3.3 e. u. Parks and Huffman[8] predict a value of 55.8 e. u.

Summary

The thermal decomposition of *t*-butyl iodide was found to be heterogeneous; however, a successful study was made of the equilibrium involved, *e. g.*

$$(CH_3)_3CI \rightleftharpoons (CH_3)_2C{=}CH_2 + HI$$

The heat of the reaction in the temperature range of 408 to 464°K. was found to be 19,150 ± 1000 cal. endothermic. The standard entropy of the liquid iodide was calculated as $S^0_{298} = 60.2 \pm 3.3$ e.u. and the free energy of formation of the gaseous iodide as $\Delta F^0_{298} = 6260$ cal.

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[8] Parks and Huffman, "Free Energy of Some Organic Compounds," Chemical Catalog Co., N. Y., 1932, p. 210.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

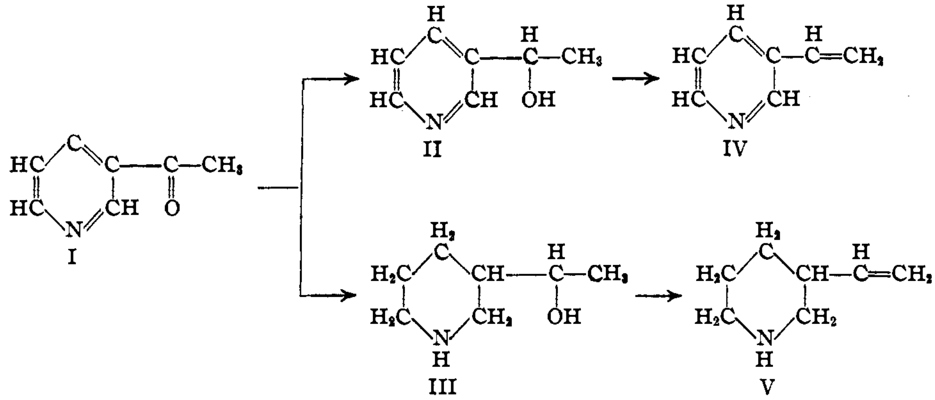
β-Vinylpyridine and β-Vinylpiperidine

BY H. A. IDDLES, E. H. LANG AND D. C. GREGG

β-Vinylpyridine and β-vinylpiperidine are of interest because of the structural relationship of the latter to the meroquinine structure and to that of the normal cinchona alkaloids.[1] Previously α-vinylpyridine,[2,3] γ-vinylpyridine,[4] α-vinylpiperidine[2] and β-vinylpiperidine[5] have been prepared.

In this study β-vinylpyridine has been prepared and characterized and β-vinylpiperidine has been prepared by a different synthesis and further characterized.

β-Acetylpyridine (I), prepared by the sequence of reactions developed by Strong and McElvain,[6] was reduced with hydrogen and Adams platinum oxide catalyst to β-pyridylmethylcarbinol (II).[6] In separate runs, after the addition of one molecular equivalent of hydrogen, hydrochloric acid was added, and the reduction continued further, producing both β-ethylpiperidine and β-piperidylmethylcarbinol (III).[6] These products were separated by fractional distillation. The secondary carbinols were dehydrated successfully to yield the corresponding vinyl derivatives (IV and V) which were characterized by the formation of solid salts. The properties of the β-vinylpiperidine prepared by the dehydration of the secondary alcohol (III) agreed with those recorded in a previous preparation of the compound[5] from the primary alcohol, 2-β-piperidylethanol-1.



Experimental

β-Acetylpyridine.—β-Acetylpyridine hydrochloride prepared according to the directions of Strong and McElvain,[6] was dissolved in water and treated with an excess of a saturated solution of sodium carbonate solution. The free base was recovered as an oily layer and by ether extraction. After drying and removal of ether, the free base was distilled at 100–110° (10–15 mm.). The average yield was 95–96%.

β-Pyridylmethylcarbinol, b. p. 135–140° (10–15 mm.), was prepared as described by Strong and McElvain[6] with an average yield of 75–90%.

β-Piperidylmethylcarbinol, distilling at 130–135° (10–15 mm.), was produced with an average yield of

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[1] Henry, Solomon and Gibbs, *J. Chem. Soc.*, 593 (1937).

[2] Ladenburg, *Ber.*, **22**, 2585 (1889).

[3] Einhorn, *Ann.*, **265**, 229 (1891).

[4] Meisenheimer, *ibid.*, **420**, 208 (1919).

[5] Merchant and Marvel, THIS JOURNAL, **50**, 1197 (1928).

[6] Strong and McElvain, *ibid.*, **55**, 816 (1933).

40% and solidified on cooling. It was used later as the mixture of the two diastereoisomeric forms which were characterized separately by Strong and McElvain.[6]

β-Vinylpyridine.—Five grams of the β-pyridylmethylcarbinol was treated with 6 g. of thionyl chloride, with slow addition and cooling. To the reaction mixture 200 ml. of a saturated solution of potassium hydroxide in alcohol was added and the whole solution refluxed for one hour. Then 100 ml. of water and 25 ml. of a 50% solution of potassium hydroxide were added and the solution steam distilled. The free base may be extracted from the distillate with ether and gave yields averaging 18–20% of the theoretical. The β-vinylpyridine was a light-yellow liquid which polymerized at ordinary temperatures and very rapidly upon heating. The free base was soluble in ether, partially soluble in alcohol and very slightly soluble in water. It decolorized bromine water and potassium permanganate solution. A small sample, when oxidized by means of nitric acid yielded nicotinic acid, m. p. 228–229°, proving the presence of the side-chain in the β-position of the pyridine ring. Likewise a sample subjected to reduction with hydrogen, platinum oxide and hydrochloric acid gave as the product β-ethylpiperidine hydrochloride, m. p. 140–141°.

As an alternative method of dehydration, 5 g. of β-pyridylmethylcarbinol was treated with 30 g. of phosphorus pentoxide. Two hundred ml. of dry xylene was added and the mixture refluxed in an oil-bath for two to three hours. After cooling, excess phosphorus pentoxide was decomposed by the addition of ice. The water layer was separated, made strongly alkaline with sodium hydroxide and steam distilled. The product could be obtained by extraction with ether or by the formation of the picrate salt.

Derivatives of β-Vinylpyridine.—The fresh steam distillate obtained in the preparation of β-vinylpyridine was heated with a hot concentrated alcoholic solution of picric acid. Upon cooling in an ice-bath β-vinylpyridine picrate separated as yellow crystals. They were recrystallized from benzene and gave a m. p. of 143–144°. The picrate salt was insoluble in absolute alcohol, ether and water. The salt gave a good test for unsaturation, decolorizing bromine water and potassium permanganate solution.

Anal. Calcd. for $C_7H_7N{\cdot}C_6H_2(NO_2)_3OH$: N, 16.77. Found: N, 16.32, 16.15.

The β-vinylpyridine hydrochloride was obtained by passing dry hydrogen chloride into the free base. A white solid was obtained which was insoluble in ether, water and cold absolute alcohol. It was recrystallized from hot absolute alcohol and melted at 114–115°.

Anal. Calcd. for $C_7H_7N{\cdot}HCl$: Cl, 25.09. Found: Cl, 24.96, 24.99.

An absolute alcoholic solution of the free base was treated with an equivalent of an alcoholic solution of mercuric chloride. Fine, white crystals separated and after three purifications with absolute alcohol gave a m. p. of 145–150°. From the analysis this product corresponds to a 1:1 addition product[7,8] rather than the mercuric chloride–hydrochloride double salt.

Anal. Calcd. for $C_7H_7N{\cdot}HgCl_2$: Hg, 53.26. Found: Hg, 52.64, 52.70.

An absolute alcoholic solution of the free base was treated with chloroplatinic acid dissolved in absolute alcohol. The light orange chloroplatinate separated and was washed with hot absolute alcohol to remove any hydrochloride. It melted at 158–160°.

Anal. Calcd. for $(C_7H_7N)_2{\cdot}H_2PtCl_6$: Pt, 31.48. Found: Pt, 31.65, 31.74, 31.49.

An absolute alcoholic solution of chloroauric acid was added to an alcoholic solution of β-vinylpyridine. Fine yellow crystals of the chloroaurate separated and were purified by recrystallization from hot alcohol, m. p. 138–140°.

Anal. Calcd. for $C_7H_7N{\cdot}HAuCl_4$: Au, 44.30. Found: Au, 44.43, 44.50.

β-Vinylpiperidine.—A mixture of 8 g. of β-piperidylmethylcarbinol, 4 g. of glacial acetic acid and 16 g. of concentrated sulfuric acid was heated in a bath at 180° for two hours. The mixture was then made strongly basic with sodium hydroxide, steam distilled and the product recovered by ether extraction. Upon evaporation and distillation 0.8 g. of material having a b. p. of 150–155° was obtained. The product is much more stable than the corresponding pyridine derivative. In the previous preparation[5] of this compound by dehydration of the primary alcohol, 2-β-piperidylethanol-1, a b. p. of 152–155° was recorded.

In further characterizing the product an alcoholic solution of the free base was treated with alcoholic picric acid to form the yellow, crystalline picrate. After recrystallizing from benzene it melted at 162–164°.

Anal. Calcd. for $C_7H_{13}N{\cdot}C_6H_2(NO_2)_3OH$: N, 16.47. Found: N, 16.45, 16.01.

The chloroplatinate was formed and found to melt at 221–225°, agreeing with earlier values.[5]

Summary

1. β-Vinylpyridine has been prepared by the dehydration of β-pyridylmethylcarbinol and has been characterized by the formation of five salts.

2. β-Vinylpiperidine has been prepared by a new synthesis, involving the dehydration of β-piperidylmethylcarbinol. In properties the product agreed with those previously recorded in the literature.

DURHAM, N. H. RECEIVED JULY 20, 1937

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[7] Lang, *Ber.*, **21**, 1586 (1888).

[8] Schroeder, *Z. anorg. Chem.*, **44**, 9 (1905).