sively until no more precipitate appeared. The crystalline product, when filtered off, washed with aqueous alcohol and dried, weighed between 9 and 10 g.; m. p., 92–130°. This precipitate was washed with hot water, in order to remove any traces of salt, and recrystallized from boiling alcohol. After four recrystallizations 5 g. of ester, m. p. 103–104°, was obtained.

Anal. Calcd. for $C_{16}H_{18}O_5N_2$: N, 8.80. Found: 8.85, 8.76.

This ester is very soluble in boiling methyl alcohol (10 g. in 50 cc.) from which it separates in the form of a meshwork of fine, white needles which tend to turn yellow on the surface when exposed to air containing traces of hydrogen chloride.

The higher-melting modification of methyl N-3-methyl-4-anisalhydantoin-N-1-propionate, m. p. 142–143°, was obtained by dissolving the lower-melting isomer in methyl alcohol and saturating the solution with hydrogen chloride. The transformation was complete in the course of a few hours and was noticeably much more rapid than the corresponding change in the case of 1,3-dimethyl-anisalhydantoin. The crude product which separates from the acid solution melts at 141–143°. After one recrystallization from methyl alcohol the substance melts at 142–143° and is halogen-free.

Anal. Calcd. for $C_{16}H_{18}O_5N_2$: N, 8.80. Found: 8.84, 8.90.

This ester is less soluble than the lower-melting modification in boiling methyl alcohol (4 g. in 50 cc.) from which it separates in large, well-defined, slightly yellow needles or prisms. It imparts a yellow color to all of its solutions.

Summary

Hydantoin compounds which contain unsaturated ethylene linkages of the type $-\overset{|}{C}=CHR$ seem to show geometrical isomerism only when the hydrogen atoms in both the N-1- and N-3- positions have been substituted.

In the case of the five esters studied the lower-melting forms are all very similar in physical properties and the differences between them and their higher-melting isomers are almost constant. The former may all be transformed into the latter by saturating their alcoholic solutions with hydrogen chloride.

South Hadley, Massachusetts

[Contribution from the Chemical Laboratory of Mount Holyoke College]

THE ABSORPTION SPECTRA OF SOME DERIVATIVES OF ANISALHYDANTOIN

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A study of the ultraviolet absorption spectra of some derivatives of anisalhydantoin has been of particular interest in its relation to the structure of these compounds and has necessitated a revision of the conclusions based on earlier evidence.[1]

The substances under investigation were the propionate derivatives of anisalhydantoin, which had been prepared and studied by Dr. Hahn and her collaborators in this Laboratory. The results led to the conclusion

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[1] Hahn, Kelley and Schaeffer, This Journal, 45, 843 (1923).

that the two isomers, m. p. 176° and 143°, which had been obtained by the condensation of ethyl bromopropionate with the sodium derivative of anisalhydantoin were geometrical isomers, in which the propionate group was in the N-3 position. When, however, ethyl bromopropionate prepared from another specimen of propionic acid, was used in the condensation, a new compound, m. p. 158°, was obtained. It was thought that this substance might be a position isomer, that is, an N-1-propionate, of the esters melting at 176° and 143°, respectively, and the present investigation was undertaken to obtain additional evidence for the interpretation of the structures of these three esters.

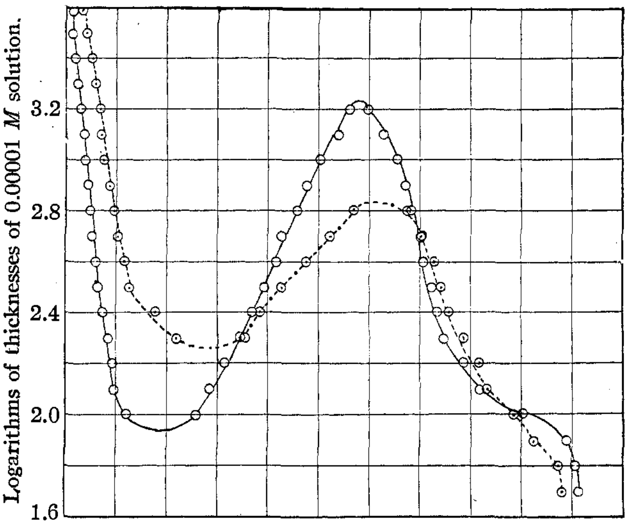

Fig. 1.

————Ethyl-4-anisalhydantoin-N-1-acetate, m. p. 176°.

- - - - -Ethyl-1-methyl-4-anisalhydantoin-N-3-acetate, m. p. 110°.

In order to make the study of the absorption spectra according to the well-known Hartley method, it was necessary to determine the absorption curves of anisalhydantoin derivatives of known structure for purposes of comparison. Ethyl 4-anisalhydantoin-N-1-acetate, m. p. 176°, had been prepared and its constitution established.[2]

A monosubstituted derivative of anisalhydantoin, where the substituent is definitely known to be in the N-3 position, was not available, but the acetate derivative of N-1-methyl-anisalhydantoin, where the acetate group must be in the N-3 position had been prepared and studied.[3] The absorption curves of (I) ethyl 4-anisalhydantoin-N-1-acetate, m. p. 176°,

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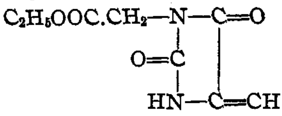
[2] Johnson and Hahn, This Journal, 39, 1255 (1917).

[3] Hahn and Renfrew, *ibid.*, 47, 147 (1925).

and (II) ethyl N-1-methyl-4-anisalhydantoin-N-3-accetate, m. p. 110°, are given in Fig. 1.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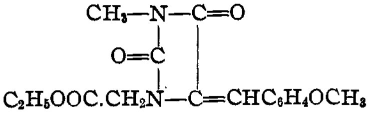
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The curves of these two substances are distinctly different and since it is well known that the substitution of methyl for hydrogen has practically no effect on the absorption spectra, these differences must be due primarily to the fact that in (I) the acetate group is in the N-1 position and in (II) in the N-3 position.

The absorption spectra of the three substances obtained by the condensation of the different samples of ethyl α-bromopropionate with the sodium derivatives of anisalhydantoin were examined and found to be identical with that of ethyl 4-anisalhydantoin-N-1-acetate. These results led to the conclusion that these three esters must all be N-1 substitution products, a conclusion which has been completely confirmed by a further study of the chemical relationships by Dr. Hahn.[4]

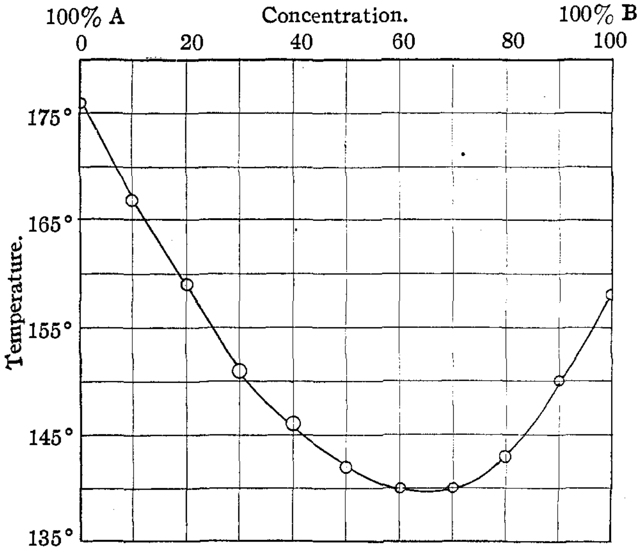

Fig. 2.—*A* = Ethyl-4-anisalhydantoin-N-1-acetate. *B* = Ethyl-4-anisalhydantoin-N-1-propionate.

The relationship among these three substances which melt at 176°, 143° and 158°, respectively, has been shown by a study of the melting-point curve of ethyl 4-anisalhydantoin-N-1-acetate, m. p. 176°, and ethyl

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[4] Hahn, This Journal, 47, 2941 (1925).

4-anisalhydantoin-N-1-propionate, m. p. 158°. It seemed possible that the ester, m. p. 176°, obtained from the ethyl α-bromopropionate condensation might be the acetate derivative which would be formed if the ethyl bromopropionate contained appreciable quantities of ethyl bromoacetate. The melting points of mixtures containing various proportions of the two esters, ethyl 4-anisalhydantoin-N-1-acetate, m. p. 176°, and ethyl 4-anisalhydantoin-N-1-propionate, m. p. 158°, were determined and the results plotted in the form of a curve, using the temperatures as ordinates and concentrations as abscissas (Fig. 2). The curve shows a minimum at a temperature of 140°, corresponding quite closely to the melting point of the third substance, 143°, which had been obtained in the ethyl α-bromopropionate reaction.[5] A fusion mixture of 60% of ethyl 4-anisalhydantoin-N-1-acetate, m. p. 176°, and 40% of ethyl 4-anisalhydantoin-N-1-propionate, m. p. 158°, was mixed with the ester melting at 143° and the melting point taken. This mixture melted at 140–142°, indicating that the two were of similar composition.

Consideration of the curve shows that it is characteristic of a system where the two components form mixed crystals and that therefore the substance, m. p. 143°, is probably a mixture of the two substances, ethyl 4-anisalhydantoin-N-1-acetate and ethyl 4-anisalhydantoin-N-1-propionate. This conclusion has been confirmed by Dr. Hahn and is reported separately.

A separation of the ester, m. p. 143°, into its two components by fractional crystallization was only partially successful. When allowed to crystallize *very* slowly from a dilute solution of alcohol, the ester melting at 158° was obtained, and on longer standing the long asbestos-like needles which are characteristic of the ester melting at 176°, appeared. This substance melted at 170–174°.

It was found that chloroform used as a solvent acted as an associating medium for the two esters and facilitated the formation of the mixed crystals. Since chloroform had been used in the extraction of the condensation mixture, this may account, in part, for the ease with which these mixed crystals were formed.

Experimental Part

The absorption spectra of the alcoholic solutions in thicknesses varying from 3 to 40 mm. were photographed and the limits of absorption plotted according to the usual Hartley method. The apparatus consisted of a Ferý spectrograph, made by Adam Hilger, a Baly absorption tube and the carbon-uranium-molybdenum arc as a source of light. Uniform time of 30 seconds was given to each exposure and every precaution was taken to

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[5] The determinations of the melting point of this ester gave 140–142° on the standard thermometer, but the previously published melting point of 143° has been retained in this discussion to avoid confusion.

insure uniformity of conditions as far as possible. The graphs are plotted in the usual way with the oscillation frequencies of the limits of absorption as abscissas and the logarithms of the thicknesses of an 0.000,01 *M* solution as ordinates. Since the absorption spectra of the three substances obtained by the condensation of ethyl α-bromopropionate with the sodium derivative of anisalhydantoin, coincide exactly with the curve for ethyl 4-anisalhydantoin-N-1-acetate, the one curve represents the results obtained for the four substances.

In the determination of the melting-point curve of mixtures of ethyl 4-anisalhydantoin-N-1-acetate, m. p. 176°, and ethyl 4-anisalhydantoin-N-1-propionate, m. p. 158°, intimate mixtures of known concentration were obtained by the following procedure. A 0.01 *M* solution of each in chloroform was made; different volumes of each solution were then transferred to watch glasses by means of a graduated pipet, and the mixtures evaporated to dryness in an electric oven at a temperature of 100°. The residues were finely powdered and the melting points taken on a standard thermometer. The curve was plotted using as ordinates the mean temperature of the melting points of the various mixtures and the percentage composition as abscissas. The mixture of minimum melting point (140°) melted quite sharply within 2°, while the other mixtures melted over a range of from 6° to 16°.

Summary

1. From a study of the ultraviolet absorption spectra, it has been shown that the esters obtained by the condensation of ethyl-α-bromopropionate with the sodium derivative of anisalhydantoin are N-1 substitution products, and not N-3-, as previously reported by Hahn, Kelley and Schaeffer.[1]

2. The ester melting at 176° which was believed to be ethyl 4-anisalhydantoin-N-3-propionate, is ethyl 4-anisalhydantoin-N-1-acetate. Its formation can be explained only by the fact that the propionic acid from which the ethyl bromopropionate was prepared must have been contaminated with a considerable amount of acetic acid.

3. From a study of the melting-point curve it has been shown that the third product in this condensation is a mixture, probably in the form of mixed crystals, of the N-1-acetate and N-1-propionate derivatives of anisalhydantoin.

SOUTH HADLEY, MASSACHUSETTS