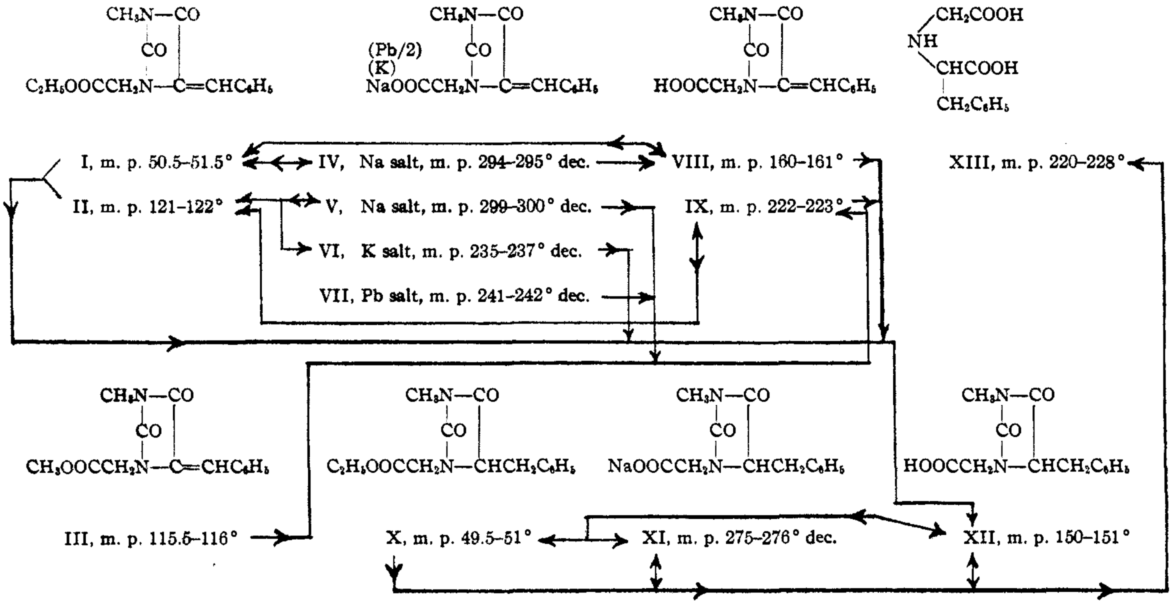
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

The Synthesis of Ethyl N-3-Methyl-5-benzalhydantoin-N-1-acetate and Certain of its Derivatives[1]

BY ANNE LITZINGER

The object of the present investigation is to establish the chemistry of hydantoins intermediate in the synthesis of β-phenylalanine-N-acetic acid, an imino-dibasic acid whose preparation has been reported.[2] These hydantoins may be divided into two classes, unsaturated and saturated. In the case of the former the number of isomers obtained corresponds to that theoretically required on the basis of geometrical isomerism. As has been observed in other cases[3] the modification which was obtained as the primary product resulting from condensations in alkaline or neutral solutions, was readily converted into the corresponding isomer under the action of dry hydrogen chloride. The nature of the isomerism was established by the fact that in the case of the ethyl esters both modifications were observed on reduction and bromination, respectively, to yield the same compound. The inter-relationships of the unsaturated derivatives together with their conversion into the saturated acid, N-3-methyl-5-benzylhydantoin-N-1-acetic, are indicated in the accompanying chart. Additional evidence in support of these formulas is furnished by the fact that the above acid, its ethyl ester and its sodium salt, are all transformed into β-phenylalanine-N-acetic acid under the prolonged action of barium hydroxide.



Experimental

Ethyl N-3-methyl-5-benzalhydantoin-N-1-acetate, I, m. p. 50.5–51.5°, and b. p. 215–216° (5.5 mm.), was obtained by condensing ethyl chloroacetate with N-3-methyl-5-benzalhydantoin. The latter was prepared by alkylating benzalhydantoin[4] with methyl iodide using the same procedure as has been described in the case of N-3-methyl-5-anisalhydantoin.[5] This method of preparation is new but the product so obtained was found to be identical in all respects with the compound previously described as resulting from the desulfurization of N-3-methyl-2-methylmercapto-5-benzalhydantoin.[6] The best percentage yields of condensation product were obtained by means of the following method.

Fifty grams of methyl-benzalhydantoin, m. p. 220–221°, was added under constant shaking to 500 cc. of absolute alcohol containing 1.2 equivalents (7.0 g.) of sodium. The yellow sodium derivative, which precipitated immediately, dissolved almost completely after refluxing for five hours on a steam-bath. At the end of this time 1.1 equivalents (37.5 g.) of ethyl chloroacetate (dried over calcium chloride) was added to the hot solution and the heating continued. Within twenty-five minutes a heavy

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[1] Offered in partial fulfilment for the degree of Master of Arts at Mount Holyoke College in consultation with Dr. Dorothy A. Hahn.

[2] Hahn and Litzinger, THIS JOURNAL, **54**, 4665 (1932).

[3] Hahn and Gilman, *ibid.*, **47**, 2953 (1925).

[4] Hahn and Evans, *ibid.*, **50**, 811 (1928).

[5] Johnson and Nicolet, *Am. Chem. J.*, **47**, 469 (1912); Hahn and Renfrew, THIS JOURNAL, **47**, 149 (1925).

[6] Johnson and Nicolet, *ibid.*, **34**, 1052 (1912).

white powder had precipitated and simultaneously the color of the solution had changed from a brownish-yellow to a pale lemon. However, since the reaction mixture was still alkaline the heating was continued for a period of from nineteen to twenty hours, or until the solution was neutral to turmeric.

On cooling and standing no additional precipitate was formed and the mixture was therefore filtered and washed with absolute alcohol. The precipitate on examination was found to consist of sodium chloride mixed with a small quantity of unacted upon methyl-benzalhydantoin (6.0 g.[7]). Since in preliminary experiments the filtrate and alcohol washings from this precipitate when concentrated to 100 cc. in a vacuum did not crystallize even after standing for months,[8] it was taken up in ether and the ether solution washed repeatedly with water.[9] After drying over calcium chloride, the ether was removed as completely as possible and the residual oil subjected to vacuum distillation. Under these conditions after the metal bath had reached a temperature of 255–260°, a clear colorless oil (51.4 g.) was collected which boiled between 215–216° at a pressure of 5.5 mm. Crystallization of this oil took place spontaneously but very slowly. When, however, ether was added (one-third the volume) a solid mass of heavy white crystals of m. p. 49–51° was immediately formed.[10] This substance was further purified by dissolving it in dry ether and allowing the ether to evaporate almost completely in a partial vacuum when large transparent plates, m. p 50.5–51.5°, were obtained.

Anal. Calcd. for $C_{15}H_{16}O_4N_2$: N, 9.72. Found: N, 9.55, 9.51.

The substance is extremely soluble in all organic solvents and begins to crystallize slowly only after the solvent has been almost or completely removed. Traces of alcohol appear to retard while traces of ether accelerate crystallization. As indicated in the chart and more specifically in other parts of this paper, ester I was readily transformed into its isomer II, the sodium salt IV, the unsaturated acid VIII and the saturated acid XII.

Ethyl N-3-methyl-5-benzalhydantoin-N-1-acetate, II, of m. p. 121–122° was obtained by dissolving the pure ester I in 95% alcohol and passing hydrogen chloride into the hot solution. It was, however, prepared more conveniently in quantity by starting with the crude oil resulting from the above condensation, without purification by vacuum distillation and subsequent recrystallization. For example, oil obtained from a condensation in which 43.5 g. of methylbenzalhydantoin had reacted, was dissolved in 150 cc. of alcohol and during a period of three and one-half hours was alternately saturated with hydrogen chloride and refluxed on a steam-bath. The dark red fuming solution on cooling was slowly filled with fine white needles growing in rosets. Isomerization was accompanied by a change of color from pale lemon to deep red which was completely discharged when precipitation had ceased. After filtering and washing the precipitate with alcohol, the now almost colorless solution was first concentrated and then treated with hydrogen chloride until it again became red and fuming. By repeating this process seven or eight times 48.2 g. of an almost pure substance melting at 119–121° was accumulated[11] and in a series of experiments yields averaging from 80 to 90% were obtained. After three recrystallizations from alcohol from which it separates in long hard translucent needles growing in rosets this substance melted at 121–122°.

Anal. Calcd. for $C_{15}H_{16}O_4N_2$: N, 9.72. Found: N, 9.82, 9.89.

This ester is less soluble than its isomer and crystallizes on cooling from hot saturated solutions of alcohol (1 g. in 5 cc. hot and in 60 cc. cold), and carbon tetrachloride (1 g. in 4 cc. hot). It passes quantitatively into the sodium salt V, potassium salt VI, the unsaturated acid IX and the saturated acid XII.

Methyl N-3-methyl-5-benzalhydantoin-N-1-acetate, III, m. p. 115.5–116°, was prepared by alkylating the sodium derivative of N-3-methyl-5-benzalhydantoin with methyl bromoacetate in exactly the same manner as has been described in the preparation of the ethyl ester II.[12] In this case the first crop of fine white needles which separated from the dark red fuming alcohol solution amounted to 60% and no attempt was made to accumulate additional quantities from the filtrate. This substance[11] (m. p. 111–114°) after four recrystallizations from 90% aqueous methyl alcohol separated in sheaves of long white needles of m. p. 115.5–116°.

Anal. Calcd. for $C_{14}H_{14}O_4N_2$: N, 10.22. Found: N, 10.16, 10.35.

The ester is very soluble in absolute methyl alcohol (1 g. in 2 cc. hot and 11 cc. cold) and less soluble in aqueous 90% methyl alcohol (1 g. in 8 cc. hot and 33 cc. cold). It passes quantitatively into the higher melting unsaturated acid IX when boiled for ten minutes with aqueous hydrochloric acid (1:1).

Sodium N-3-methyl-5-benzalhydantoin-N-1-acetate, IV, m. p. 294–295° with decomposition, was obtained by treating the crude oil, resulting from the condensation of methyl-benzalhydantoin with ethyl chloroacetate in the preparation of the ester I, with alcoholic sodium hydroxide. Under the conditions of the experiment the hydrolysis was incomplete but the results are interesting because of the fact that unacted upon ester I was isolated from the reaction mixture in crystalline condition.[13] For example, an oil resulting from a condensation in which 18 g. of

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(7) The same constant percentage of methyl-benzalhydantoin was recovered in a series of eleven condensations.

(8) It seems probable from later observations that the presence of small quantities of alcohol interferes with crystallization.

(9) The water extract when acidified and then evaporated to dryness left no deposit.

(10) Small quantities of this same ester were obtained in a less pure condition from the reaction mixture resulting from the alkaline hydrolysis of the crude oily condensation product in the preparation of the salt IV.

(11) The crystals obtained in this way were always characterized by a strong odor of benzaldehyde, indicating that isomerization was accompanied by partial cleavage at the ethylene double bond. The substance when pure also developed this odor faintly (without noticeable change in melting point) but only after standing in bottles for more than a year. Compare Hahn and Evans, THIS JOURNAL, **50**, 811 (1928).

(12) A lower melting modification of this ester (corresponding to the ethyl ester I) was never isolated although it was probably represented in the oily product resulting from the condensation.

(13) The experiment when repeated gave the same results and represents the only instance when crystals of this ester were obtained from the oil prior to its vacuum distillation.

methylbenzalhydantoin had reacted, was dissolved in 150 cc. of alcohol and refluxed for one hour with sodium hydroxide (1.1 equivalents in 3 cc. of water). Since no precipitate separated on cooling an equal volume of ether was added when 9.8 g. of a white crystalline powder, m. p. 290–294° with decomposition, was obtained. This was filtered and washed with alcohol–ether mixtures (1:1). The filtrate was evaporated almost to dryness when 9.4 g. of the ester I, m. p. 45–49°, crystallized. The salt obtained in this way was pure after three recrystallizations, separating from alcohol–ether mixtures in the form of transparent prisms which rapidly became opaque during the process of filtration but which decomposed sharply at 294–295°.

Anal. Calcd. for $C_{13}H_{11}O_4N_2Na$: N, 9.93. Found: N, 10.13.

The salt dissolves readily in water and in hot alcohol (1 g. in 25 cc.) to form colorless solutions. It is insoluble in ether and may be conveniently precipitated from cold saturated alcohol solutions on the addition of two volumes of ether. When its aqueous solutions are acidified with hydrochloric acid it passes quantitatively into the unsaturated acid VIII. Attempts to prepare the crystalline ester I corresponding to this acid by dissolving the salt in absolute alcohol and running in dry hydrogen chloride were unsuccessful, the product consisting of an oil mixed with small quantities of the isomeric ester II.

Sodium N-3-methyl-5-benzalhydantoin-N-1-acetate, V, m. p. 299–300° with decomposition, and **potassium N-3-methyl-5-benzalhydantoin-N-1-acetate, VI,** m. p. 235–237° with decomposition, were both prepared in quantity by dissolving the ester II in alcohol and treating, respectively, with 1.1 equivalents of concentrated aqueous sodium or potassium hydroxide. After refluxing for one hour and then cooling both solutions became filled with soft white crystals which were filtered and washed. The sodium salt was recrystallized from alcohol and the potassium salt from alcohol–ether mixtures. After several recrystallizations the sodium salt was obtained in the form of fine white needles which decomposed sharply at 299–300° and which when dried in the oven at 110° suffered no loss in weight.

Anal. Calcd. for $C_{13}H_{11}O_4N_2Na$: N, 9.93. Found: N, 9.41, 9.26.

The potassium salt after several recrystallizations from alcohol was obtained in the form of hard compact crystals which first melted at 80°, resolidified at about 130° and then melted with decomposition at 235–237°. After being heated to constant weight at 110° the crystals became opaque but again melted with decomposition at 235–237°.

Anal. Calcd. for $C_{13}H_{11}O_4N_2K \cdot C_2H_5OH$: C_2H_5OH, 13.38. Found: C_2H_5OH, 11.23, 11.22. Calcd. for $C_{13}H_{11}O_4N_2K$: N, 9.40. Found: N, 9.43, 9.23.

Both salts passed quantitatively into the unsaturated acid IX when their aqueous solutions were acidified with hydrochloric acid, and into the saturated acid XII under the action of hydrogen iodide. The sodium salt when suspended in absolute alcohol and the solution saturated with dry hydrogen chloride was transformed quantitatively into the corresponding ester II.

Lead N-3-methyl-5-benzalhydantoin-N-1-acetate, VII, m. p. 241–242° with decomposition, was formed immediately as a heavy white precipitate, m. p. 236–240°, when aqueous lead nitrate was added to an aqueous solution of the salt V. The crude product was recrystallized twice from boiling water, from which it separated in long white needles resembling cellulose fibers and completely filling the solution. The pure substance melted at 241–242° with decomposition but when exposed to light for even a short time its decomposition point was lowered and this was accompanied by a change in color from white to yellow.

Anal. Calcd. for $C_{13}H_{11}O_4N_2Pb_{1/2} \cdot 2H_2O$: N, 7.03. Found: N, 7.02, 6.89.

This salt was not very soluble in water (1 g. in 210 cc. of hot and 400 cc. cold). It passed quantitatively into the corresponding acid IX when its hot aqueous solution was treated with hydrochloric acid. The same acid IX was formed when the salt was suspended in 50% alcohol and boiled with an excess of either methyl or ethyl iodide.[14]

N-3-methyl-5-benzalhydantoin-N-1-acetic acids, VIII, m. p. 160–161° and **IX,** m. p. 222–223°, were obtained by hydrolyzing the sodium salts IV and V, respectively. In each case an aqueous solution of the salt was cooled with ice before treatment with hydrochloric acid. Under exactly the same conditions the acid VIII always separated as an oil while its isomer was precipitated as a fine white powder. This behavior in aqueous solutions was so characteristic that it served as a method for distinguishing the salts as well as the acids. Both acids were purified by recrystallization from 1:1 acetone–water mixtures from which VIII separates in the form of transparent rhombic prisms and IX in the form of glistening transparent plates.

Anal. VIII. Calcd. for $C_{13}H_{12}O_4N_2$: N, 10.76. Found: N, 10.81, 10.65. IX. Calcd. for $C_{13}H_{12}O_4N_2$: N, 10.76. Found: N, 10.73.

The two acids are both very soluble in acetone but differ considerably in their solubility in water, one gram of VIII dissolving in 110 cc. hot and 1000 cc. cold and IX in 1100 cc. hot and 2200 cc. cold. When suspended in 95% alcohol and saturated with hydrogen chloride with warming both acids dissolved almost immediately to form colorless solutions. Although of exactly the same strength these two solutions behaved quite differently. In the case of VIII no precipitate was formed on cooling but under the renewed action of hydrogen chloride the solution suffered a color change and in the course of time finally precipitated small amounts of the ester II. In the case of IX, a crystalline precipitate consisting of the same ester II was formed immediately in quantitative amounts upon cooling the solution. Both acids passed quantitatively into the saturated acid XII under the action of hydrogen iodide.

N-3-methyl-5-benzylhydantoin-N-1-acetic acid, XII, m. p. 150–151°, was prepared from I, II, V, VI, VIII, and IX, respectively. In every case the reaction proceeded smoothly, the saturated acid being generated in yields ranging from 90 to 95%. For example, 20 g. of the ester II, m. p. 120–122°, and 3.5 g. of red phosphorus were suspended in 60 cc. of hydrogen iodide (sp. gr. 1.7)

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[14] This experiment was undertaken in the hope of obtaining the corresponding esters. Compare Pitts, *J. Chem. Soc.*, **97**, 1889 (1910).

and distilled under reduced pressure over a metal bath kept at 110–120°. When the hydrogen iodide had ceased coming off (one and one-half to two hours) the residue of reddish gum was dissolved in 300 cc. of boiling water and filtered. On cooling 15.6 g. of almost pure acid separated and on concentrating the filtrates additional quantities were obtained, making a total of 96% of the theoretical yield.[15] After three recrystallizations from water the substance separated in the form of long white needles,[16] m. p. 150–151°.

Anal. Calcd. for $C_{13}H_{14}O_4N_2$: N, 10.69. Found: N, 10.74, 10.61.

The acid is very soluble in cold alcohol (1 g. in 8 cc.) and less soluble in water (1 g. in 13 cc. hot and 100 cc. cold). It passes quantitatively into the ester X under the action of hydrogen chloride in alcohol solution, into the sodium salt XI under the action of sodium hydroxide in aqueous alcohol and into the imino acid XIII on intensive hydrolysis in the presence of barium hydroxide.

Ethyl N-3-methyl-5-benzylhydantoin-N-1-acetate, X, m. p. 49.5–51°, was prepared by suspending 14 g. of XII, m. p. 149–150°, in 40 cc. of alcohol and saturating the solution with dry hydrogen chloride. After refluxing for one hour on a steam-bath the clear solution was placed in an open beaker and evaporated under successive additions of alcohol until most of the hydrogen chloride had been removed. Since nothing separated on cooling the concentrated solution and since additions of water resulted in the precipitation of an oil, the mixture was extracted with ether. The combined extracts when washed with aqueous sodium bicarbonate and water, dried and evaporated in a partial vacuum, deposited 12.7 g. of a crystalline substance, m. p. 46–49°. The alkaline aqueous washings when concentrated and acidified with hydrochloric acid yielded 2.2 g. of the acid XII, thus indicating that under the conditions of the experiment esterification was incomplete. The ester was purified by repeated recrystallizations from ether solutions evaporated under reduced pressure when large transparent cubes of m. p. 49.5–51° were obtained.

Anal. Calcd. for $C_{15}H_{18}O_4N_2$: N, 9.66. Found: N, 9.59, 9.47.

The ester is extremely soluble in all organic solvents and (even in the case of ether) crystallizes only after the solvent has been almost completely removed. It is insoluble in water. Under the action of aqueous hydrochloric acid it hydrolyzes readily to give XII (yield 85%) and under the prolonged action of aqueous barium hydroxide, to give the imino acid XIII (yield 80%).

Sodium N-3-methyl-5-benzylhydantoin-N-1-acetate, XI, m. p. 275–276° with decomposition, was prepared by treating 10 g. of the acid XII, m. p. 149–150°, dissolved in 60 cc. of absolute alcohol, with 1.1 equivalents of sodium hydroxide (1.7 g.), dissolved in 3 cc. of water, without warming. Five volumes of ether were then added immediately to the cold clear solution, when a crystalline precipitate consisting of 10.5 g. of salt, m. p. 273–275°, was obtained (97%). After three recrystallizations from alcohol–ether mixtures (1:2) the substance separated in transparent glistening plates which decompose sharply at 275–276°. When heated to constant weight at 110° the crystals became opaque, losing the equivalent of more than one mole of alcohol.

Anal. Calcd. for $C_{13}H_{13}O_4N_2Na \cdot 2C_2H_5OH$: C_2H_5OH, 24.20. Found: C_2H_5OH, 16.07, 16.08. Calcd. for $C_{13}H_{13}O_4N_2Na \cdot C_2H_5OH$: N, 8.49. Found: 8.33, 8.18.

The salt is very soluble in cold water (1 g. in 2.5 cc.), less soluble in cold absolute alcohol (1 g. in 24 cc.) and insoluble in ether. It is almost completely precipitated from its saturated alcohol solutions on the addition of twice the volume of dry ether. When treated with hydrochloric acid in aqueous solution it passes quantitatively into the acid XII and on intense hydrolysis with aqueous barium hydroxide is transformed into the imino acid XIII (80%).

β-Phenylalanine-N-acetic acid, XIII, has already been obtained from the acid XII under the action of barium hydroxide.[2] Its preparation from the ethyl ester and sodium salt of this acid has now been accomplished by the application of the same general method. A number of derivatives of the acid have been prepared but their description will be reserved for a later paper.

In conclusion attention is called to the fact that further evidence in support of the geometrical isomerism of the esters I and II is to be found in the fact that both add bromine to give the same product. This addition takes place instantly in carbon tetrachloride and also in ether solution between equimolecular quantities of the reacting substances. In both cases the transformation proceeds in exactly the same way and under the same conditions except for the fact that at the beginning of any experiment ester I is completely dissolved while ester II is partly dissolved and partly suspended in the given solvent, a difference which quickly disappears as the reaction proceeds. For example, one mole of bromine (5.5 g.) dissolved in 60 cc. of carbon tetrachloride was added rapidly (five minutes) to a solution containing 10 g. of the ester I, m. p. 50.5–51.5°, in 40 cc. of the same solvent, the color of the bromine being discharged as rapidly as added. As soon as the reaction was complete the pale reddish-brown solution was evaporated rapidly on a hot-plate to 50 cc. The heating was accompanied by the evolution of dense fumes of hydrobromic acid which had not been observed previously. In order to remove hydrogen bromide as completely as possible 100 cc. of absolute alcohol was added in portions of 50 cc. each under continued heating. When a volume of 50 cc. was again reached the heating was discontinued and the now almost colorless solution on cooling deposited 7.0 g. of a white crystalline solid, m. p. 110–112°, additional quantities of which were obtained on concentrating the filtrates. After one recrystallization from alcohol it melted sharply at 113–113.5° to form a clear liquid which at 195–200° evolved a colorless gas and at 250–260° developed a deep red color.

Anal. Calcd. for $C_{15}H_{15}O_4N_2Br \cdot C_2H_5OH$: N, 6.78; Br, 19.35. Found: N, 6.98, 7.06; Br, 19.92, 20.01.

The substance is very soluble in alcohol (1 g. in 3 cc. hot and 25 cc. cold) and insoluble in water. When

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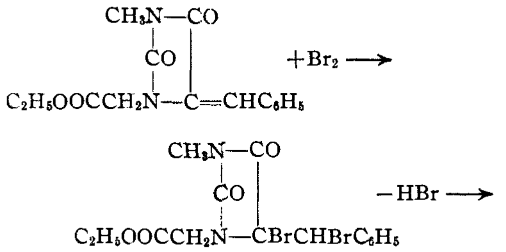
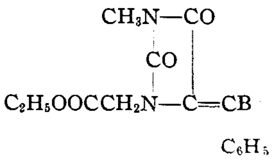
[15] When desired in quantity this acid may be obtained most conveniently and in yields approximating 90% by treating the crude oil described under ester I with hydrogen iodide in the usual way.

[16] When its hot aqueous solutions are too concentrated the acid is precipitated as an oil.

warmed with dilute aqueous sodium hydroxide it slowly hydrolyzes to form a salt. While the complete elucidation of the chemistry of this substance depends upon a more detailed investigation of its derivatives, it seems probable that its formation takes place in the following way.[17]





Summary

The existence of geometrical isomerism in the hydantoin series has again been demonstrated. The substances described together with their various derivatives may all be transformed under the action of various reagents into β-phenylalanine-acetic acid.

[17] Compare Limpricht, *Ann.*, **165**, 265 (1873); Rupe, *Ann*, **256**, 18 (1890).

SOUTH HADLEY, MASS.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

A Quantitative Study of the Reaction between Some Primary Aliphatic Alcohols and Sulfuric Acid

BY C. M. SUTER AND ELMER OBERG[1]

It has been shown by other investigators that the reaction between sulfuric acid and a primary aliphatic alcohol at ordinary temperatures gives only the mono-alkyl ester regardless of whether the acid[2] or the alcohol[3] is present in excess. Quantitative studies of the equilibrium involved in this reaction have, however, been limited to ethyl alcohol.[4] It therefore seemed desirable to compare the extent of ester formation in the reaction of several common aliphatic alcohols with sulfuric acid of various concentrations and to determine the optimum conditions for preparing the corresponding alkyl hydrogen sulfates. The salts of the latter are of value in some alkylation reactions such as the preparation of mercaptans and sulfides[5] and the higher members of the series have become commercially valuable as detergents.

The alcohols studied include the primary straight chain alcohols through *n*-hexyl, ethylenechlorohydrin and *i*-butyl alcohol. Isopropyl alcohol gave a mixture of products apparently containing *i*-propyl ether under the conditions employed, and benzyl alcohol undergoes a condensation[6] reaction when treated with sulfuric acid, so equilibrium measurements could not be completed with these compounds. Four concentrations of sulfuric acid were used. These were 96.70% sulfuric acid, and 5.20, 22.61 and 31.98% sulfur trioxide in sulfuric acid. The use of acid containing sulfur trioxide (or pyrosulfuric acid) results in the formation of the alkyl hydrogen sulfates by the irreversible reaction

$$RCH_2OH + SO_3 = RCH_2OSO_3H$$

in which no water is produced, as well as by the normal esterification reaction. This makes possible the preparation of reaction mixtures containing a smaller concentration of water than would otherwise be obtained. This is useful in the preparation of the alkyl hydrogen sulfates particularly since the value for K in the expression

$$K = [RHSO_4][H_2O]/[H_2SO_4][ROH]$$

increases considerably in most cases as the concentration of the water decreases. In general the acids containing the two higher percentages of sulfur trioxide could not be used with alcohols above *n*-butyl because colored by-products were formed in appreciable quantities accompanied in some cases by the evolution of a trace of sulfur dioxide.

The reaction mixtures were kept in a thermo-

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[1] Eastman Kodak Company Fellow, 1931–1932.

[2] Oddo and Scandola, *Gazz. chim. ital.*, **39**, II, 1 (1909); *Chem. Abs.*, **5**, 879 (1911).

[3] Popelier, *Bull. soc chim. Belg.*, **35**, 264 (1926).

[4] (a) Zaitschek, *Z. physik. Chem.*, **24**, 1 (1879); (b) Kailan, *Monatsh.*, **30**, 1 (1909); (c) Kremann, *ibid.*, **31**, 245, 1031 (1910); (d) Evans and Albertson, THIS JOURNAL, **39**, 456 (1917); (e) Dunnicliff and Butler, *J. Chem. Soc.*, **119**, 1384 (1921).

[5] Gray and Gutekunst, THIS JOURNAL, **42**, 856 (1920).

[6] Cannizzaro, *Ann.*, **92**, 114 (1854); Senderens, *Compt. rend.*, **182**, 612 (1920).