodesoxyinositols

BY BEAT ISELIN AND HERMANN O. L. FISCHER

The synthesis of nitrodesoxyinositols by cyclization of 6-nitrodesoxyaldohexoses has been reported from this Laboratory.[1] Further attempts have been made since to convert these compounds to the corresponding inososes by means of the Nef reaction.[2] This method was used successfully for the removal of the nitro substituent in nitrodes-

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(1) J. M. Grosheintz and H. O. L. Fischer, THIS JOURNAL, **70**, 1479 (1948).

(2) J. U. Nef, *Ann.*, **280**, 263 (1894).