The author is indebted to Dr. G. E. Hilbert, Dr. T. B. Johnson and Dr. P. A. Levene for the samples of the compounds examined, to Dr. F. F. Heyroth for lending the graphs of his absorption curves to facilitate replotting them for comparison, and to Dr. Emma P. Carr for her help throughout the investigation.

Summary

1. The absorption spectra of uracil, 1-methyluracil, 3-methyluracil, 1,3-dimethyluracil, 1,3-diethyluracil, 1-methyl-3-ethyluracil, 1-methyl-3-benzyluracil, 1-benzyl-3-methyluracil, 1,2-dihydro-2-keto-1-methyl-4-methoxypyrimidine, 1,2-dihydro-2-keto-1-methyl-4-ethoxypyrimidine, 1,2-dihydro-2-keto-1-tetraacetylglucosido-4-methoxypyrimidine, 2,4-dimethoxypyrimidine, 2,4-diethoxypyrimidine, 3-benzyl-5-methyluracil and 5,6-dihydrouracil have been determined for the region 32,000 to 46,000 cm.$^{-1}$.

2. The absorption curves for these compounds indicate that the absorption spectra depend upon the position of the substituent in the molecule and are only slightly dependent upon the nature of the substituent.

3. From the spectrographic evidence it appears that the tautomeric group in the 1,2-position of uracil in alcohol solution, and by analogy in hydantoin, exists predominantly in the lactim form, that in the 3,4-position in the lactam form.

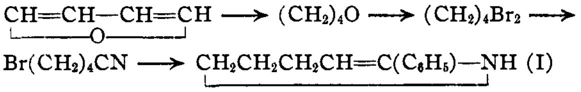
SOUTH HADLEY, MASS. RECEIVED JULY 13, 1934

[CONTRIBUTION FROM THE WALKER LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

The Formation of Alpha-Phenyltetrahydropyridine by the Action of Phenylmagnesium Bromide on Delta-Bromovaleronitrile[1]

BY JOHN B. CLOKE AND OSBORN AYERS

Some time ago a method was described for the synthesis of α-substituted pyrrolines by the action of Grignard reagents on γ-chlorobutyronitrile.[2] The present communication describes a method for the formation of α-substituted tetrahydropyridines by an extension of the same general reaction. Our α-phenyltetrahydropyridine (I) was obtained by means of the following transformations



$$\underbrace{CH{=}CH{-}CH{=}CH}_{O} \longrightarrow (CH_2)_4O \longrightarrow (CH_2)_4Br_2 \longrightarrow$$

$$Br(CH_2)_4CN \longrightarrow \underbrace{CH_2CH_2CH_2CH{=}C(C_6H_5){-}NH}_{} \text{ (I)}$$

Experimental Part

Reduction of Furan with the Raney Catalyst.—A mixture of 10 g. of nickel catalyst,[3] 100 g. of *n*-butyl alcohol and 100 g. of furan[4] was heated to 50° in an electrically heated bottle of a Burgess–Parr outfit and shaken with hydrogen until the pressure became practically constant. Distillation of the filtered solution gave, as a rule, 80% yields of the tetrahydrofuran of b. p. 63–67°.

1,4-Dibromobutane.—A part of the tetramethylene dibromide was obtained by the method of Smyth and Walls[5] and part as follows. A weight of 39 g. of red phosphorus was placed in a flask, which was immersed in ice water, and provided with a stirrer, condenser and dropping funnel; 400 g. of bromine was then added slowly to the well-stirred mixture, and this was followed by 54 g. of tetrahydrofuran, when the mixture was heated on a water-bath for half an hour. The separation and purification of the dibromide in the usual way gave a 53% yield.

δ-Bromovaleronitrile was prepared by the addition of 39 g. of potassium cyanide in 40 cc. of water to a boiling and well-stirred solution of 108 g. of 1,4-dibromobutane in 175 cc. of alcohol. The mixture was refluxed for about three hours, when the nitrile was purified by a procedure similar to that described by Allen[6] for γ-chlorobutyronitrile. The δ-bromovaleronitrile, which was obtained in a 33% yield, boiled at 110–111° at 11 mm. It possessed a density d_4^{20} of 1.3989 and a refractive index n_D^{20} of 1.47811, which correspond to a molecular refractivity (n^2) of 32.83 as compared with the calculated value of 32.75.

Anal. Calcd. for C_5H_8NBr: N, 8.64. Found: N, 8.72, 8.68.

α-Phenyltetrahydropyridine.—A Grignard reagent was prepared from 4.8 g. of magnesium, 100 cc. of ether and 31 g. of bromobenzene. To this reagent 16.1 g. of the δ-bromovaleronitrile in ether was added during the course of a half hour. The stirring and refluxing were then continued for a two and a half hour period, when the cooled solution was added slowly from a separatory funnel to 250 cc. of liquid ammonia, which was contained in a Dewar flask. When the ammonia had evaporated, the residue was extracted with ether. The extract was evaporated to 50 cc. and treated with a slight excess of aqueous hydro-

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(1) From a thesis presented by Osborn Ayers to the Rensselaer Polytechnic Institute in partial fulfilment of the requirements for the degree of Chemical Engineer.

(2) Cloke, THIS JOURNAL, **51**, 1174 (1929).

(3) Covert and Adkins, *ibid.*, **54**, 4116 (1932).

(4) Wilson, "Organic Syntheses," Vol. VII, 1927, p 40.

(5) Smyth and Walls, THIS JOURNAL, **54**, 2262 (1932).

(6) Allen, "Organic Syntheses," Vol. VIII, 1928, p. 52.

chloric acid. The aqueous solution was then extracted with ether and steam distilled for some time. At this point sodium hydroxide was added in excess and the α-phenyltetrahydropyridine was removed by steam distillation. Extraction of the distillate gave a 48% yield of the compound, which was characterized by its hydrochloride (m. p. 86–87°), picrate (m. p. 180–181°) and chloroplatinate, as described by Gabriel.[7]

α-Phenyltetrahydropyridine chloroplatinate was precipitated from an alcoholic solution of the hydrochloride by the addition of alcoholic chloroplatinic acid. According to Gabriel the compound sinters at about 190°, foams at 191–192°, then resolidifies, softens again and gives an almost clear red-brown melt at 202°. In the case of our compound the final melting did not appear to take place until 210–211°.

Anal. Calcd. for $C_{22}H_{28}N_2Cl_6Pt$: Pt, 26.80. Found: Pt, 26.52, 26.97.

Summary

A method has been described for the synthesis of α-phenyltetrahydropyridine by the action of phenylmagnesium bromide on δ-bromovaleronitrile, which may be obtained by the action of potassium cyanide on 1,4-dibromobutane. The latter compound may be prepared by the action of phosphorus pentabromide on tetrahydrofuran, which, in turn, may be obtained by the hydrogenation of furan, in the presence of Raney catalytic nickel.

Other communications will follow on the synthesis of other α-, α,β-, etc., substituted tetrahydropyridines, their hydrogenation products and related derivatives.

TROY, N. Y. RECEIVED JULY 14, 1934

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[7] Gabriel, *Ber.*, **41**, 2010 (1908).

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, NO. 139]

The Action of Phosphorus Pentahalides and Thionyl Chloride on Some Saturated and Unsaturated 1,4-Diketones and 2,5-Diphenylfurans

BY ROBERT E. LUTZ AND FRANK N. WILDER

The action of phosphorus pentachloride on various saturated and unsaturated 1,4-diketones and diphenylfurans has been mentioned in previous communications, and it is the object of this report to collect, extend and correlate the data. The end-product of most of these reactions is the known 2,5-diphenyl-3,4-dichlorofuran (II).[1]

Hydrogens or acetoxy groups in the beta positions in the diphenylfurans are easily replaced by halogens on short heating with phosphorus pentahalides. Diphenylfuran (I) reacts with phosphorus pentachloride at 25–40° giving the monochlorofuran III which under more drastic conditions at 100° is converted into the dichlorofuran II. Diphenylacetoxyfuran V reacts at 25–40° through replacement of the one beta hydrogen with chlorine giving the chloroacetoxyfuran VI; the acetoxy group of the latter is itself replaced with chlorine under more drastic conditions at 100°. The acetoxy groups of 2,5-diphenyldiacetoxyfuran IV are also replaceable, stepwise; the first may be replaced by means of acetyl chloride and sulfuric acid.[2] These reactions are illustrated in Diagram 1.

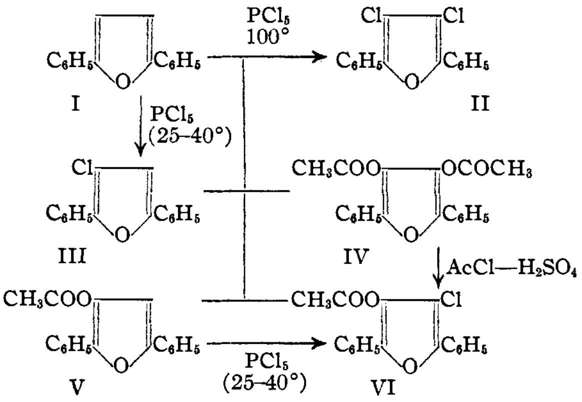

DIAGRAM 1.

The replacement of aromatic hydrogen with halogen by means of phosphorus pentachloride is not a common reaction; it has been accomplished in the case of anisole.[3] The substitution in the furan series occurs with great ease, even in the absence of activating substituents such as methoxyl, hydroxyl and acetoxy. The furan nucleus is therefore to some extent comparable in activity with the benzene nucleus of anisole, a phenomenon in accord with the so-called super-aromatic character of the furan nucleus.[4] The reactions

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[1] *Cf.* (a) Conant and Lutz, THIS JOURNAL, **47**, 881 (1925); (b) Lutz and Wilder, *ibid.*, **56**, 978 (1934).

[2] Lutz and Wilder, *ibid.*, **56**, (a) 1980, (b) 1987 (1934).

[3] Henry, *Ber.*, **2**, 711 (1869); Hayashi, *J. prakt. Chem.*, **123**, 306 (1929).

[4] *Cf.* Gilman and Towne, *Rec. trav. chem.*, **51**, 1054 (1932); Gilman and Calloway, THIS JOURNAL, **55**, 4197 (1933); Gilman and Young, *ibid.*, **56**, 464 (1934).