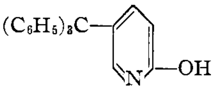
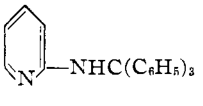
sulfuric acid. This behavior indicated that N-alkylation had occurred to produce V or VI. The attempted condensation of triphenylcarbinol with 2-aminopyridine using larger amounts of acidic catalyst gave only dark tarry products which could not be crystallized.


IV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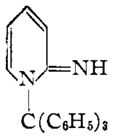
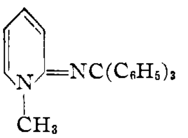
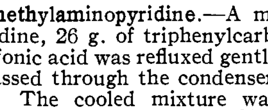

VI

The product obtained was shown to be 2-triphenylmethylaminopyridine (V) by reaction with methyl iodide to yield N-methyl-2-pyridonetriphenylmethylimide(VII), the latter also being obtained in low yield by the reaction of N-methyl-2-pyridoneimide(I) with triphenylchloromethane. Thus, triphenylcarbinol reacts differently than do the methyl and benzyl halides.


VII

It is noteworthy that the free bases having the quinoid structure, as shown by I, III and VII, have a yellow color. The color is lost upon preparing the hydrochlorides. Since color is lacking in N-alkyl-2-pyridones (VIII), the color in the imide-type structures may be because the latter do not have as great a tendency to exist in a "zwitterion" structure as do the N-alkyl-2-pyridones as shown by IX. The zwitterion structure results in the loss of the quinoid structure and the attendant color.


VIII IX

Experimental

2-Triphenylmethylaminopyridine.—A mixture of 40 g. of 2-aminopyridine, 26 g. of triphenylcarbinol and 0.1 g. of *p*-toluenesulfonic acid was refluxed gently for two hours, steam being passed through the condenser to remove the water formed. The cooled mixture was recrystallized from 90% ethanol to yield 18.2 g. (54%) of light cream-colored crystals. Recrystallization from 95% ethanol gave glistening white crystals, m. p. 152–153° (cor.).

Anal. Calcd. for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.57; H, 6.02; N, 8.18.

Cleavage of 2-Triphenylmethylaminopyridine. (A) **By Nitrous Acid.**—A suspension of 4.97 g. of powdered 2-triphenylmethylaminopyridine in 25 ml. of concd. hydrochloric acid was stirred at room temperature as a solution of 1.1 g. of sodium nitrite in 15 ml. of water was dropped in over a period of fifteen minutes. The mixture was stirred for one hour after the addition was complete. The white product was then collected on a filter and washed well with water. The yield was 3.50 g. (91%). Two recrystallizations from 95% ethanol gave pure triphenylcarbinol, m. p. 162°, as shown by the melting point of a mixture with an authentic sample.

(B) **By Sulfuric Acid.**—Upon dissolving 2-triphenylmethylaminopyridine in concd. sulfuric acid and pouring the solution into water, a nearly quantitative yield of triphenylcarbinol resulted.

N-Methyl-2-pyridonetriphenylmethylimide. (A) **From 2-Triphenylmethylaminopyridine.**—A solution of 1 g. of 2-triphenylmethylaminopyridine and 5 ml. of methyl iodide in 20 ml. of absolute ethanol was refluxed for five hours and then diluted with 50 ml. of petroleum ether. The precipitate of hydroiodide was collected on a filter and washed well with petroleum ether. It was then dissolved in 50 ml. of a 3:2 mixture of hot ethanol and water and the solution made basic with dilute aqueous sodium hydroxide. The mixture was warmed and stirred a few minutes and then cooled overnight in the ice-box. The yellow crystalline precipitate was collected on a filter and washed well with 50% ethanol. The yield was 0.52 g. (50%). Two recrystallizations from 95% ethanol gave yellow crystals, m. p. 151–152° (cor.). A melting point of this compound mixed with 2-triphenylmethylaminopyridine gave a large depression.

Anal. Calcd. for $C_{25}H_{22}N_2$: C, 85.67; H, 6.33; N, 8.00. Found: C, 85.84; H, 6.46; N, 7.98.

(B) **From N-Methyl-2-pyridoneimide.**—To a suspension of 2.36 g. of the hydroiodide of N-methyl-2-pyridoneimide[1] in 50 ml. of hot benzene was added 5 ml. of 10% aqueous sodium hydroxide and the mixture quickly shaken. The benzene layer was separated, dried over anhydrous sodium sulfate and the benzene removed on the steam-cone. To the green residual oil was added 2.8 g. of triphenylchloromethane and the mixture heated on the steam-cone one hour. Then 30 ml. of benzene was added and the mixture boiled a few minutes. After cooling overnight in the ice-box, the precipitate of hydrochloride was collected on a filter, washed well with benzene and dried. It was then taken up in 10 ml. of boiling ethanol and the solution made basic with the addition of 10% aqueous sodium hydroxide. After cooling in the ice-box, 0.20 g. of dark yellow crystalline material was collected on a filter. Recrystallization from 95% ethanol gave yellow crystals, m. p. 151–152° (cor.), identical with the product obtained above, as shown by a melting point of the mixture.

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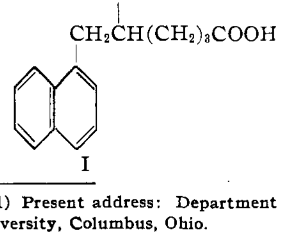
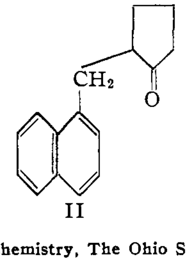
Preparation of the Isomeric 2-(Naphthylmethyl)-cyclopentanones

BY W. E. BACHMANN AND N. C. DENO[1]

Condensation of α-chloromethylnaphthalene with the sodio derivative of 2-carbethoxycyclopentanone gave the substituted cyclic keto ester, which was hydrolyzed by alkali with ring cleavage to α-(1′-naphthylmethyl)-adipic acid (I). Cyclization of the diacid with the aid of acetic anhy-



I



II

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dride or by dry distillation with calcium oxide yielded 2-(1′-naphthylmethyl)-cyclopentanone (II). The ultraviolet absorption spectrum of II was similar to that of 1-methylnaphthalene.

2-(2′-Naphthylmethyl)-cyclopentanone was prepared in a similar manner from β-chloromethylnaphthalene. An excellent yield of the crystalline ketone was obtained by cyclization of the intermediate α-(2′-naphthylmethyl)-adipic acid with acetic anhydride. The ketone was obtained also by acid hydrolysis of 2-carbethoxy-2-(2′-naphthylmethyl)-cyclopentanone.

Experimental[2]

α-(1′-Naphthylmethyl)-adipic Acid (I).—A mixture of 15.6 g. (0.1 mole) of 2-carbethoxycyclopentanone, sodium methoxide (prepared from 2.3 g. of sodium and dried at 100° and 20 mm.), and 150 cc. of dry benzene was refluxed for five minutes; any lumps present were crushed with a spatula. After the addition of 17.6 g. (0.1 mole) of α-chloromethylnaphthalene, the mixture was refluxed for six hours. After the removal of the benzene under reduced pressure, 40 cc. of 40% aqueous potassium hydroxide and 60 cc. of methanol were added and the solution was refluxed for eighteen hours. After being cooled and diluted with water to 300 cc., the solution was washed twice with ether and then acidified with hydrochloric acid. The substituted adipic acid, which was isolated by extraction with two 200-cc. portions of ether and removal of the ether, was triturated with 30 cc. of benzene; yield of colorless granular crystals, 15 g., m. p. 116–121°. An additional 1.17 g. of the acid (m. p. 110–118°) was obtained by further treatment of the non-crystalline portion with 40 cc. of 20% aqueous potassium hydroxide at 100° for twenty-four hours; total yield, 56%. After several recrystallizations from benzene the acid melted at 126–127.4°.

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.30, H, 6.33; neut. equiv., 143. Found: C, 71.42; H, 6.37; neut. equiv., 144.

2-(1′-Naphthylmethyl)-cyclopentanone (II).—The acetic anhydride was distilled slowly from a solution of 0.5 g. of the aforementioned acid in 1.5 cc. of acetic anhydride. After the apparatus had been filled with nitrogen, the temperature was raised to 300° in the course of five minutes; the pressure was then lowered to 30 mm. in order to complete the distillation; yield of colorless liquid, 71%. **The 2,4-dinitrophenylhydrazone** (m. p. 232.2–233.2°), which was prepared in 76% yield by addition of 1 cc. of concentrated hydrochloric acid to a refluxing solution of 100 mg. of the ketone and 150 mg. of 2,4-dinitrophenylhydrazine in ethanol, crystallized in fine, yellow needles.

Anal. Calcd. for $C_{22}H_{20}N_4O_4$: C, 65.33; H, 4.99. Found: C, 65.47; H, 5.16.

When the diacid alone was distilled, the yield of ketone was low and much acid was recovered. By dry distillation of an intimate mixture of 2 g. of the diacid and 0.4 g. of powdered calcium oxide under nitrogen and redistillation of the dark distillate at 130–170° and 0.1 mm., 1.02 g. of the ketone was obtained.

2-(2′-Naphthylmethyl)-cyclopentanone.—The cyclic keto ester prepared from 11.2 g. of β-chloromethylnaphthalene and an equivalent amount of 2-carbethoxycyclopentanone was completely hydrolyzed and cleaved by refluxing with aqueous methanolic alkali for eighteen hours. Recrystallization of the crude diacid from acetone–benzene gave two crops: 12.8 g., m. p. 149–150°, and 2 g., m. p. 144–146°; total yield, 81%. The highest m. p. obtained for α-(2′-naphthylmethyl)-adipic acid was 152.3–152.8°.

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.30; H, 6.33; neut. equiv., 143. Found: C, 71.50; H, 6.50; neut. equiv., 142.5.

By the procedure described for the isomer, 3.63 g. (93%) of the cyclic ketone (m. p. 57–63°) was obtained from 5 g. of the diacid and 15 cc. of acetic anhydride. The **2-(2′-naphthylmethyl)-cyclopentanone** crystallized from ether–petroleum ether in colorless glistening flakes; weight, 2.9 g. (75%), m. p. 70.3–71.3°.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.66; H, 7.19. Found: C, 85.78; H, 7.45.

A 38% yield of the ketone (m. p. 65.5–67°) was obtained when the diacid was distilled from calcium oxide and a 53% yield of ketone (m. p. 57–65°) resulted from refluxing a solution of 3.6 g. of the 2-carbethoxy-2-(2′-naphthylmethyl)-cyclopentanone in 10 cc. of acetic acid and 10 cc. of concentrated hydrochloric acid for twelve hours and evaporatively distilling the neutral product up to 180° at 0.1 mm.

The 2,4-dinitrophenylhydrazone (prepared in quantitative yield as described for the isomer except that the mixture was refluxed for five minutes and then allowed to stand for several days) crystallized in fine, short yellow needles; m. p. 138–139°, raised to 144.2–145° by recrystallization from ethanol.

Anal. Calcd. for $C_{22}H_{20}N_4O_4$: C, 65.33; H, 4.99. Found: C, 65.48; H, 4.95.

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[2] All melting points are corrected.

Derivatives of Indole-2-carboxylic Acid

BY WARREN J. BREHM

This report of work originally aimed at a synthesis of lysergic acid, but now discontinued, is prompted by Uhle's successful synthesis of 5-keto-1,3,4,5-tetrahydrobenz[cd]indole.[1] It was hoped that an abrine suitably protected at the 2-position to permit closure of the (α-methylamino)-propionic acid side-chain into the 4-position could be prepared by following the tryptophan syntheses developed by Snyder[2] or Robson.[3] The choice of the carboxypiperidide as the protective group made subsequent decarboxylation or its equivalent a necessary step. In an attempt to avoid the difficulties often attendant upon decarboxylation of indole-2-acids, 2-hydroxymethylindole was prepared. When this compound did not lose formaldehyde on treatment with base this alternate scheme had to be abandoned.

Experimental

Ethyl Indole-2-carboxylate.—Crude ethyl *o*-nitrophenylpyruvate, obtained as an oil by the method of Wislicenus and Thoma,[4] was dissolved in glacial acetic acid (35 g. of ester in 225 cc. of solvent). It was reduced with hydrogen at a pressure of 3 atm. over Adams catalyst (0.2 g.). At the end of the very rapid reduction the catalyst was filtered off and the solution diluted with water. This gave 22 g. (80%) of ethyl indole-2-carboxylate, m. p. 121–123°.

2-Hydroxymethylindole.—Lithium aluminum hydride (4.75 g.) was dissolved in 180 cc. of dry ether. With mechanical stirring a solution of 18.9 g. of ethyl indole-2-carboxylate in 250 cc. of dry ether was added dropwise at a rate sufficient to keep the solution boiling. When the addition was complete, stirring was continued for fifteen minutes, and then 100 cc. of water added slowly to decompose the excess reducing agent. The ether layer was

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(1) Uhle, THIS JOURNAL, **71**, 761 (1949).

(2) Snyder and Smith, *ibid.*, **66**, 351 (1944).

(3) Miller and Robson, *J. Chem. Soc.*, 1910 (1938).

(4) Wislicenus and Thoma, *Ann.*, **436**, 45 (1924).