Apparently, some of the alcohols used in this work were not of the highest purity, since the 2-propanol, 2-pentanol and 3-pentanol gave weakly cloudy solutions with concd. hydrochloric acid alone. However, the tests for distinguishing the alcohols as developed herein are believed to be reliable, since the amounts of these impurities were small.

The reaction time is lower if the proportion of reagent to alcohol is smaller, or if the temperature is lower. At a six to one ratio 2-butanol gave the test in two minutes at 26° and in seven minutes at 20°; at a four to one ratio, in five and nine minutes, respectively; while at a two to one ratio (approximately mole per mole) the test was given in two and one-half to three hours.

Summary

The lower saturated alcohols may be readily differentiated by the fact that the tertiary alcohols react rapidly with concentrated hydrochloric acid alone to form insoluble liquid chlorides, the secondary react with hydrochloric acid–zinc chloride mixture within five minutes at 26°, while the primary alcohols react with neither. Allyl alcohol resembles a secondary alcohol.

The presence of a secondary or a tertiary alcohol in another compound may be demonstrated by these reagents, provided the concentration of the alcohol is not too low.

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SYNTHESIS OF N-PHENYLPYRROLIDINE AND N-HEXAHYDROPHENYLPYRROLIDINE

BY LYMAN C. CRAIG WITH R. M. HIXON

In a study of the insecticidal action of nicotine and related compounds, pyrrolidine and a series of its derivatives were desired. The methods reported in the literature[1] for the preparation of pyrrolidine are all difficult and tedious. During the progress of the studies reported below, Anderson and McElvain[2] published their work on the catalytic reduction of pyrrole using specially purified pyrrole, glacial acetic acid, a large quantity of platinum-oxide platinum black catalyst and shaking for four to five days.

The catalytic reduction is much more convenient with the platinum-oxide platinum black catalyst using as a solvent absolute alcohol contain-

[1] Ciamician and Magnaghi, Ber., 18, 2079 (1885); Ladenburg, ibid., 19, 780 (1886); 20, 2215 (1887); Wohl, Schafer and Theile, ibid., 38, 4157 (1906); Gabriel, ibid., 42, 1254 (1912); Keil, ibid., 59, 2816 (1926); Putochin, ibid., 55, 2742 (1922); Willstätter and Hatt, ibid., 45, 1477 (1912); Willstätter and Waldschmidt, ibid., 54, 125 (1921); Hess, ibid., 46, 3113 (1913).

[2] Anderson and McElvain, THIS JOURNAL, 51, 887 (1929).

ing a slight excess over an equivalent of hydrogen chloride. With the latter solvent 0.2 g. of catalyst can be used for three successive reductions of 10-cc. portions of pyrrole, the reduction being complete in six hours and the yield being 80% of the theoretical.

A mixture of α- and β-methylpyrroles was prepared according to the method reported by Anderson and McElvain. Reduction of these compounds by the above method was as unsuccessful as in glacial acetic acid. A small amount of reduction did take place but the basic oil obtained in recovery proved to be pyrrolidine, which indicated the presence of pyrrole in the fraction taken. These compounds are more unstable and go over to pyrrole red derivatives much more easily than does pyrrole.

In the N-substituted pyrrolidine series, the aliphatic derivatives can be prepared by treating the free base with RX. The aromatic derivatives are more difficult to prepare. It was expected that N-phenylpyrrole could be selectively reduced in alcohol and hydrochloric acid. This is not the case for under these conditions the benzene ring apparently reduces as easily as the pyrrole ring. Five moles of hydrogen are rapidly absorbed (two and one-half hours) and a constant boiling tertiary base is obtained which is N-hexahydrophenylpyrrolidine. If the reduction is stopped when two moles of hydrogen have been absorbed, some unreduced N-phenylpyrrole and a base which does not have a constant boiling point (206–247°) are the products obtained. The identity of the N-hexahydrophenylpyrrolidine was proved by condensing bromocyclohexane with pyrrolidine.

In attempting to prepare the N-phenylpyrrolidine, several other methods were tried without success. LeSueur[3] has prepared the compound N-phenyl-α,α'-dicarboxypyrrolidine. This compound evolves carbon dioxide when subjected to dry distillation under reduced pressure. Small amounts of N-phenylpyrrolidine are produced but the method cannot be recommended for purposes of preparation.

Piperidine when heated in a sealed tube with bromobenzene to 250–260° gives a small yield of N-phenylpiperidine.[4] The analogous synthesis fails with pyrrolidine although reaction takes place at 220°. Apparently ring cleavage takes place under these conditions since a very stable amine was isolated with too high a ratio between hydrogen and carbon to permit of its containing a benzene nucleus.

The N-phenylpyrrolidine can be prepared with satisfactory yields by condensing aniline with tetramethylene chloride.

Experimental

Preparation of Pyrrole.—The method of preparation used was that of Schwanert.[5] Five hundred grams of mucic acid was converted to the neutral ammonium salt with

[3] LeSueur, *J. Chem. Soc.*, **95**, 273 (1909).

[4] Lellmann and Geller, *Ber.*, **21**, 2279 (1888).

[5] Schwanert, *Ann.*, **116**, 278 (1860).

excess ammonia and subjected to dry distillation in an iron retort. The pyrrole was extracted from the distillate with ether, the ether evaporated off and the residue distilled. Fifty cc. of a fraction boiling at 125 to 130° was obtained which is 32% of the theoretical yield. By use of glycerol according to the method of Goldschmidt,[2,6] a higher yield is obtained (40–50% of the theoretical) but dry distillation is much less trouble and considering the relative price of mucic acid and glycerol is to be preferred.

Reduction of Pyrrole to Pyrrolidine.—The platinum-oxide platinum black catalyst was prepared according to the method of Adams and Shriner.[7] The shaking machine was a modification of that ordinarily used in that the connections and tubing were all metal with a rubber gasket for the bottle. A pressure of approximately 90 lb. was used. Pyrrole not freshly distilled and colored reduced slowly if at all. Commercial samples freshly distilled reduced as easily as the samples freshly prepared from ammonium mucate. The pyrrole was dried over anhydrous calcium chloride before the final distillation.

To 100 cc. of absolute alcohol, 0.2 g. of catalyst, 10 cc. of pyrrole and a slight excess over an equivalent of concentrated hydrochloric acid (6 cc.) were added. The pyrrole reduced the catalyst at once; previous reduction of the catalyst before addition of pyrrole did not increase the rate of reduction. Absolute alcohol containing a calculated amount of dry hydrogen chloride did not increase the rate of reduction, although there is less pyrrole red formed. If 95% alcohol is used the reduction is slower and there is considerable pyrrole red formed. The reduction was completed in about six hours. The catalyst was allowed to settle and the reduction products decanted. To the catalyst fresh portions of alcohol, acid and pyrrole were added. A third reduction could also be run on the same catalyst without seriously impairing the efficiency. No occasion was had to run more than three reductions on the same catalyst but there appeared to be no tendency for it to become poisoned if good pyrrole was used. After decantation, the alcohol was removed by evaporation under reduced pressure, the unreduced pyrrole was extracted with ether, solid potassium hydroxide was added to the solution of the salt until an oil separated and the oil finally dried over solid potassium hydroxide. It distilled at 86–88°, small residues of a high-boiling fraction being left behind. Derivatives showed the constant boiling fraction to be pyrrolidine.

Preparation of N-Phenylpyrrole.—The method of preparation was essentially that of Feist.[8] Two hundred grams of mucic acid was added with constant stirring to an excess of aniline heated to a temperature just below boiling. This mixture was then placed in an iron retort and heated until no more liquid came over. The distillate was extracted with ether and the aniline removed by washing with a dilute solution of hydrochloric acid. After evaporating off the ether, the residue was distilled under reduced pressure; yield, 25%. As N-phenylpyrrole colors slightly on standing, it was recrystallized from 95% alcohol immediately before use. It crystallized in lustrous leaves, melted at 60–61° and boiled at 234°, as reported in the literature.

Reduction of N-Phenylpyrrole to N-Hexahydrophenylpyrrolidine.—A 10-g sample was dissolved in 100 cc. of absolute alcohol, a slight excess over one equivalent of concd. hydrochloric acid and 0.2 g. of catalyst were added. The reduction was rapid, being complete in two and one-half hours, 5 moles of hydrogen being absorbed. The reaction mixture was colorless and on recovery in the same way as with pyrrolidine, a constant boiling oil (209–211°) was obtained, the yield being quantitative. It did not react with phenyl isothiocyanate. It gave a picrate which on repeated crystallization from alcohol

[6] Goldschmidt, Z. Chem., 280 (1867); Khotinsky, Ber., 42, 2506 (1909).

[7] Adams and Shriner, THIS JOURNAL, 45, 2171 (1923).

[8] Feist, Ber., 35, 1655 (1902).

melted at 163–164°. The hydrochloride was hygroscopic and not suitable for a melting point determination.

Stopping the reduction when two moles of hydrogen were absorbed gave 6 cc. of an oil that did not show a constant boiling point (206–247°). It was probably a mixture of N-phenyl- and N-hexahydrophenylpyrrolidine. Separation by chemical means failed and all attempts at fractional crystallization of picrates gave only the N-hexahydro derivative.

Proof of Structure of N-Hexahydrophenylpyrrolidine.—Six cc. of pyrrolidine and an excess of bromocyclohexane were refluxed for two hours. Two layers were present, showing that a reaction had taken place. The base when recovered in the usual way with solid potassium hydroxide gave a small amount of a high-boiling fraction. A picrate of this recrystallized from alcohol melted at 163°. Mixed melting points proved its identity with that from the reduction product of N-phenylpyrrole.

Preparation of N-Phenylpyrrolidine.—To 8 g. of tetramethylene chloride[9] two equivalents of freshly distilled aniline were added and the mixture kept at 100° for four hours. On cooling, the mixture became solid with crystals. A dilute solution of hydrochloric acid was added and the unreacted tetramethylene chloride removed by extracting with ether. The free base was liberated by strong caustic and the two layers separated. The excess aniline was removed from the oily layer with benzenesulfonyl chloride in dilute alkali. The tertiary amine fraction was extracted with ether and precipitated with dry hydrogen chloride. The free base was then recovered and dried with potassium hydroxide. It had a slight red color and did not react with acetyl chloride. When the free base was subjected to distillation at atmospheric pressure, the boiling point did not remain constant and a colorless oil distilled over that reacted vigorously with acetyl chloride. Evidently the pyrrolidine ring must partially rupture during distillation. The undistilled base formed a chloroplatinate that crystallized from alcohol acidified with hydrochloric acid in yellow needles and melted with decomposition at 174–175° varying slightly with the rate of heating.

Anal. Calcd. for $(C_{10}H_{13}N)_2 \cdot H_2PtCl_6$: Pt, 27.7. Found: Pt, 27.6, 27.7.

A crystalline picrate could not be obtained for the N-phenylpyrrolidine. On addition of an ether solution of oxalic acid to an ether solution of the base, a white precipitate formed that could be recrystallized from a mixture of acetone and petrolic ether; m. p. 156°. The only oxalate that corresponds to the analysis is the tetroxalate with $1/2$ molecule of water of crystallization.

Anal. Calcd. for $C_{10}H_{13}N \cdot (COOH)_4 \cdot 1/2H_2O$: C, 49.9; H, 5.36. Found: C, 50.00, 50.10; H, 5.46, 5.52.

Dry Distillation of α,α'-Dicarboxy-N-phenylpyrrolidine.—This compound could be best prepared by the method given by LeSueur. On dry distillation of α,α'-dicarboxy-N-phenylpyrrolidine under reduced pressure, an oil with a slight red color distilled over. It gave an oxalate that corresponded with that of the N-phenylpyrrolidine reported above. Mixed melting points showed the oxalates to be identical.

Reaction of Pyrrolidine with Bromobenzene.—Ten cc. of pyrrolidine was heated with an equivalent of bromobenzene in a sealed tube at 220° for six hours. Experiment had shown this to be the minimum temperature at which reaction takes place. Two layers had separated in the tube and on recovery and distillation 6 cc. of a very stable oil (b. p. 250 to 256°) was obtained. It reacted vigorously with acetyl chloride but a crystalline derivative could not be isolated. It gave a non-hygroscopic hydrochloride when dry hydrogen chloride was passed through its ether solution. This was recrystallized from absolute alcohol and analyzed.

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[9] Prepared from pyrrolidine according to the method of Braun and Beschke, *Ber.*, **39**, 4119 (1906).

Anal. Found: C, 52.8, 53.1; H, 10.02, 10.05; Cl, 26.43, 26.46.

The ratio of carbon to hydrogen is too high for this compound to contain a benzene ring. When shaken with water the free base formed leaf-like crystals that melted slightly above room temperature. It also gave a picrate with a melting point of 155°.

Summary

It has been shown that pyrrole can be reduced easily to pyrrolidine in absolute alcohol–hydrochloric acid solution This method is more rapid and convenient than the glacial acetic acid method.

Reduction of N-phenylpyrrole yields N-hexahydrophenylpyrrolidine. The reduction cannot be stopped at the intermediate N-phenylpyrrolidine.

Bromobenzene does not react with pyrrolidine as with piperidine. Pyrrolidine is less stable and rupture of the ring appears to take place.

N-phenylpyrrolidine can be prepared in satisfactory yields by condensing tetramethylene chloride with aniline. The compound can also be prepared by dry distillation under reduced pressures of α,α'-dicarboxy-N phenylpyrrolidine but the yields are very low.

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THE FATTY ACIDS ASSOCIATED WITH WHEAT STARCH

BY LEO LEHRMAN

The occurrence of fatty acids combined with carbohydrate in several natural starches is quite well known.[1] In two of these starches, corn and rice, the fatty acids have been determined qualitatively and quantitatively.[2] A review of the literature revealed that there is very little known about the non-carbohydrate constituents, if any, of wheat starch. Should fatty acids be found combined with carbohydrate in wheat starch, it is logical to assume that there are at least two components, α- and β- amylose,[3] comparable to those found in corn and rice starch and that the fatty acids constitute part of the α-amylose component.[3]

The work was accordingly carried out first with the object of establishing whether or not fatty acids occurred combined with carbohydrate. After this had been shown, the next thing was to determine the total amount of fatty material, "fat by hydrolysis,"[1b] which would give a means of comparison with other starches. A qualitative and quantitative analysis by means of iodine numbers of the fatty acids[2] present in the "fat by

[1] (a) Sostegni, *Gazz. chim. ital.*, 15, 376 (1885); (b) Taylor and Nelson, THIS JOURNAL, 42, 1726 (1920); (c) Aoi, *J. Chem. Soc. Japan*, 44, 755 (1923).

[2] (a) Taylor and Lehrman, THIS JOURNAL, 48, 1739 (1926); (b) Lehrman, *ibid.*, 51, 2185 (1929).

[3] Taylor and Iddles, *Ind. Eng. Chem.*, 18, 713 (1926).