acid forms an insoluble mono-K-salt stable at pH 4.6–4.8, and an insoluble mono-Na-salt stable at about the same pH. The acid is quickly and completely precipitated by barium chloride from aqueous solution neutralized with ammonia.

Summary

The reaction between formaldehyde and phenol in alkaline medium has been investigated with the object of determining which of the several possible mono- and polymethylols of phenol are formed as initial products of the reaction, and to what relative extent. Evidence in the form of the corresponding methoxybenzenecarboxylic acids has been obtained for the formation of 10–15 mole % o-methylol phenol, 35–45% p-methylol, 30–35% 2,4-dimethylol and 4–8% trimethylol phenol, plus 5–10% of unreacted phenol as the primary products of reaction of 1 mole of phenol with 1.4 moles of formaldehyde. No 2,6-dimethylol phenol was detected nor was any evidence found for the presence of methylol groups in the meta-position to the phenolic hydroxyl.

The respective methoxybenzenecarboxylic acids have also been synthesized by other means. A method is described for the separation of anisic acid, o-methoxybenzoic acid, 4-methoxyisophthalic acid, 2-methoxyisophthalic acid, and methoxytrimesic acid when present as a mixture.

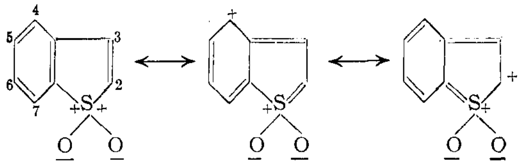
EAST PITTSBURGH, PA. RECEIVED JULY 8, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Benzothiophene[1] Chemistry. IV.[2] Some Addition Reactions of Benzothiophene-1-dioxide[3]

BY F. G. BORDWELL AND W. H. MCKELLIN

Benzothiophene-1-dioxide (I) may be looked on as containing a heteroaromatic system if resonance forms such as Ia and Ib, which give the sulfur atom ten electrons, are recognized as important. Chemically, carbon–carbon bonds in aromatic systems differ from olefinic bonds in showing less susceptibility to attack by addition-type reagents. Therefore, it seemed of interest to see whether or not the 2–3 bond in I would undergo, under comparable conditions, the reactions typical of the similarly situated bond in other α,β-unsaturated sulfones.



I Ia Ib

Kohler and Potter[4] reported that β-phenylvinyl p-tolyl sulfone ($C_6H_5CH{=}CHSO_2C_7H_7$), which is somewhat analogous to I in structure, underwent addition reactions with hydrogen (incomplete in the presence of platinum catalyst), bromine (irradiation was necessary), phenylmagnesium bromide, thiocresol (basic catalyst used) and sodiomalonic ester. It was found that I underwent reaction with all of these reagents under conditions similar to those used by Kohler and Potter.[4] The addition of one mole of hydrogen to I was complete in a short time in the presence of palladium on charcoal catalyst. Addition of bromine was brought about either by irradiation in carbon tetrachloride solution or by heating in acetic acid solution.[2] Thiophenol was added in benzene solution according to the directions of Kohler and Potter,[4] or in alcohol solution. The latter method was more convenient but the product was less pure, probably due to contamination by the alcohol-addition product. The product from the reaction with phenylmagnesium bromide resisted attempts at purification, and no identifiable substance was obtained.

Vinyl sulfone has been reported[5] to undergo addition reactions with: (1) hydrobromic and hydroiodic acids; (2) water, methanol, ethanol, 3-methylbutanol and phenol (all with basic catalysis); (3) hydrogen sulfide and thiophenol; (4) glycine and phenylhydrazine. As representative of these and other reagents mentioned in the literature,[6] hydrobromic acid, water, ethanol, 2-propanol, 2-methyl-2-propanol, diethylamine, morpholine, piperidine, phenol and malonic ester were chosen. The addition reactions were successful with all of these except phenol.[7] In general the reactions proceeded rapidly and gave excellent yields of addition products.

By analogy with a large number of examples

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[1] The name *thianaphthene* was adopted in the first three papers of this series, following the current usage in *Chemical Abstracts*. Prior to 1937 the name *thionaphthene* was preferred by *Chemical Abstracts*. Since both *thia* and *naphthene* have meanings which are not borne out in the structure, the name *thianaphthene* appears to be an unfortunate choice. Henceforth it will be abandoned in favor of *benzothiophene*, as suggested by Ball and Haines, *Chem. Eng. News*, **24**, 2765 (1946), and by the committee on nomenclature of the Petroleum Division of the American Chemical Society.

[2] For Paper III see Bordwell, Lampert and McKellin, THIS JOURNAL, **71**, 1702 (1949).

[3] This work was supported by a grant from The Texas Company, New York, N. Y.

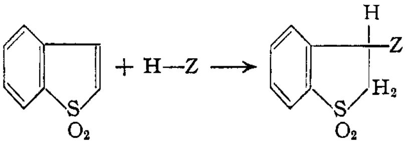
[4] Kohler and Potter, THIS JOURNAL, **57**, 1316 (1935).

[5] Alexander and McCombie, *J. Chem. Soc.*, 1913 (1931).

[6] See Suter, "Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., p. 727–728, for further references.

[7] After this work had been completed Challenger and Clapham, *J. Chem. Soc.*, 1615 (1948), reported the addition of hydrogen iodide, methanol, ethanol and hydrogen to I.

in the literature reporting the addition of similar reagents to α,β-unsaturated ketones, esters, sulfones, nitro compounds, etc., most of the reactions are formulated as proceeding by attack of the electron-donating atom at the β-position (3-position) of I, as shown. The structures of the products were not, in general, rigorously proven. The correctness of the structures assigned for the addition compounds from the reaction of water and thiophenol with I were confirmed by qualitative evidence. The water-addition product was stable when evaporated in acidic solutions showing that it was a β-hydroxy sulfone rather than an α-hydroxysulfone.[8] Oxidation of the thiophenol-addition product gave a disulfone which was insoluble in alkali indicating a γ-disulfone rather than a β-disulfone. The structure of the hydrobromic acid addition product was definitely established. The isomeric 2-bromo-2,3-dihydrobenzothiophene-1-dioxide was prepared by the reaction of 2,3-dihydrobenzothiophene-1-dioxide with ethylmagnesium bromide, and treatment of the magnesium derivative so formed with bromine. The 3-bromo product was also prepared by the reaction of phosphorus tribromide or hydrobromic acid on 3-hydroxy-2,3-dihydrobenzothiophene-1-dioxide and by bromination of 2,3-dihydrobenzothiophene-1-dioxide in a carbon tetrachloride solution irradiated with ultraviolet light. The α-position in sulfones is resistant to bromination under the latter conditions as shown by the failure of benzyl sulfone and phenyl ethyl sulfone to be attacked. The activating influence of the phenyl group apparently makes the β-position in 2,3-dihydrobenzothiophene-1-dioxide more susceptible to attack by bromine atoms than that in phenyl ethyl sulfone.



Z = OR, SC_6H_5, OH, Br, NR_2, $CH(COOEt)_2$

It is evident from the above that the 2–3 bond in I undergoes addition reactions in a manner comparable to that of other α,β-unsaturated sulfones, and no aromatic characteristics are detectable in this way. In line with this it was found that I was oxidized rapidly by cold aqueous potassium permanganate to *o*-sulfobenzoic acid.

Experimental[9]

Hydrogenation of Benzothiophene-1-dioxide.—Hydrogenation of 8.3 g. (0.05 mole) of benzothiophene-1-dioxide[2] was accomplished in a Parr hydrogenation apparatus in fifteen minutes under an initial pressure of 45 pounds using 150 cc. of ethanol as the solvent and 0.2 g. of 5% palladium-on-charcoal catalyst. Evaporation of the solution, after removal of the catalyst, gave a quantitative yield of 2,3-dihydrobenzothiophene-1-dioxide, m. p. 88–89°. One crystallization from dilute alcohol gave material melting at 91–92°.[10]

3-Hydroxy-2,3-dihydrobenzothiophene-1-dioxide.—Water was added to 5.0 g. (0.030 mole) of benzothiophene-1-dioxide by stirring in 150 cc. of 1 *N* sodium hydroxide until all the solid had dissolved (six days). The solution was acidified with hydrochloric acid and evaporated to dryness with the aid of a stream of air. A clear, yellow oil was obtained by treating the residue with dry acetone and evaporating the acetone. Treatment of 0.1 g. of the crude product with 1 cc. of acetyl chloride gave, after evaporation of the excess acetyl chloride, a material, m. p. 87–90°. Crystallization from dilute alcohol gave **3-acetoxy-2,3-dihydrobenzothiophene-1-dioxide**, m. p. 89.5–90°.

Anal. Calcd. for $C_{10}H_{10}SO_4$: C, 53.08; H, 4.46. Found: C, 52.88; H, 4.55.

A solution of 0.5 g. (0.0027 mole) of crude 3-hydroxy-2,3-dihydrobenzothiophene-1-dioxide with 5.0 g. of benzoyl chloride was refluxed for twenty minutes, cooled, diluted with 50 cc. of water, and made strongly alkaline with sodium hydroxide. On standing, the resulting oil solidified and was collected on a filter; 0.6 g. of solid, m. p. 100–105° was obtained. Crystallization from dilute alcohol gave **3-benzoxy-2,3-dihydrobenzothiophene-1-dioxide**, m. p. 104–106° (89% yield). A sample purified for analysis melted at 107–108°.

Anal. Calcd. for $C_{15}H_{12}SO_4$: C, 62.48; H, 4.20. Found: C, 62.80; H, 4.28.

3-Bromo-2,3-dihydrobenzothiophene-1-dioxide.—A solution of 0.5 g. (0.003 mole) of benzothiophene-1-dioxide in 20 cc. of 48% hydrobromic acid was refluxed for one hour. On cooling 0.45 g. (60%) of 3-bromo-2,3-dihydrobenzothiophene-1-dioxide, m. p. 88–91°, was obtained. This material gave no depression in melting point when mixed with samples of the compound prepared by the methods described below.

A solution of 2.0 g. (0.012 mole) of 2,3-dihydrobenzothiophene-1-dioxide and 2.0 g. (0.0125 mole) of bromine in 25 cc. of carbon tetrachloride was decolorized after irradiation with ultraviolet light for four days. The product was crystallized from dilute alcohol; m. p. 91.5–92.5°.

Anal. Calcd. for $C_8H_7SO_2Br$: C, 38.88; H, 2.86. Found: C, 38.88; H, 2.87.

Addition of two drops of liquid bromine to a mixture of 0.1 g. of crude 3-hydroxy-2,3-dihydrobenzothiophene-1-dioxide and 0.5 g. of phosphorus tribromide caused the formation of a solid. After thirty minutes 20 cc. of water was added and the mixture heated to effect solution. On cooling 0.12 g. (90%) of 3-bromo-2,3-dihydrobenzothiophene-1-dioxide, m. p. 90–92°, precipitated.

A solution of 0.25 g. of crude 3-hydroxy-2,3-dihydrobenzothiophene-1-dioxide and 10 cc. of 48% hydrobromic acid was refluxed for two days and then diluted with 20 cc. of water. On cooling, 0.3 g. (89%) of solid product, m. p. 88–92°, was obtained.

2-Bromo-2,3-dihydrobenzothiophene-1-dioxide.—To a Grignard reagent prepared from 0.875 g. (0.036 mole) of magnesium turnings and 4.0 g. (0.036 mole) of ethyl bromide in 50 cc. of anhydrous ether, was added with stirring 5.0 g. (0.030 mole) of 2,3-dihydrobenzothiophene-1-dioxide in 50 cc. of dry benzene. A white, gummy precipitate formed on addition of the sulfone solution; 50 cc. more dry benzene was added and the solution was refluxed five minutes. The solution was cooled in an ice-bath and 5.75 g. (0.036 mole) of bromine was added in 75 cc. of dry benzene with rapid stirring. After two hours stirring, the clear solution was poured into 200 cc. of water, enough sodium bisulfite added to use up the excess bromine and the benzene solution separated and washed with water. Removal of the solvent gave an oil which yielded a crystalline product from dilute alcohol. The yield of crude material

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(8) Kohler and Reimer, *Am. Chem. J.*, **31**, 163 (1904).

(9) Microanalyses were by Misses Hines, Guy, Gibbs and Nielsen.

(10) This constitutes the easiest route to this compound, compare, Challenger and Clapham, ref. 7; Fricke and Spilker, *Ber.*, **58B**, 1589 (1925).

was 6.2 g. (84%); m. p. 107–112°. A sample crystallized for analysis melted at 116–117°.

Anal. Calcd. for $C_8H_7SO_2Br$: C, 38.88; H, 2.86. Found: C, 39.21; H, 2.88.

Attempted Bromination of Ethyl Phenyl and Benzyl Sulfones.—A solution of 5.0 g. (0.0294 mole) of ethyl phenyl sulfone and 5.0 g. (0.0312 mole) of bromine in 50 cc. of carbon tetrachloride was illuminated with ultraviolet light for seven days. There was no apparent decoloration of the solution and when the bromine was taken up with sodium bisulfite, the solution washed with water and the solvent evaporated, 4.3 g. of unchanged sulfone was obtained, 86% recovery. Benzyl sulfone showed no inclination to brominate when refluxed in contact with bromine in carbon tetrachloride solution for two hours under ultraviolet irradiation (quartz flask).

3-Ethoxy-2,3-dihydrobenzothiophene-1-dioxide.—A solution of 2.0 g. (0.012 mole) of benzothiophene-1-dioxide, 0.1 g. of potassium hydroxide and 50 cc. of ethanol was refluxed for twenty-four hours. On cooling, 1.8 g. (94%) of crystalline product separated, m. p. 103–105°. A sample recrystallized from dilute alcohol for analysis gave colorless platelets m. p. 108–109°. Challenger and Clapham[7] report a melting point of 107–108°.

Anal. Calcd. for $C_{10}H_{12}SO_3$: C, 56.61; H, 5.66. Found: C, 56.80; H, 5.68.

3-Isopropoxy-2,3-dihydrobenzothiophene-1-dioxide.—One gram (0.006 mole) of benzothiophene-1-dioxide and 0.1 g. of potassium hydroxide were dissolved in 50 cc. of isopropyl alcohol and the solution refluxed for twenty-four hours. The solvent was removed with the aid of a stream of air, the solid suspended in water and the suspension filtered. There was obtained 1.25 g. (93%) of product, m. p. 87–90°. A sample recrystallized for analysis from dilute alcohol melted at 96–97°.

Anal. Calcd. for $C_{11}H_{14}SO_3$: C, 58.38; H, 6.24. Found: C, 58.18; H, 6.39.

3-(1,1-Dimethylethoxy)-2,3-dihydrobenzothiophene-1-dioxide.—A solution of 1.0 g. (0.006 mole) of benzothiophene-1-dioxide and 0.1 g. of potassium hydroxide dissolved in 50 cc. of dry *t*-butyl alcohol was refluxed forty hours. The solution was evaporated to dryness with a stream of air and the residue taken up in 20 cc. of water. Filtration of the water suspension yielded 0.55 g. of product, m. p. 110–114° (38% yield). After crystallization from dilute alcohol for analysis the material melted at 115–116°.

Anal. Calcd. for $C_{12}H_{16}SO_3$: C, 59.97; H, 6.71. Found: C, 60.01; H, 6.75.

3-Piperidino-2,3-dihydrobenzothiophene-1-dioxide.—A solution containing 1.0 g. (0.006 mole) of benzothiophene-1-dioxide, 1.0 g. (0.012 mole) of piperidine and 15 cc. of 95% alcohol was refluxed fifteen minutes and the alcohol removed in a current of air. A quantitative yield of solid was obtained, m. p. 103–110°. Recrystallization from dilute alcohol gave an analytical sample m. p. 109–110°.

Anal. Calcd. for $C_{13}H_{15}SO_2N$: C, 62.12; H, 6.82. Found: C, 62.11; H, 6.83.

3-Morpholino-2,3-dihydrobenzothiophene-1-dioxide.—A mixture containing 0.5 g. (0.003 mole) of benzothiophene-1-dioxide and 0.5 g. (0.0057 mole) of morpholine dissolved in 20 cc. water was refluxed one and one-half hours. Upon cooling, a precipitate formed, m. p. 176–179° (100% yield); recrystallized for analysis from alcohol the melting point was 177.5–178.5°.

Anal. Calcd. for $C_{12}H_{13}SO_3N$: N, 5.53. Found: N, 5.76.

3-Diethylamino-2,3-dihydrobenzothiophene-1-dioxide.—A solution containing 2.0 g. (0.012 mole) of benzothiophene-1-dioxide, 2.0 g. (0.027 mole) of diethylamine and 80 cc. of water was refluxed one hour. On cooling, 2.6 g. (90%) of a precipitate formed, m. p. 95–97°. A sample was recrystallized from dilute alcohol for analysis; m. p. 97.5–98°.

Anal. Calcd. for $C_{12}H_{17}SO_2N$: N, 5.85. Found: N, 5.53.

3-Thiophenoxy-2,3-dihydrobenzothiophene-1-dioxide.—To 0.14 g. (0.006 mole) of sodium sand suspended in 50 cc. of dry benzene, 1.33 g. (0.012 mole) of thiophenol in 25 cc. of dry benzene was added, and the mixture refluxed for four hours. The suspension obtained was cooled, 1.0 g. (0.006 mole) of benzothiophene-1-dioxide was added, and the suspension again refluxed. After twenty hours the mixture was cooled, 100 cc. of water added, the benzene layer separated and washed with 10% sodium hydroxide solution, and finally with water. Evaporation of the benzene gave 1.65 g. (quantitative yield) of an oil which crystallized from alcohol; m. p. 67–70°. Recrystallized from alcohol for analysis the product melted at 69–70°.

Anal. Calcd. for $C_{14}H_{12}S_2O_2$: C, 60.84; H, 4.38. Found: C, 61.12; H, 4.38.

In the presence of sodium ethoxide, prepared by the addition of 0.05 g. of sodium to 20 cc. absolute alcohol, 1.0 g. (0.006 mole) of benzothiophene-1-dioxide was refluxed seventeen hours with 1.33 g. (0.012 mole) of thiophenol. Evaporation of the alcohol yielded a yellow oil from which the excess thiophenol was removed by adding 50 cc. water, acidifying with hydrochloric acid, and steam distilling. The yellow oil obtained slowly solidified on cooling; 1.65 g. of material melting at 55–65° was obtained. After recrystallization from alcohol a mixed melting point with a sample of the product described above showed no depression.

3-Phenylsulfonyl-2,3-dihydrobenzothiophene-1-dioxide.—To 0.2 g. (0.0007 mole) of 3-thiophenoxy-2,3-dihydrobenzothiophene-1-dioxide dissolved in 5 cc. of glacial acetic acid was added 1.0 cc. (0.01 mole) of 30% hydrogen peroxide and the mixture refluxed five minutes. Addition of 5 cc. of water and cooling caused a precipitate to form; m. p. 176–177°. After crystallization from alcohol an 81% yield melting at 177–178° was obtained.

Anal. Calcd. for $C_{14}H_{12}S_2O_4$: C, 54.53; H, 3.92. Found: C, 54.54; H, 3.99.

Attempted Addition of Phenol to Benzothiophene-1-dioxide.—To 0.28 g. (0.012 mole) of sodium sand suspended in 50 cc. of dry benzene was added 2.28 g. (0.024 mole) of phenol. To the fluffy precipitate obtained by refluxing the mixture two hours was added 2.0 g. (0.012 mole) of benzothiophene-1-dioxide, and the refluxing continued sixteen hours. The suspension obtained on cooling the reaction mixture was poured over 200 g. of ice and the mixture allowed to come to room temperature. The benzene solution was washed with 5% sodium hydroxide solution, then with water and the benzene removed with a current of air. The solid product obtained was shown to be benzothiophene-1-dioxide by a mixed melting point comparison. The recovery was practically quantitative.

3-Dicarbethoxymethyl-2,3-dihydrobenzothiophene-1-dioxide.—To 0.28 g. (0.012 mole) of sodium sand suspended in 75 cc. of dry benzene was added 3.86 g. (0.024 mole) of malonic ester and the mixture refluxed overnight. To the white suspension obtained when the mixture was cooled was added 2.0 g. (0.012 mole) of benzothiophene-1-dioxide in 50 cc. of dry benzene. The mixture was stirred at 50° for six days without any change in appearance. When 100 cc. of water was slowly added, the solution made strongly acid with concentrated hydrochloric acid, and the benzene layer separated, washed and the benzene evaporated, there was obtained 3.35 g. of crystal, m. p. 65–80°; 86% yield. Traces of unreacted benzothiophene-1-dioxide were removed by treatment of a benzene solution of the product with a few drops of 2% potassium permanganate solution. The excess permanganate was destroyed with dilute sodium bisulfite solution, the benzene solution washed and the product recovered by evaporation of the benzene. The product was recrystallized for analysis from alcohol; m. p. 84.5–85.5°.

Anal. Calcd. for $C_{15}H_{18}SO_6$: C, 55.20; H, 5.56. Found: C, 55.14; H, 5.50.

Oxidation of Benzothiophene-1-dioxide.—A mixture of 0.3 g. (0.0018 mole) of benzothiophene-1-dioxide, 1.4 g. (0.0065 mole) of potassium permanganate and 25 ml. of water was heated on the steam-bath for five hours, acidified with concentrated hydrochloric acid, and the solution clarified with 30% hydrogen peroxide. Addition of a solution of benzylthiouronium chloride to this solution yielded 0.6 g. (60%) of the dibenzylthiouronium salt of *o*-sulfobenzoic acid, m. p. 205–206°, which did not depress the melting point of an authentic sample.[11]

Summary

The 2–3 bond in benzothiophene-1-dioxide (I) was found to be readily hydrogenated and oxidized, and was shown to undergo addition reactions with a variety of reagents. These reactions are typical of an α,β-unsaturated sulfone, and no indication of aromatic character in the 2–3 bond was revealed.

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 1, 1949

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[11] Veibel, *Bull. soc. chim.*, [5] **5**, 1153 (1938); Campaigne and Suter, THIS JOURNAL, **64**, 3040 (1942).

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Some α-Substituted β-Pyridylethylamines

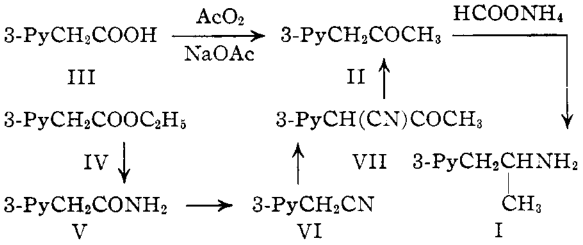
BY ALFRED BURGER AND C. ROBERT WALTER, JR.[1,2]

The three isomeric β-pyridylethylamines exhibit characteristic differences in their physiological activity depending on the position of the side-chain in the pyridine ring. The 2-isomer resembles histamine, while the 3- and 4-isomers are pressor amines,[3,4] perhaps because only the β-(2-pyridyl)-ethylammonium ion can exist in a chelated form like the histamine ion.[3]

It could be expected that these properties would be more pronounced in the corresponding β-pyridylisopropylamines since these compounds should be more refractory to enzymatic deamination than the unbranched ethylamine derivatives. In fact, β-(2-pyridyl)-isopropylamine has been found to have pronounced histamine-like activity.[5] We are now reporting the synthesis of β-(3-pyridyl)-isopropylamine (I). This compound was obtained from 3-pyridylacetone (II) by the Leuckart reaction.

Two different routes were used in preparing 3-pyridylacetone. The more rewarding one was patterned on the preparation of phenylacetone from phenylacetic acid, sodium acetate and acetic anhydride.[6] 3-Pyridylacetic acid[7] (III) furnished the ketone under analogous conditions. The second method started with 3-pyridylacetamide[7a] (V), which we prepared by the action of ammonia on ethyl 3-pyridylacetate (IV). Dehydration of the amide led to 3-pyridylacetonitrile (VI) which, when condensed with ethyl acetate, produced 3-pyridylacetylacetonitrile (VII). The latter yielded 3-pyridylacetone on acid hydrolysis.

Another series of experiments designed to lead to I began with ethyl α-nicotinoylpropionate (VIII) which we hoped to reduce to ethyl α-methyl-β-(3-pyridyl)-propionate (XI). However, this reduction could not be forced beyond ethyl α-methyl-β-hydroxy-β-(3-pyridyl)-propionate (IX) which proved singularly hard to dehydrate; only its acetate was pyrolyzed to ethyl α-methyl-β-(3-pyridyl)-acrylate (X). This unsaturated ester absorbed one mole of hydrogen but the reaction product, presumably XI, could not be characterized, and its degradation to I was not pursued further.



$$\underset{\text{VIII}}{\text{3-PyCOCH(CH}_3\text{)COOC}_2\text{H}_5} \longrightarrow \underset{\text{IX}}{\text{3-PyCHOHCH(CH}_3\text{)COOC}_2\text{H}_5} \longrightarrow \underset{\text{X}}{\text{3-PyCH=C(CH}_3\text{)COOC}_2\text{H}_5} \longrightarrow \underset{\text{XI}}{\text{3-PyCH}_2\text{CH(CH}_3\text{)COOC}_2\text{H}_5}$$

It was also considered pertinent to prepare pyridine analogs of α-phenyl substituted phenethylamines ($C_6H_5CH_2CH(C_6H_5)NH_2$] since some of the latter possess marked analgetic properties.[8] Two pyridine derivatives of this type (XIV and XVI) were therefore prepared by way of the corresponding ketones.

Ethyl nicotinate was condensed with phenylacetonitrile, and the resulting α-(3-nicotinoyl)-phenylacetonitrile (XII) was hydrolyzed and decarboxylated to benzyl-(3-pyridyl) ketone (XIII). The latter was converted to α-(3-pyridyl)-phenethylamine (XIV).

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[1] Smith, Kline and French Laboratories Fellow, 1947–1949.

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[3] Nieman and Hays, THIS JOURNAL, **64**, 2288 (1942).

[4] Walter, Hunt and Fosbinder, *ibid.*, **63**, 2771 (1941).

[5] Burger and Ullyot, *J. Org. Chem.*, **12**, 342 (1947).

[6] Magidson and Garkusha, *J. Gen. Chem.* (*U. S. S. R.*), **11**, 339 (1941); *Chem. Abstr.*, **35**, 5868[6] (1941).

[7] (a) Hartman and Bosshard, *Helv. Chim. Acta*, **24**, 28E (1941); *Soc. pour l'ind. Chim. à Bâle*, British Patent 558,774 (1944); (b) Malan and Dean, THIS JOURNAL, **69**, 1797 (1947).

[8] Dodds, Lawson and Williams, *Nature*, **151**, 614 (1943); **154**, 514 (1944); *Proc. Roy. Soc.* (*London*), **132B**, 119 (1944).