amalgam and mercury, the solution was made distinctly alkaline with ammonium hydroxide and then extracted with ether. This ether solution was dried over sodium sulfate and after removing the ether in the usual manner the base was distilled. Since 2-ethyl-4-methylaniline is not stable, we immediately converted the base into its sulfuric acid salt by solution in equal volumes of dilute sulfuric acid and 50% alcohol. A crystalline product separated upon standing. This product was crystallized twice from dilute alcohol, out of which it separated in characteristic plates melting approximately at 178°. It is soluble in alcohol and ether. Yield, 4 g.

Calc. for $(C_9H_{13}N)_2H_2SO_4$: N, 7.609; found: 7.506, 7.72.

2-Ethyl-4-methylaniline, XIV.—This compound was previously synthesized by Willgerodt and Brandt[1] by the action of molecular quantities of *p*-toluidine, ethyl alcohol and zinc-chloride at 280°. The writers obtained this same amine by the reduction of 2-acetylamido-5-methyl-chloroacetophenone with zinc-amalgam and hydrochloric acid. The procedure followed in this reduction was similar to that employed in the reduction of 3-acetylamido-6-methyl-chloroacetophenone. The product of the reaction was an oil which distilled at 217–220°. Willgerodt and Brandt assign a boiling point of 218–220° to their compound. Owing to the instability of the base, it was converted into its sulfuric acid salt by solution in 50% alcohol and sulfuric acid. The salt soon separated in characteristic platy crystals melting at 241°. The physical and chemical properties of this sulfate are entirely in accord with those of the sulfate described by Willgerodt and Brandt.

Calc. for $(C_9H_{13}N)_2H_2SO_4$: N, 7.608; found: N, 7.60, 7.55.

NEW HAVEN, CONN.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON HYDANTOINS. XXXI. A NEW SYNTHESIS OF *o*-TYROSINE.[2]

BY TREAT B. JOHNSON AND WALTER M. SCOTT.

Received June 8, 1915.

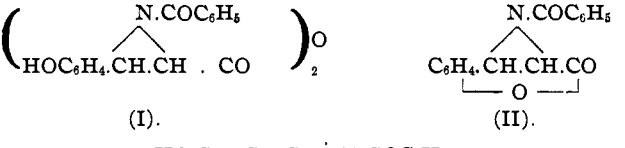
It has already been demonstrated that the *hydantoin-method* of synthesizing α-amino acids is one of quite general application. In fact, the results obtained thus far, and discussed in previous papers from this laboratory, show that the methylene radical of the polypeptide grouping—$NH.CH_2.CO$—in a hydantoin is as reactive towards the aldehyde group as is the same combination in the hippuric acid molecule $C_6H_5CONHCH_2$-

[1] *J. prakt. Chem.*, [2] **69**, 436 (1904).

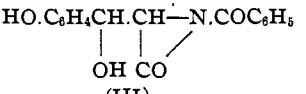
[2] Part of a dissertation presented by Mr. Walter Moody Scott to the Faculty of the Graduate School of Yale University, 1915, in Candidacy for the Degree of Doctor of Philosophy.

COOH. Twelve aldehydes have thus far been included in our researches, of which every one has interacted smoothly with hydantoin or 2-thiohydantoins with formation of the corresponding condensation products. The choice of aldehydes, however, has purposely been confined to representatives of the aromatic series. The only possible exception is that of cinnamic aldehyde, which may be viewed either as an aromatic or an aliphatic representative. Attempts are now being made to apply our method of α-amino acid synthesis with aliphatic aldehydes. In order to obtain still further evidence of the utility of our method we deemed it desirable, for several reasons, to demonstrate its application for the synthesis of *o*-tyrosine from salicylic aldehyde. This has now been accomplished and likewise the complete synthesis of the methyl ether of *o*-tyrosine from methyl salicylic aldehyde. A complete description of these two syntheses is now recorded in this paper.

That salicylic aldehyde will condense with hippuric acid in the presence of acetic anhydride was first observed by Plöchl and Wolfrum.[1] They represented the condensation product as an anhydride, corresponding to Formula I, which was converted on hydrolysis into a benzoylimidocumarin represented by Formula II. Rebuffat[2] later applied the same reaction and apparently obtained the same products as described by Plöchl and Wolfrum. He assigned, however, to his primary condensation product the structural formula III. Both of these interpretations were,



(I). (II).



(III).

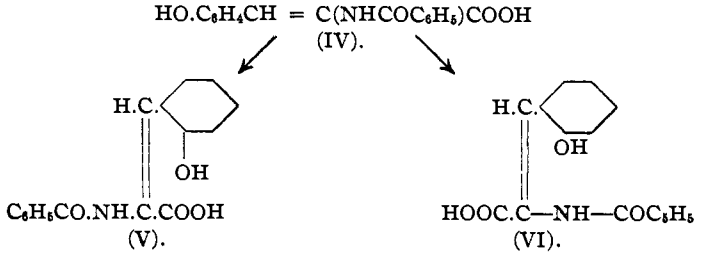
however, shown to be incorrect. The true explanation of the nature of these aldehyde condensation products was given by Erlenmeyer, Jr., in a series of papers published several years later.[3] Erlenmeyer and Stadlin[4] showed that salicylic aldehyde, for example, condenses normally with hippuric acid giving first the unsaturated acid IV, which they assumed was capable of existing in two stereoisomeric modifications as represented by Formulas V and VI. In the presence of the acetic anhydride these two acids then underwent further characteristic changes. The acid (V)

[1] *Ber.*, **18**, 1183 (1885).

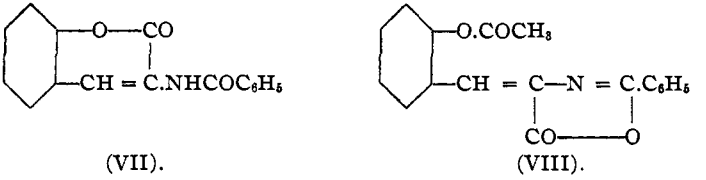
[2] *Gaz.*, **19**, 43 (1889).

[3] *Ann.*, **271**, 137 (1892); **275**, 1 (1893); Erlenmeyer and Stadlin, *Ibid.*, **237**, 265, 283; Erlenmeyer and Arbenz, *Ibid.*, **337**, 302 (1904).

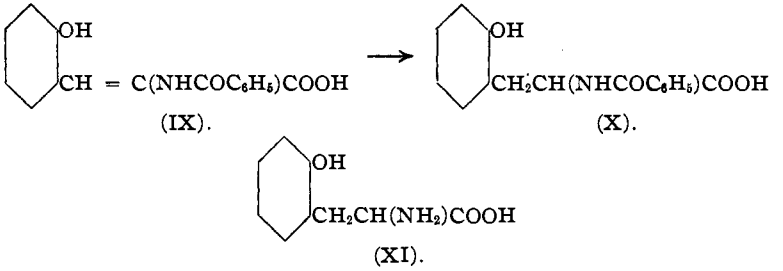
[4] *Loc. cit.*



was transformed into a colorless benzoylaminocumarin (VII), which was identical with Plöchl and Wolfrum's *benzoylimidocumarin*, while its stereoisomer (VI) underwent acetylation and finally an inner condensation, giving the azlactimide corresponding to Formula VIII.



In 1908, Blum[1] repeated this work of Erlenmeyer and Stadlin's and converted the azlactimide (VIII), by hydrolysis with alkali, into the acrylic acid (IX). The latter, on reduction with sodium amalgam, was then transformed into the acid (X), which was converted into *o*-tyrosine



(XI), by hydrolysis with hydrochloric acid. This is the only method of synthesizing this acid, which has hitherto been described in the literature.

The starting point in our synthesis of *o*-tyrosine was 2-thiohydantoin NH.CS.NH.CH_2.CO, which is now an easily obtainable reagent if glycocoll is available. If glycocoll is not available any acyl derivative of this amino acid, as hippuric acid, will serve for its preparation. Several hundred grams of the reagent have been prepared in this laboratory during the progress of our hydantoin researches. This thiohydantoin was selected for our investigation after we had made the observation that hydantoin does not react smoothly with salicylic aldehyde to give the corre-

[1] *Arch. Exp. Pathol. u. Pharm.*, **59**, 273 (1908).

sponding condensation product, namely, hydroxybenzalhydantoin (XV). On the other hand, 2-thiohydantoin and salicylic aldehyde interact smoothly, when heated together in acetic acid solution and in the presence of fused sodium acetate, giving an excellent yield of the 2-thio-4-hydroxybenzalhydantoin (XVI). The hydantoin (XV), which theoretically should be formed by condensation of hydantoin with salicylic aldehyde, is obtained in almost a quantitative yield by desulfurization of this thiohydantoin (XVI), by digesting with chloroacetic acid.

The thiohydantoin (XVI) undergoes reduction normally by the action of sodium amalgam in an alkaline solution, forming the corresponding saturated derivative—2-thio-4-hydroxybenzylhydantion (XIV). When the latter compound was digested with chloroacetic acid it was converted smoothly into the hydantoin of *o*-tyrosine (XIII). This same hydantoin (XIII) is also found by reducing the hydroxybenzalhydantoin (XV) with sodium amalgam. In fact, we found that the best method for preparing this hydantoin (XIII) in quantity is to first desulfurize the original thiohydantoin (XVI) with formation of the hydantoin (XV) and then to subject this to reduction with sodium amalgam. By proceeding in the reverse manner, namely, by reduction to the hydantoin (XIV) and then desulfurizing this with chloroacetic acid, a much poorer yield is obtained. By long digestion of the hydantoin (XIII) with an excess of barium-hydroxide solution a good yield of *o*-tyrosine is obtained with evolution of ammonia and formation of barium carbonate. A description of the properties of this acid is given in the experimental part of this paper.

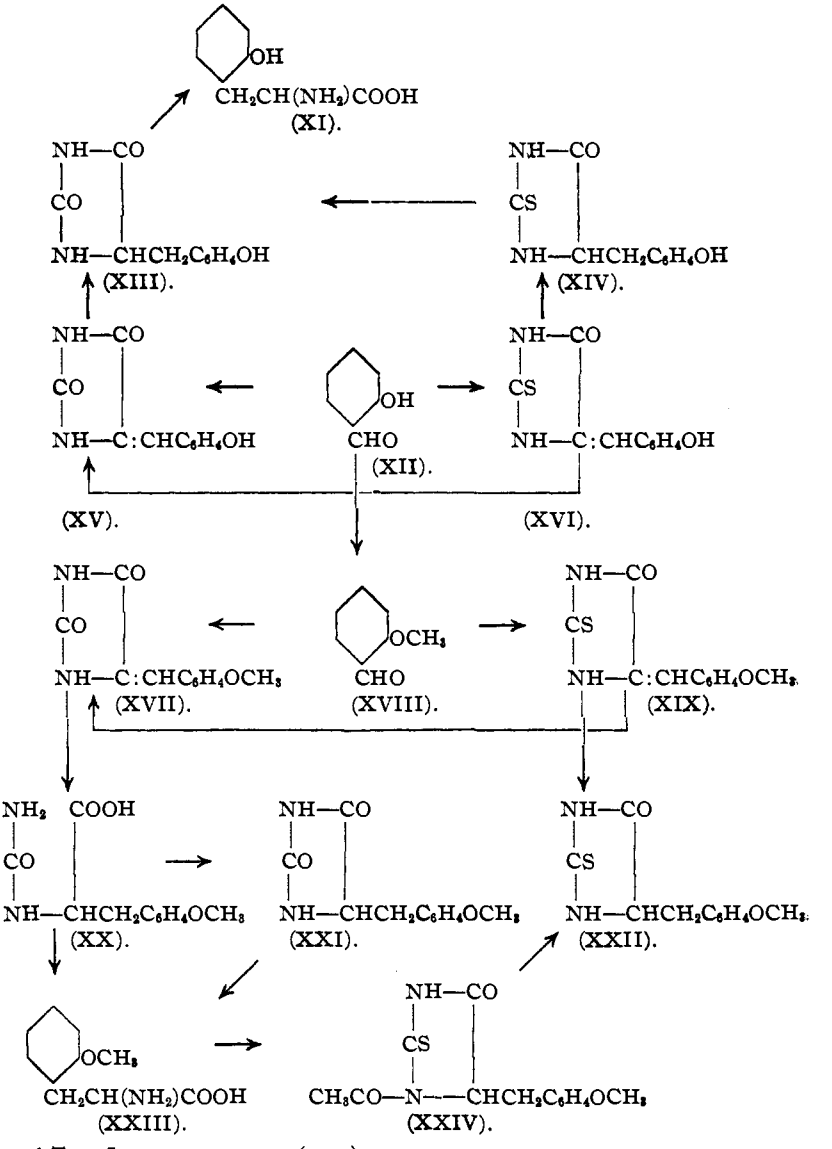
In order to synthesize the methyl ether of *o*-tyrosine (XXIII) we first prepared the methyl ether of salicylic aldehyde according to the method of Voswinckel.[1] Here again we made the observation that 2-thiohydantoin showed a greater tendency to interact with this aldehyde than did plain hydantoin. The condensation product (XVII) could be obtained by interaction of the aldehyde and hydantoin, but the yield was small. On the other hand, 2-thiohydantoin and methylsalicylic aldehyde combined to give an excellent yield of 2-thio-4-methoxybenzalhydantoin (XIX). This hydantoin is easily converted into the hydantoin (XVII) when digested with chloroacetic acid.

While 2-thio-4-methoxybenzalhydantoin (XIX) undergoes reduction with sodium amalgam, in the usual manner, forming the hydantoin (XXII), on the other hand, the hydantoin (XVII) is reduced abnormally by the same reagent, giving the hydantoic acid (XX). This new acid is converted smoothly into the normal hydantoin (XXI), by digesting with concentrated hydrochloric acid. The *o*-methoxyphenylalanine (XXIII) is easily obtained by hydrolysis of the hydantoin (XXI) or its corresponding

[1] *Ber.*, **15**, 2024 (1882).

acid (XX) with barium hydroxide. A description of this acid is given in the experimental part of this paper.

Johnson and Nicolet's[1] thiohydantoin reaction can be applied successfully with this amino acid. It reacted normally with ammonium thiocyanate in acetic anhydride solution, giving smoothly the 2-thio-3-acetyl-4-methoxybenzylhydantoin represented by Formula XXIV. When this



[1] THIS JOURNAL, 33, 1973 (1911).

was warmed with hydrochloric acid it underwent hydrolysis with formation of 2-thio-4-methoxybenzylhydantoin (XXII). The various changes involved in the synthesis of these two α-amino acids are represented by the preceding structural formulas.

Our researches on hydantoins will be continued.

Experimental Part.

The 2-thiohydantoin, which was used in this investigation, was prepared according to the method of Johnson and Nicolet[1], namely: by the action of ammonium thiocyanate on hippuric acid in the presence of acetic anhydride.

2-Thio-4-*o*-hydroxybenzalhydantoin (XVI).—This hydantoin is obtained in nearly a quantitative yield by condensing salicylic aldehyde (XII) with 2-thiohydantoin. Thirty grams of the hydantoin, 37.5 g. of salicylic aldehyde, 90 g. of fused sodium acetate and 230 cc. of glacial acetic acid were heated together in an oil bath for 4 hours at 140–150°. While the reaction mixture was still hot, it was then poured into a large volume of cold water, whereupon the above hydantoin separated immediately. After complete disintegration, to remove sodium acetate, the crude hydantoin was then separated by filtration and purified by crystallization from hot, glacial acetic acid. It separated from this solvent, on cooling, in small clusters of radiating needles which melted at 248°.

Calc. for $C_{10}H_8O_2N_2S$: N, 12.72. Found: N, 12.86, 12.60.

Desulfurization of 2-Thio-4-*o*-hydroxybenzalhydantoin with Formation of 4-*o*-Hydroxybenzalhydantoin (XV).—Fifty grams of the thiohydantoin, 150 g. of monochloroacetic acid and 400 cc. of water were placed in a flask and the mixture then digested in an oil bath for 2 hours at 140–150°. Owing to the insolubility of both the thio- and oxyhydantoins a clear solution was never obtained. However, even under such conditions the sulfur was displaced smoothly and an 80% yield of the hydantoin was obtained. After the reaction was complete the benzalhydantoin was separated by filtration, washed thoroughly with water and then purified by crystallization from a large volume of alcohol. It was difficultly soluble in this solvent and separated, on cooling, in the form of short needles which melted at 271° with decomposition.

Calc. for $C_{10}H_8O_3N_2$: N, 13.72. Found: N, 13.57, 13.87.

Attempts were made to prepare this new hydantoin directly by condensing salicylic aldehyde with hydantoin. The reaction was applied by digesting the reagents in acetic acid solution in the presence of anhydrous sodium acetate and also in the presence of acetic anhydride. In no case, however, did we observe a smooth formation of the hydantoin. This marked difference in reactivity of hydantoin and thiohydantoin has

[1] *Loc. cit.*

been observed in the case of other aldehydes which we have incorporated in our work.

2-Thio-4-*o*-hydroxybenzylhydantoin (XIV).—After several unsuccessful attempts to reduce 1-thio-4-hydroxybenzalhydantoin to the above benzylhydantoin with stannous chloride in hydrochloric acid solution and with hydriodic acid, we finally succeeded in effecting the reduction by using sodium amalgam. Our procedure was as follows: Four grams of the thiohydantoin were dissolved in 45 cc. of a mixture of equal volumes of water and a 10% solution of sodium hydroxide. The hydantoin dissolves with formation of a deep red solution. This solution was then heated to 75° and held at this temperature while 150 g. of 3% sodium amalgam were added, in small portions at a time. As the compound underwent reduction the solution finally became almost colorless. The solution was then separated from the mercury and acidified with hydrochloric acid. The hydantoin did not separate under these conditions; consequently the solution was concentrated by evaporation until the crude hydantoin had partially separated as a semisolid. The supernatant liquor was then poured off and cooled when the hydantoin was obtained in a crystalline condition. More of the same compound was obtained by digesting the semisolid residue with fresh water. By repeated extractions an excellent yield of the hydantoin was finally obtained. It crystallized from water in rosettes of needles which melted at 107° to an oil.

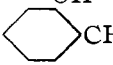
Calc. for $C_{10}H_{10}O_2N_2S$: N, 12.63. Found: N, 12.40.

Desulfurization of 2-Thio-4-orthohydroxybenzylhydantoin with Formation of *o*-Tyrosinehydantoin (XIII).—This change is easily effected by digesting the thiohydantoin with chloroacetic acid. Three and five-tenths grams of the thiohydantoin were suspended in 10 cc. of water containing 3 g. of monochloroacetic acid. After heating this mixture for about one hour, in an oil bath at 130°, a clear solution was obtained. This was then cooled, when the hydantoin of tyrosine separated in a crystalline condition. This hydantoin was purified by crystallization from water, and separated in clusters of stout, prismatic crystals which melted at 205–206°.

Calc. for $C_{10}H_{10}O_3N_2$: N, 13.59. Found: N, 13.56.

o-Tyrosinehydantoin (XIII) is also formed by reduction of 4-orthohydroxybenzylhydantoin (XV) with sodium amalgam. In fact, this is the better method of the two for the synthesis of this compound. The reduction is easily accomplished as follows: Ten grams of the unsaturated hydantoin are dissolved in a mixture of 30 cc. of 10% sodium hydroxide and 75 cc. of water. The resulting solution is then warmed to about 80° and the hydantoin reduced by gradual addition of 100 g. of 3% sodium amalgam. At the end of one hour add slowly 100 g. more of the amalgam

and finally heat for 3–4 hours at 75–80°. Practically a colorless solution is obtained. This is then cooled, separated from the mercury and acidified with an excess of hydrochloric acid. There is generally no precipitation of hydantoin at this point. On concentrating the solution, however, and cooling the hydantoin will separate in a crystalline condition. It melted at 205–206° and the yield was 85% of the theoretical.

Hydrolysis of *o*-Tyrosinehydantoin with Barium Hydroxide, *o*-Tyrosine,  $CH_2.CH(NH_2)COOH$.—For complete conversion into this α-amino acid, it is necessary to digest this hydantoin with strong barium hydroxide solution for several hours. Working with 7 g. of the hydantoin, it was our experience that the hydrolysis was complete after 48 hours' digestion. In order to isolate the amino acid the barium was exactly precipitated as barium sulfate and the colorless solution of the amino acid then concentrated and cooled. The *o*-tyrosine then separated in a crystalline condition. The acid dissolves with difficulty in water and when once in solution separates again only on long standing. Our procedure was to dissolve the acid in hot water and then allow the solution to evaporate spontaneously in a vacuum over concentrated sulfuric acid. In this manner the acid was obtained nearly colorless and in a crystalline condition. The acid gave Millon's test and also a violet coloration in aqueous solution when allowed to interact with ferric chloride. Blum[1] assigned to this amino acid a melting point of 249–250°. It was our experience that this acid has an indefinite decomposition point. If our product was heated slowly it underwent a noticeable change at about 232–3°, decomposing with effervescence and forming an oil which solidified again. The latter substance did not undergo further change until the temperature of the bath was raised to 270° when it finally melted to an oil. The temperature of primary decomposition was indefinite depending on the rate of heating. If heated rapidly there was no evidence of a change at 232° but the substance decomposed at 247–250°. It is probable that *o*-tyrosine undergoes an inner condensation on melting with loss of a molecule of water.

Calc. for $C_9H_{11}O_3N$: N, 7.73. Found: N, 7.72.

Hydrochloride of *o*-Tyrosine.—Crystallizes from dilute hydrochloric acid in prismatic crystals which decompose at 180°.

Calc. for $C_9H_{12}O_3NCl$: N, 6.44. Found: N, 6.39, 6.53.

The methylsalicylic aldehyde (XVIII) which was used in the following work was prepared according to the directions of Voswinckel[1] by alkylation of salicylic aldehyde (XII) with methyl iodide in the presence of sodium methylate.

[1] *Loc. cit.*

From 20 g. of salicylic aldehyde we obtained 17.5 g. of its methyl ether boiling at 236–240°. Voswinckel assigned to the oil a boiling point of 238°

Condensation of Methylsalicylic Aldehyde with 2-Thiohydantoin.

2-Thio-4-*o*-methoxybenzalhydantoin (XIX).—The following proportions were taken for the preparation of this compound: 10.3 g. of thiohydantoin, 12 g. of the aldehyde, 30 g. of fused sodium acetate and 75 cc. of glacial acetic acid. This mixture was then heated in an oil bath at 140–150° for 6 hours, when it was poured while warm into a large volume of cold water. The thiohydantoin separated at once in a crystalline condition. The yield was 20.5 g. which was almost equal to the theoretical amount. The hydantoin was purified by crystallization from alcohol and melted at 227° to an oil. It crystallized in the form of needles.

Calc. for $C_{11}H_{10}O_2N_2S$: N, 11.96. Found: N, 11.82, 11.91.

Condensation of Methylsalicylic Aldehyde with Hydantoin.

4-*o*-Methoxybenzalhydantoin (XVII). — The following proportions were taken for the preparation of this hydantoin: 2.5 g. of hydantoin, 3.5 g. of the aldehyde, 7.5 g. of sodium acetate and 25 cc. of glacial acetic acid. This mixture was then heated at 130–140° for 4 hours when a clear solution was obtained, which solidified on cooling. This product was then dissolved in a small volume of hot water and the solution cooled when the above hydantoin separated. The yield was only 2.2 g. It was purified by crystallization from alcohol and melted at 178°.

A 75% yield of this same hydantoin is obtained by desulfurization of 2-thio-4-*o*-methoxybenzalhydantoin (XIX). Eight grams of the thiohydantoin were digested with 16.3 g. of chloroacetic acid and 50 cc. of water for 4 hours at 130–140°. A clear solution was obtained from which the above hydantoin immediately separated on cooling. It crystallized from 95% alcohol in long, slender prisms or needles which melted at 178° to an oil.

Calc. for $C_{11}H_{10}O_3N_2$: N, 12.84. Found: N, 12.81, 12.91.

Reduction of 4-*o*-Methoxybenzalhydantoin with Sodium Amalgam.

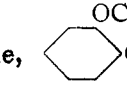
***o*-Methoxybenzylhydantoic Acid (XX).**—One hundred and seventy-five cubic centimeters of a 10% solution of sodium hydroxide were mixed with 300 cc. of water and 30 g. of the above hydantoin dissolved in the solution with the aid of heat. If this solution was cooled after complete solution of the hydantoin its sodium salt separated immediately in colorless crystals. In order to keep this salt in solution the latter was heated to 80–90° and then 600 g. of 3% amalgam slowly added. After the final addition of amalgam the solution was then warmed for 3–4 hours and finally acidified with dilute hydrochloric acid. There was an immediate precipitation of the hydantoic acid. The yield was 29 g. This new acid

crystallized from alcohol in rectangular prisms which melted at 189° with effervescence.

Calc. for $C_{11}H_{14}O_4N_2$: N, 11.76. Found: N, 11.87, 11.64.

4-*o*-Methoxybenzylhydantoin (XXI).—The 29 g. of the hydantoic acid from the preceding experiment were converted into this hydantoin by warming with dilute hydrochloric acid. The hydantoic acid dissolved in this solvent on warming, but as the heating was continued the hydantoin finally deposited from the hot solution. The hydantoin is practically insoluble in cold hydrochloric acid. It is easily purified by crystallization from alcohol and separates from this solvent in prisms which melt at 186° to an oil. The yield was quantitative.

Calc. for $C_{11}H_{12}O_3N_2$: N, 12.73. Found: N, 12.57, 12.68.

***o*-Methoxyphenylalanine,**  $CH_2.CH(NH_2)COOH$. — This amino acid is easily obtained by hydrolysis of the above hydantoic acid or the hydantoin (XXI), with strong barium hydroxide solution. Our procedure was practically the same as that applied in the preparation of *o*-tyrosine from its hydantoin. From 7.5 g. of the hydantoic acid we obtained 4 g. of the α-amino acid. It was purified by crystallization from hot water and separated in rosettes of needles. The acid melted at 206° with effervescence.

Calc. for $C_{10}H_{13}O_3N$: N, 7.18. Found: N, 7.21, 7.14.

Condensation of *o*-Methoxyphenylalanine with Ammonium Thiocyanate in Acetic Anhydride Solution.

2-Thio-3-acetyl-4-*o*-methoxybenzylhydantoin (XXIV).—This hydantoin is easily obtained by warming 1.5 g. of the α-amino acid and 0.7 g. of dry ammonium thiocyanate with 8 cc. of acetic anhydride and 1 cc. of glacial acetic acid for 30 minutes at 100°. On pouring the resulting solution into water the hydantoin separated immediately. The yield was excellent. The hydantoin was purified by crystallization from alcohol and melted at 168°.

Calc. for $C_{13}H_{14}O_3N_2S$: N, 10.07. Found: N, 10.05.

2-Thio-4-*o*-methoxybenzylhydantoin (XXII).—A quantitative yield of this compound was obtained by hydrolysis of the preceding hydantoin with hydrochloric acid. It was purified for analysis by crystallization from alcohol and melted at 190°.

This same 2-thiohydantoin was also obtained by reduction of the above 2-thio-4-*o*-methoxybenzalhydantoin (XIX) with sodium amalgam. This was accomplished by dissolving 5 g. of the thiohydantoin in dilute alkali and then reducing with 100 g. of sodium amalgam at 70–80°. When the reduction was complete the solution was then acidified with hydrochloric acid when an oil separated which soon solidified. This substance

was then warmed with an excess of hydrochloric acid to convert any hydantoic acid present into hydantoin and then finally purified by crystallization from alcohol. It melted at 190°.

Calc. for $C_{11}H_{12}O_2N_2S$: N, 11.86. Found: N, 11.80.

NEW HAVEN, CONN.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON HYDANTOINS. XXXII. SYNTHESIS OF THE HYDANTOIN OF 2-HYDROXY-5-AMINOPHENYLALANINE.[1]

BY TREAT B. JOHNSON AND WALTER M. SCOTT.

Received June 11, 1915.

The hydantoins of aminophenylalanine derivatives have become of especial interest to us because it now seems very probable that they will find application for the synthesis of α-amino acids of biochemical interest, which it is now practically impossible to prepare easily by other methods. They should be valuable for operations where it is desired to introduce groups into the benzene nucleus by application of the diazo reaction, because the basic influence of the α-amino group of the acid is completely neutralized in such combinations. Furthermore, it has been our experience that the incorporation of the hydantoin nucleus tends to bestow physical properties which are very essential for synthetical work. Such cyclic combinations should be especially valuable for developing methods of synthesizing new, isomeric halogen derivatives of phenylalanine and tyrosine. The iodine derivatives of these two acids are of special physiological interest at the present time. Investigations dealing with methods of synthesis, and other phases of these interesting problems are now in progress in this laboratory.

The only aminohydantoin derivatives of phenylalanine or tyrosine which have hitherto been available for synthetical work are the hydantoins of 3-aminotyrosine (III), and its corresponding methyl ether (II), which have been described by Johnson and Bengis[2] in a previous paper from this laboratory. They were prepared by the reduction of 3-nitro-4-methoxybenzalhydantoin (I) with hydriodic acid, and tin and hydrochloric acid, respectively. Johnson and Bengis employed the hydantoin (II), for the synthesis of monobromotyrosine (V).[3] This was accomplished by diazotization of the amino group and by subsequent introduction of bromine into the benzene ring in the usual manner. On subjecting the resulting bromohydantoin to hydrolysis 3-bromo-4-methoxyphenyl-

[1] Part of a dissertation presented by Mr. Walter M. Scott to the Faculty of the Graduate School of Yale University, 1915, in candidacy for the Degree of Doctor of Philosophy.

[2] THIS JOURNAL, 34, 1054 (1912).

[3] *Ibid.*, 34, 1061 (1912).