tolyl methyl ether[6] with stannous chloride and hydrochloric acid. However, since this procedure is likely to give extensive chlorine substitution on the benzene nucleus, the compound was obtained by catalytic reduction using a platinum catalyst.

2-Nitro-*m*-tolyl methyl ether (0.31 mole, 53 g.) was placed in the hydrogenation flask with 250 ml. of ethanol and 0.6 g. of Adams catalyst and hydrogenated at a pressure of 50 lb./sq. in. at room temperature. At the end of three hours the catalyst was filtered off and the alcohol removed *in vacuo*. The oil which remained (40 g., 0.29 mole) was subjected to the next step after purification by vacuum distillation.

ω-Chloro-2-methoxy-6-methylacetanilide.—The amine from above was dissolved in 255 ml. of glacial acetic acid and cooled in an ice-bath to 10°. Chloroacetyl chloride (37.2 g., 0.33 mole) was added with constant stirring followed by a solution of 99 g. of $NaOAc \cdot 3H_2O$ in 414 ml. of water. After shaking mechanically for one-half hour the heavy white precipitate was filtered off with suction and dried in the air. Upon recrystallization from dilute ethanol the product appeared as a felted mass of white needles, m.p. 128–129°, with a yield of 37 g. (59%).

Anal. Calcd. for $C_{10}H_{12}ClNO_2$: N, 6.56. Found: N, 6.38.

ω-Chloro-2,6-dimethoxyacetanilide.[3]—2-Aminoresorcinol dimethyl ether[7] (50 g., 0.33 mole) was treated as above with chloroacetyl chloride (41.3 g., 0.37 mole) to yield 52 g. (69%) of fine colorless needles, m.p. 165–166°. This compound was recrystallized from benzene.

Anal. Calcd. for $C_{10}H_{12}ClNO_3$: N, 6.10. Found: N, 6.02.

ω-Chloro-2,6-dichloroacetanilide.—2,6-Dichloroaniline (27.3 g., 0.17 mole), synthesized as directed by Seikel,[8] was dissolved in 55 ml. of glacial acetic acid, and 20.3 g. (0.18 mole) of chloroacetyl chloride was added. The reaction mixture, containing a heavy white precipitate, was warmed on the steam-bath until no further evolution of HCl gas was apparent (about 15 minutes), and then 250 ml. of cold water was added. The resulting thick sludge was filtered with suction, washed with a little water, and dried in the air. Upon recrystallization from 50% acetic acid, 29.3 g. (72%) of long, colorless needles was obtained, m.p. 176–177° with sublimation.

Anal. Calcd. for $C_8H_6Cl_3NO$: N, 5.87. Found: N, 5.70.

The ω-Dialkylaminoacetanilides (Table I).—The appropriate ω-chloro-2,6-disubstituted acetanilide (0.044 mole) was refluxed for five hours with 0.122 mole of the dialkylamine in 100 ml. of dry benzene. After cooling, the colorless precipitate of the dialkylamine hydrochloride was filtered off with suction and washed with a little dry benzene. The combined filtrates were then evaporated to a thick sirup *in vacuo*, the residue taken up in sufficient 3 *N* HCl, shaken out with a little ether, and finally made strongly basic with 20% NaOH solution. The oil or solid which separated was isolated by ether extraction or suction filtration and distilled under diminished pressure.

To produce compounds 1, 9 and 17, dry dimethylamine gas was bubbled through a hot solution of the starting material in benzene for five hours and subsequently worked up as described above.

The hydrochlorides were obtained by passing dry hydrogen chloride gas through a solution of the free base in anhydrous ether. After recrystallization from methyl ethyl ketone–ether mixture the product usually appeared as a white microcrystalline powder.

CHICAGO 11, ILLINOIS

(7) H. Kaufmann and W. Franck, *Ber.*, **40**, 3999 (1907).

(8) M. K. Seikel, *Organic Syntheses*, **24**, 47 (1944).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Synthesis of DL-α-Amino-β-(6-methyl-3-indazolyl)-propionic Acid

BY H. R. SNYDER AND JOHN K. WILLIAMS[1]

RECEIVED SEPTEMBER 21, 1953

The indazole analog of 6-methyltryptophan, α-amino-β-(6-methyl-3-indazolyl)-propionic acid, has been synthesized *via* the sequence: nitro-*p*-xylene, the sodium enolate of ethyl 2-nitro-4-methylphenylpyruvate, the oxime of sodium 2-nitro-4-methylphenylpyruvate, 2-nitro-4-methylphenylacetonitrile, 2-amino-4-methylphenylacetonitrile, 6-methyl-3-cyanoindazole, 6-methylindazole-3-carboxylic acid, methyl 6-methylindazole-3-carboxylate, the dimethylamide of 6-methylindazole-3-carboxylic acid, 6-methyl-3-dimethylaminomethylindazole, 6-methyl-3-dimethylaminomethylindazole methiodide, ethyl α-acetamido-α-carbethoxy-β-(6-methyl-3-indazolyl)-propionate, α-acetamido-α-carboxy-β-(6-methyl-3-indazolyl)-propionic acid, α-acetamido-β-(6-methyl-3-indazolyl)-propionic acid, and α-amino-β-(6-methyl-3-indazolyl)-propionic acid.

In connection with studies of the antimetabolic activity of substances related to tryptophan the indazole analog of 6-methyltryptophan has been prepared. The steps employed in the synthesis are shown in the accompanying equations.

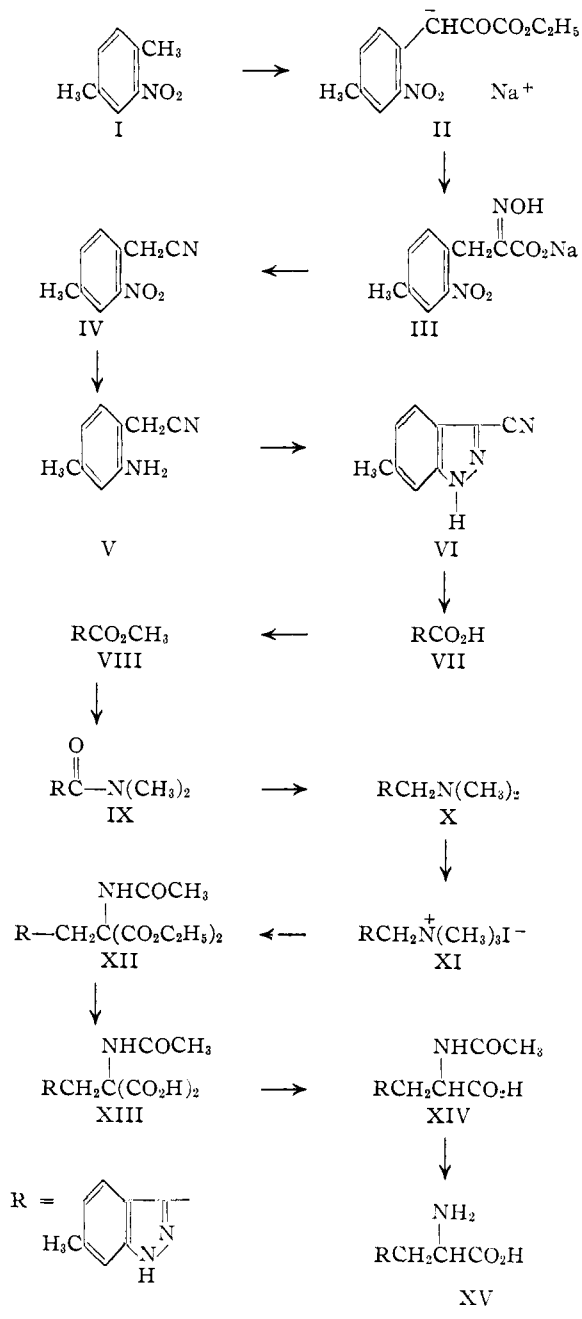
The nitro-*p*-xylene (I) was prepared as reported previously.[2] The sodium enolate of ethyl 2-nitro-4-methylphenylpyruvate (II) separated as a dark purple solid when I was allowed to react with diethyl oxalate and sodium ethoxide in absolute ether. When II was dissolved in warm water, it presumably decomposed to give the ester and sodium hydroxide, which then interacted to give sodium 2-nitro-4-methylphenylpyruvate in solution. When aqueous hydroxylamine was added to this solution, the sodium salt of the oxime III separated. The decarboxylation and dehydration of III were accomplished in one step by adding III to a mixture of acetic anhydride and glacial acetic acid heated to 70–100°. If acetic anhydride was used alone, as has been reported[3] for the conversion of the oxime of 2-nitrophenylpyruvic acid to 2-nitrophenylacetonitrile, the sodium salt III decomposed violently and was converted to a black intractable mass. When 2-nitro-4-methylphenylacetonitrile (IV) was shaken with hydrogen over palladium on carbon at room temperature, it was converted smoothly to 2-amino-4-methylphenylacetonitrile (V). Diazotization of V resulted in cyclization to 3-cyano-6-methylindazole (VI).

Hydrolysis of VI produced 6-methylindazole-3-carboxylic acid (VII) in high yield. Conversion of VII to 3-carbomethoxy-6-methylindazole (VIII) was accomplished by heating the acid with absolute methanol in the presence of sulfuric acid. When VIII was heated at 100° in a pressure bottle with 70% methanolic dimethylamine, the dimethylamide (IX) was obtained. The amide IX was converted to 3-dimethylaminomethyl-6-methyl-

(1) Allied Chemical and Dye Corporation Fellow, 1952–1953.

(2) H. R. Snyder and F. J. Pilgrim, THIS JOURNAL, **70**, 3787 (1948).

(3) V. Rousseau and H. Lindwall, *ibid.*, **72**, 3047 (1950).



indazole (X) by reduction with lithium aluminum hydride in ether solution. Because of the insolubility of the amide in ether, the Soxhlet technique[4] had to be employed.

Conversion of the tertiary amine X to the methiodide XI was effected in quantitative yield by allowing it to stand at 8° with a slight excess of methyl iodide in absolute ethanol solution. Acetamidomalonic ester was alkylated by XI when a solution of these two compounds in absolute ethanol was heated with sodium ethoxide. The substituted malonic ester XII was hydrolyzed to the acid XIII which was decarboxylated to α-acetamido-β-(6-methyl-3-indazolyl)-propionic acid (XIV) when heated in aqueous suspension. The amino acid XV was obtained when XIV was hydrolyzed with aqueous barium hydroxide.

(4) W. G. Brown in Adams, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 487.

Experimental[5]

Preparation of Sodium Enolate of Ethyl 2-Nitro-4-methylphenylpyruvate (II).—Ethanol-free sodium ethoxide was prepared by allowing 63 g. of sodium to dissolve in 400 ml. of absolute ethanol. When solution was complete, 800 ml. of absolute benzene was added and the resulting slurry of sodium ethoxide was distilled to dryness by gentle heating at water pump pressure. To the dry ethoxide which remained were added 2 l. of absolute ether, 408 g. of nitro-*p*-xylene and 400 g. of freshly distilled diethyl oxalate. The mixture was stirred at the reflux temperature for 42 hours during which time a heavy, dark purple precipitate of the enolate separated. The enolate was collected by filtration, washed with ether until the washings were only light yellow, and air dried. The yield of crude material, pure enough for the next step, was 555 g. (80.7%). Samples of this enolate have been kept for periods of several days exposed to the atmosphere without evidence of hydrolysis or other decomposition.

Preparation of the Oxime of Sodium 2-Nitro-4-methylphenylpyruvate (III).—The crude enolate (495 g.) was dissolved in 1 l. of water and the solution was heated on the steam-bath for one hour. The resulting red-brown solution was filtered through a fluted paper. To the filtrate was added 250 g. of sodium chloride, followed by a solution of 174 g. of hydroxylamine hydrochloride and 100 g. of sodium hydroxide in 400 ml. of water. As soon as the hydroxylamine solution was added a light tan precipitate began to appear. The mixture was allowed to stand at room temperature for one hour and then at 8° overnight. The solid which had been deposited was collected, washed with 200 ml. of cold water then with three 350-ml. portions of 95% ethanol, and air dried. The yield of light cream colored powder was 281 g. (60.3%). An additional 46 g. of product was obtained after the filtrate had been allowed to stand at room temperature for one week. The total yield of salt, of sufficient purity for conversion to the nitrile, was 327 g. (70.2%).

Preparation of 2-Nitro-4-methylphenylacetonitrile (IV).—A mixture of 600 ml. of glacial acetic acid and 150 ml. of acetic anhydride was heated to 70° and the source of heat removed. To the hot solution was added 281 g. of III in small portions. The hot, light orange, clear reaction mixture was diluted with 900 ml. of cold water and set aside at 8° overnight. The light tan crystalline product was collected, washed with dilute acetic acid and then with water until the washings were neutral. The product weighed 195 g. and melted at 68–71°.

A sample prepared for analysis by several recrystallizations from methanol melted at 71–73°.

Anal. Calcd. for $C_9H_8N_2O_2$: C, 61.35; H, 4.58; N, 15.91. Found: C, 61.59; H, 4.47; N, 15.89.

Preparation of 2-Amino-4-methylphenylacetonitrile (V).—A suspension of 103 g. of IV and 2 g. of 5% palladium chloride-on-carbon in 500 ml. of 95% ethanol was shaken with hydrogen at one to three atmospheres until three moles of hydrogen had been absorbed. The reduction required about two hours, and during this time the temperature of the reaction mixture reached about 70°.

The catalyst was removed and washed with about 50 ml. of hot ethanol. The filtrate and washings were combined and diluted while hot to a volume of 2 l. with hot water. After refrigeration overnight, the light tan crystals which had been deposited were collected and dried. The yield of aminonitrile melting at 103–105° was 80.0 g. (93.8%).

A small sample was prepared for analysis by solution in dilute hydrochloric acid, treatment of the resulting solution with Darco, recovery by the addition of base to the colorless solution of the amine hydrochloride, and recrystallization of the free amine two times from ethanol–water. The sample prepared in this way consisted of colorless needles melting at 104–105°.

Anal. Calcd. for $C_9H_{10}N_2$: C, 73.94; H, 6.90; N, 19.16. Found: C, 74.05; H, 6.76; N, 19.21.

(5) Analyses performed by Mrs. Esther Fett, Mrs. Katherine Pih and Mr. Joseph Nemeth; infrared spectra determined and interpreted by Miss Helen P. Miklas.

Preparation of 3-Cyano-6-methylindazole (VI).—In a mixture of 99 ml. of concentrated hydrochloric acid and 500 ml. of water was dissolved 70.5 g. of V. The light brown solution was treated with Darco and filtered. The light yellow filtrate was diluted with 500 ml. of water and cooled to 5°. To this cold solution was added a solution of 37 g. of sodium nitrite in 500 ml. of water. An orange precipitate began to form immediately and the temperature rose to 15°. After three hours at room temperature, the solid which had been deposited was collected and washed well with water. One recrystallization from ethanol–water, after treatment with Darco, gave 69.0 g. (91.0%) of orange prisms which melted at 163–164.5°.

An analytical sample prepared by recrystallization from ethanol–water melted at 164.5°.

Anal. Calcd. for $C_9H_7N_3$: C, 68.77; H, 4.49; N, 26.73. Found: C, 68.82; H, 4.36; N, 26.77.

6-Methylindazole-3-carboxylic Acid (VII).—A suspension of 152 g. of VI in a solution of 152 g. of sodium hydroxide in 1 l. of water was stirred at the reflux temperature for 21 hours. The hot, clear, light orange solution was diluted with 500 ml. of 95% ethanol and 2.5 l. of hot water. The hot solution was acidified with a 1:3 mixture of concentrated hydrochloric acid–ethanol. The solid was collected, washed with water, suspended in 3.5 l. of 20% ethanol and brought into solution by the addition of concentrated ammonium hydroxide. After treatment with Darco, the solution was heated to 80° and acidified with 1:5 concentrated hydrochloric acid–ethanol. (If the solution was not acidified while hot or if aqueous acid rather than alcoholic acid was used, the product was precipitated in a form which was exceedingly difficult to filter.) After refrigeration overnight, the product was collected, washed with a little cold water, and dried in an oven at 120°. In this way 159 g. (93.5%) of light tan, long, hairy needles was obtained which melted at 286–287° with decomposition.

A small sample was prepared for analysis by recrystallization from 95% ethanol. No consistent melting point could be obtained, since it was evidently dependent to some extent both on the rate of heating during the determination and on small quantities of adsorbed water. Before a satisfactory analysis could be obtained, the sample had to be dried at 150° for 36 hours at a pressure of 0.05 mm.

Anal. Calcd. for $C_9H_8N_2O_2$: C, 61.35; N, 4.58; N, 15.91. Found: C, 61.44; H, 4.80; N, 15.79.

Preparation of Methyl 6-Methylindazole-3-carboxylate (VIII).—A mixture of 75 g. of VII, 250 ml. of absolute methanol and 19 ml. of concentrated sulfuric acid was heated under reflux on the steam-bath for five hours. The solution was adjusted to *p*H 9 by the addition of 15% methanolic dimethylamine and then, while still hot, diluted with hot water until crystallization began. After refrigeration overnight, the solid was collected, washed with water and dried. The material obtained in this way was of sufficient purity for conversion to the dimethylamide (IX) and weighed 75.4 g. (93.1%), m.p. 145–150°. The analytical sample (from aqueous methanol) melted at 150–151°.

Anal. Calcd. for $C_{10}H_{10}N_2O_2$: C, 63.14; H, 5.30; N, 14.73. Found: C, 63.20; H, 5.32; N, 14.96.

Preparation of 6-Methylindazole-3-carboxylic Acid Dimethylamide (IX).—A bottle capable of withstanding ten atmospheres pressure (such as one used for the polymerization of butadiene) was charged with 80 g. of VIII and 40 g. of 73% methanolic dimethylamine. The bottle was suspended by means of a wire in a steam-bath for 23 hours. The contents of the bottle were transferred to a beaker and the solvent and excess dimethylamine were removed on the steam-bath. The solid residue was dissolved in 400 ml. of 95% ethanol and the resulting solution was filtered while hot. The hot filtrate was diluted with 1.8 l. of hot water and set aside at 8° overnight. The solid which had been deposited was collected, washed with water and dried. The yield of amide, melting at 178–191° was 63.8 g. (74.6%). Despite the wide melting range, the crude product was suitable for reduction to the amine X.

A sample was prepared for analysis by four recrystallizations from 95% ethanol; m.p. 193–195°.

Anal. Calcd. for $C_{11}H_{13}N_3O$: C, 65.02; H, 6.45; N, 20.68. Found: C, 64.70; H, 6.36; N, 20.71.

Preparation of 3-Dimethylaminomethyl-6-methylindazole (X).—In the cup of a Soxhlet apparatus was placed 46.3 g. of IX. A suspension of 21 g. of lithium aluminum hydride in 1.2 l. of absolute ether was placed in the boiler. The ether was allowed to reflux until the amide had been completely extracted into the hydride slurry (19 hours). To the reaction mixture was added 55 ml. of 20% sodium hydroxide solution, which caused the inorganic salts to be deposited as a granular precipitate. The ether layer was decanted and extracted with a solution of 75 ml. of concentrated hydrochloric acid in 500 ml. of water which had been divided into six portions. The extracts were combined and adjusted to *p*H 6 by the addition of about 200 ml. of 10% ammonium hydroxide. The slightly cloudy solution was treated with Darco and filtered. The clear filtrate was made basic by the addition of concentrated ammonium hydroxide and cooled in ice for two hours. The white crystalline solid which was deposited was collected and sucked as dry as possible on a büchner funnel. The moist cake was dissolved in nitromethane and, after boiling to remove some water, refrigerated overnight. The yield of amine was 34.8 g. (30.8%); m.p. 91–96°.

A sample was prepared for analysis by several recrystallizations from nitromethane followed by vacuum sublimation; m.p. 97–98°.

Anal. Calcd. for $C_{11}H_{15}N_3$: C, 69.78; H, 7.99; N, 22.20. Found: C, 69.98; H, 7.90; N, 22.40.

Preparation of 3-Dimethylaminomethyl-6-methylindazole Methiodide (XI).—A solution of 40.0 g. of X in 300 ml. of absolute ethanol was cooled to 0° in an ice–salt mixture. To this cold solution was added 40.0 g. of methyl iodide. The clear solution was immediately placed in a refrigerator at 8° and allowed to remain there overnight. The long, colorless needles which had deposited were collected and dried. The yield of methiodide, melting at 211–213°, was 68.0 g. (97.0%).

Two recrystallizations from absolute ethanol produced an analytical sample which melted at 214–218°.

Anal. Calcd. for $C_{12}H_{18}N_3I$: C, 43.51; H, 5.48; N, 12.69. Found: C, 43.60; H, 5.49; N, 12.48.

Preparation of Ethyl α-Carbethoxy-α-acetamido-β-(6-methyl-3-indazolyl)-propionate (XII).—A solution of sodium ethoxide was prepared from 3.1 g. of sodium and 150 ml. of absolute ethanol. To this solution was added 29 g. of acetamidomalonic ester and 44 g. of the methiodide XI. The reaction mixture was boiled under reflux for 65 hours and then diluted with 1 l. of water. The oil which separated was extracted into chloroform and the extract was dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure gave a quantitative yield of crude XII as a light tan oil. Attempts to induce the ester to crystallize were unsuccessful. However, the crude material was sufficiently pure for conversion to the amino acid XV.

Preparation of β-(6-Methyl-3-indazolyl)-α-aminopropionic Acid (XV). A. Decarboxylation of XIII in Neutral Solution.—A mixture of 48 g. of crude ester XII and 150 ml. of 2.5 *N* sodium hydroxide was boiled under reflux for one hour. The hot solution was neutralized with the calculated amount of 2.5 *N* sulfuric acid (which had been titrated against the alkali used). The neutral solution was boiled under reflux for one hour and then the solvent was removed *in vacuo*. The crude acetylamino acid XIV was separated from inorganic material by extraction with hot 95% ethanol. The acetylamino acid (XIV) was obtained as a grey oil when the solvent was removed under reduced pressure.

A mixture of crude XIV, 75 g. of barium hydroxide hexahydrate and 600 ml. of water was boiled under reflux for 14 hours. The hot reaction mixture was acidified to *p*H 4 with 10% sulfuric acid and diluted to 3.5 l. with hot water. The mixture was boiled in a beaker for one hour. The barium sulfate was removed by filtration of the hot solution. The filtrate was adjusted to *p*H 5 by the addition of ammonium hydroxide. After refrigeration overnight 16.3 g. (56.0% over-all yield from the methiodide) of amino acid XV was collected; m.p. 264–266°.

A sample, prepared for analysis by recrystallization from water, melted at 268–271°. The infrared spectra of this sample and of an authentic sample of DL-α-amino-β-(3-indazolyl)-propionic acid[6] were nearly identical.

(6) H. R. Snyder, C. B. Thompson and R. L. Hinman, THIS JOURNAL, 74, 2009 (1952).

Anal. Calcd. for $C_{11}H_{13}N_3O_2$: C, 60.28; H, 5.98; N, 19.17. Found: C, 59.64; H, 5.99; N, 19.19.

B. **Decarboxylation of XIII in Acid Solution.**—A mixture of 90 g. of crude ester XII and 500 ml. of 2.5 *N* sodium hydroxide was boiled under reflux for 24 hours. The hot solution was treated with Darco and filtered. The clear orange filtrate was adjusted to *p*H 1 by the addition of 90 ml. of concentrated hydrochloric acid and then boiled under reflux for 24 hours. The solid which separated from this reaction mixture on cooling was collected and recrystallized from an ethanol–water mixture giving 13.0 g. of amino acid XV, m.p. 264–268°. Concentration of the liquors from this recrystallization to 200 ml. gave 5.3 g. (9%) of acetylamino acid XIV, m.p. 188–190°. A sample of the acetylated compound recrystallized from an ethanol–water mixture, m.p. 190–191°, was submitted for analysis.

Anal. Calcd. for $C_{13}H_{15}N_3O_3$: C, 59.75; H, 5.79; N, 16.08. Found: C, 59.60; H, 5.53; N, 16.19.

When the filtrate from the reaction mixture was adjusted to *p*H 4 by the addition of ammonium hydroxide and concentrated to 300 ml., an additional 8.3 g. of amino acid XV was obtained, m.p. 265–271°. Also, by evaporating all mother liquors to dryness and hydrolyzing the residue again with barium hydroxide, as described above, another 6.3 g. of amino acid was obtained giving a total yield of 27.7 g. (55.5%).

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Disproportionation of Tertiary Amines

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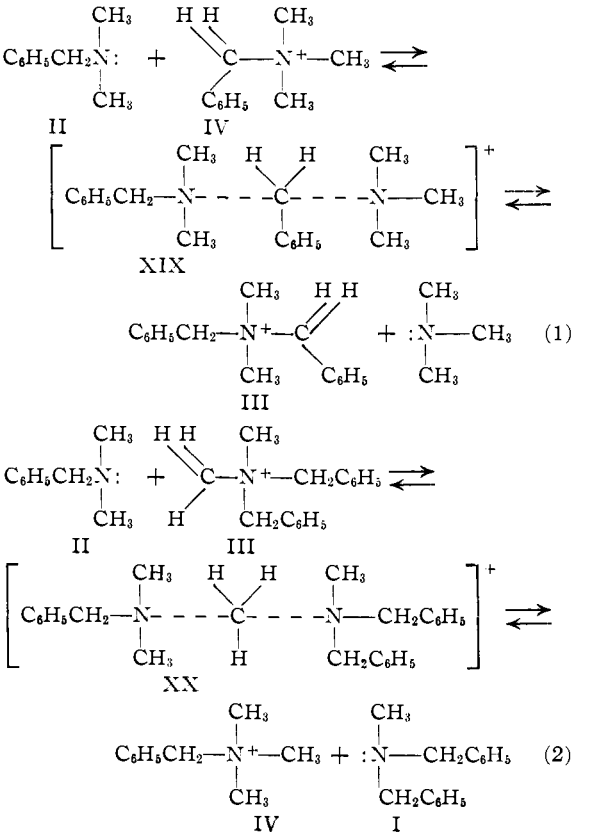
When N,N-dimethylbenzylamine is heated for 17 hours at 200° in the presence of catalytic amounts of its quaternary ammonium salt, it disproportionates to form N-methyldibenzylamine and trimethylamine. An examination of the results of subjecting various tertiary amines to the disproportionation conditions shows that an amine of the benzyl type undergoes the reaction while others do not. This observation agrees with that predicted from the proposed S_N2 displacement reaction sequence.

The formation of N-methyldibenzylamine (I) was observed as a side reaction during the alkylation of methyl cyanoacetate with N,N-dimethylbenzylamine (II).[3] Its formation was explained by the initial quaternization of the amine by the methyl cyanoacetate followed by the reaction of the amine and the salt in a cyclic process in which the dibenzyldimethylammonium cation (III) is an intermediate. When the methyl cyanoacetate was replaced by the salt itself (IV as the chloride) in a 1:1 ratio, a 78% conversion resulted; when the ratio of amine to salt was increased to 10:1, the conversion was 73%. The quaternary ammonium salt thus functioned as the catalyst. Hydrochloric acid and boron trifluoride were also found to catalyze the reaction although not so effectively, the conversions being 8.1 and 15.0%, respectively.[3] Several other tertiary amines have been subjected to the conditions for the disproportionation in an attempt to determine the generality and synthetic value of the reaction.

Those amines containing a benzyl residue were found to undergo the disproportionation to form trimethylamine and a new tertiary amine. The refluxing of N,N-dimethylfurfurylamine (V) in the presence of 0.1 mole of its methiodide for 17 hours produced N-methyldifurfurylamine (VI) in a yield of 50.0%. Similarly, N,N-dimethyl-2-thenylamine (VII) was converted to the previously unknown N-methyl-di-2-thenylamine (VIII) in 56.5% yield. Only a 30.0% conversion was achieved when N,N-dimethyl-α-naphthylmethylamine (IX) was allowed to react. N,N-Dimethyl-*p*-nitrobenzylamine (X) and gramine (XI) appeared to react but no product other than trimethylamine could be isolated although some dimethylamine was evolved by the decomposition of gramine. Tertiary amines containing no group of the benzyl type failed to react. No trimethylamine or disproportionation product was isolated from attempted reactions of N,N-dimethylaniline (XII), N,N-dimethyl-β-naphthylamine (XIII), N,N-dimethylcyclohexylamine (XIV) or N,N-dimethylallylamine (XV). An exception was noted when N-methyl-bis-β-phenethylamine (XVI) was formed to an extent of 2% from N,N-dimethyl-β-phenethylamine (XVII). Styrene



(1) Minnesota Mining and Manufacturing Co. Fellow, 1949–1950.

(2) National Science Foundation Fellow, 1952–1953.

(3) H. R. Snyder, E. L. Eliel and R. E. Carnahan, THIS JOURNAL, **72**, 2958 (1950).