refractive indices of 1.480 (±0.005) for vibrations lengthwise and 1.87 (±0.1) for vibrations crosswise. Views showing oblique extinction have refractive indices of 1.460 (±0.005) for vibrations 18° to their elongation and 1.81 (±0.01) for vibrations ⊥ to this direction. 2 V is about 60°, and double refraction is negative (−). The axial plane is // b, with Bx_a visible in end views.

Benzoselenazoleguanidine Picrate.—Yellow needles with faint if any pleochroism appear in recrystallization from water. Extinction is either parallel or about 18°. Refractive indices are: vibration crosswise, *ca.* 1.9; vibrations lengthwise, 1.495 (±0.005). The crystals are probably monoclinic.

Summary

The benzazoleguanidine series has been extended by the preparation of benzoselenazoleguanidine through the reaction between dicyandiamide and *o*-aminoselenophenol. The base, nitrate, hydrochloride, sulfate and picrate have been isolated and certain physical, chemical and crystallographical properties of these substances have been observed.

BROOKLYN, NEW YORK RECEIVED MAY 15, 1933
PUBLISHED SEPTEMBER 5, 1933

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Studies of Conjugated Systems. XIV. The Preparation and Properties of 1-Phenyl-4-aminobutadiene and 1-Phenyl-4-anilidobutadiene

BY IRVING E. MUSKAT AND LOREN B. GRIMSLEY

The characteristic properties and addition reactions of conjugated systems have been for some time the subject of an investigation in this Laboratory. One of the objects of this investigation was to throw some light on the mechanism of substitution and directive influence in the aromatic series. Some of the addition reactions of butadiene, phenylbutadiene, carboxybutadiene, chloro- and bromobutadiene have already been studied and a theory has been developed[1] which explains these addition reactions without recourse to any special hypothesis of conjugation. In this paper we shall present the results of an investigation on the preparation and properties of aminobutadiene derivatives.

The aminobutadiene derivatives are the aliphatic analogs of the aromatic amines, such as aniline, diphenylamine and α-naphthylamine. Since the aromatic amines are among the most reactive as well as among the most important of aromatic compounds, a study of the aminobutadiene derivatives may not only throw some light on the reactions of aromatic

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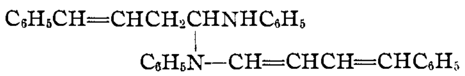
(1) Muskat and Northrup, THIS JOURNAL, **52**, 4043 (1930).

amines, but may also prove of considerable interest for synthetic work. For instance, the diazotization and subsequent coupling reactions of these aminobutadiene derivatives would lead to a most interesting group of compounds. The aminobutadiene derivatives selected for this study were 1-phenyl-4-anilidobutadiene and 1-phenyl-4-aminobutadiene.

The 1-phenyl-4-anilidobutadiene was prepared by treating 1-phenyl-4-bromobutadiene with aniline. This reaction was carried out in various solvents in order to determine the conditions for optimum yield of the amine. It was found that the best yield was obtained when aniline was used as the solvent. The amine could not be distilled even under reduced pressure; there remained in the distilling flask a dimer of the amine which readily forms a monohydrochloride salt. No effort was made to prove the structure of this dimer but the formula given is suggested. This formula would account for the fact that only the monohydrochloride salt of the dimer is formed.



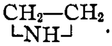
$$\begin{array}{l} C_6H_5CH{=}CHCH_2\overset{}{C}HNHC_6H_5 \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad C_6H_5N{-}CH{=}CHCH{=}CHC_6H_5 \end{array}$$

The reactions of this amine were then studied. When dry hydrogen chloride is passed into an anhydrous ether solution of the amine, the hydrogen chloride salt of 1-phenyl-4-anilidobutadiene is precipitated. This salt hydrolyzes when exposed to the atmosphere. When dry benzene is used as the solvent in place of ether, the dihydrochloride of 1-phenyl-4-anilidobutadiene is formed. This compound is the hydrogen chloride salt of what is probably 1-phenyl-3-chloro-4-anilido-Δ^1-butene. This salt hydrolyzes only very slowly when exposed to the atmosphere. The 1-phenyl-3-chloro-4-anilido-Δ^1-butene was treated with an excess of chlorine in chloroform solution. 1-Phenyl-1,2,3-trichloro-4-trichloroanilidobutane hydrochloride was formed.

It was further found that the 1-phenyl-4-anilidobutadiene readily absorbs one mole of bromine to give 1-phenyl-3,4-dibromo-4-anilido-Δ^1-butene. The structure of this compound was determined by ozonolysis. This dibromide absorbs a second mole of bromine to give 1-phenyl-1,2,3,4-tetrabromo-4-anilidobutane. On further treatment with an excess of bromine, 1-phenyl-1,2,3,4-tetrabromo-4-tribromoanilidobutane hydrobromide was formed. The 1-phenyl-4-anilidobutadiene absorbs likewise a mole of chlorine to give 1-phenyl-3,4-dichloro-4-anilido-Δ^1-butene. The hydrogen chloride salt was precipitated when dry hydrogen chloride was passed into an ethereal solution of the dichloride.

The 1-phenyl-4-aminobutadiene was prepared by the interaction of alcoholic ammonia with 1-phenyl-4-bromobutadiene. An attempt to distil the amine under reduced pressure was not successful. When dry hydrogen chloride is passed into an ether solution of the amine, the hydrogen chloride salt is formed. This salt hydrolyzes when exposed to the atmosphere. If dry benzene is used as the solvent in place of the ether, the hydrochloride salt of what is probably 1-phenyl-3-chloro-4-amino-Δ^1-butene is formed. This salt is hydrolyzed only very slowly under similar conditions.

It was likewise found possible to prepare the 1-phenyl-4-aminobutadiene by the reaction of sodium or potassium amide in liquid ammonia solution upon 1-phenyl-4-bromobutadiene, and also by the reaction of potassium phthalimide upon 1-phenyl-4-bromobutadiene, followed by the hydrolysis of the resulting product. It was further found possible to bring about the rearrangement of the acid amide of styrylacrylic acid to 1-phenyl-4-aminobutadiene by heating it with an aqueous solution of sodium hypochlorite.[2]

It is interesting to note that both the 1-phenyl-4-aminobutadiene and 1-phenyl-4-anilidobutadiene are stable in the amino form rather than in the imino form. This seems to emphasize the rather close analogy between the aliphatic conjugated compounds and aromatic compounds. Every effort to prepare aliphatic amines in which the amino group is attached to an unsaturated carbon atom has always yielded the corresponding imino derivatives or cyclic derivatives.[3] In the case of vinylamine, there is some question as to its true structure. Gabriel,[4] who first synthesized it, gave its structure as $CH_2{=}CHNH_2$. This was later disproved by Marckwald[3] who favored the cyclic structure,  $\underset{\llcorner NH \lrcorner}{CH_2\text{—}CH_2}$. A number of the unsaturated amino derivatives have been given the imide structure, $RCH_2CH{=}NH$.[3] However, the 1-phenyl-4-aminobutadiene and 1-phenyl-4-anilidobutadiene are stable in the amino form just as is aniline. A number of attempts were made to hydrolyze both these amines but in no case were we able to detect ammonia or aniline in the hydrolytic products. The addition reactions of the 1-phenyl-4-anilidobutadiene and of 1-phenyl-4-aminobutadiene eliminate the possibility of the cyclic structure.

Experimental Part

1-Phenyl-4-anilidobutadiene.—1-Phenyl-4-bromobutadiene prepared according to the method of Muskat and Grimsley[5] was treated with a large excess of aniline and allowed to stand at room temperature for twenty-four hours. The excess aniline was removed by treating with cold dilute hydrochloric acid. The resulting mixture was extracted several times with ether, the ether extract dried over anhydrous sodium sulfate and then over sodium hydroxide. The ether solution was filtered from the sodium hydroxide and dry hydrogen chloride was passed into the filtrate. A slightly yellow, crystalline precipitate was formed. The crystals were collected on a filter by means of suction, washed with dry ether to remove the excess hydrogen chloride, and then dried in a vacuum desiccator over phosphorus pentoxide. These crystals melted at 104–106° and hydrolyzed when exposed to the atmosphere. Due to this hydrolysis, the melting point may be somewhat low. The maximum yield, based upon the amount of the 1-phenyl-4-bromobutadiene which reacted, was 57%.

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(2) The relation of these studies on the reactions of conjugated amines to the problem of substitution in the benzene ring will be discussed in a later paper.

(3) Marckwald, *Ber.*, **33**, 764 (1900); Howard and Marckwald, *ibid.*, **32**, 2031 (1899); Kohler and Drake, THIS JOURNAL, **45**, 1287 (1923).

(4) Gabriel, *Ber.*, **21**, 1049 (1888); Gabriel and Stelzner, *ibid.*, **28**, 2929 (1895).

(5) Muskat and Grimsley, THIS JOURNAL, **55**, 2860 (1933).

Anal. Calcd. for $C_{16}H_{16}NCl$: Cl, 13.74. Found: Cl, 13.81, 13.91.

This chlorine analysis indicates that the compound is the hydrogen chloride salt of 1-phenyl-4-anilidobutadiene.

The hydrogen chloride salt of 1-phenyl-4-anilidobutadiene was hydrolyzed with dilute aqueous alkali and the resulting mixture was extracted with ether. The ether solution was washed free of chloride ion and then dried first over anhydrous sodium sulfate and finally over sodium hydroxide. The ether was removed by means of suction. The free base, a dark red viscous oil, remained.

Anal. Calcd. for $C_{16}H_{15}N$: N, 6.33. Found: N, 6.21, 6.26.

These analyses show that the compound is 1-phenyl-4-anilidobutadiene.

1-Phenyl-4-chlorobutadiene, prepared according to the method of Muskat and Huggins,[6] was treated with aniline in a manner exactly analogous to that described above for the corresponding bromo derivative. The hydrogen chloride salt of the anilide thus obtained was identical with the 1-phenyl-4-anilidobutadiene hydrochloride whose preparation from 1-phenyl-4-bromobutadiene was described above. Since the monochloride was definitely proved[6] to have the structure $C_6H_5CH{=}CHCH{=}CHCl$, this constitutes definite proof of the similar structure of the corresponding monobromide.

An attempt to distil, under reduced pressure, the 1-phenyl-4-anilidobutadiene was not successful but there remained in the distilling flask a red rosin-like solid which was easily pulverized into an orange powder. This powder melted at 105°.

Mol. wt. Calcd. for $(C_{16}H_{15}N)_2$: mol. wt., 442. Found: mol. wt. (freezing point method, benzene), 446.

The powder was dissolved in benzene and dry hydrogen chloride was passed into the solution; a crystalline precipitate was formed. The crystals were collected on a filter by means of suction and washed with dry ether to remove the excess hydrogen chloride. These crystals melted at 152°.

Anal. Calcd. for $(C_{16}H_{15}N)_2HCl$: Cl, 7.41. Found: Cl, 6.80, 6.89.

Reactions of 1-Phenyl-4-anilidobutadiene

Addition of Hydrogen Chloride.—The 1-phenyl-4-anilidobutadiene was dissolved in dry benzene and dry hydrogen chloride passed into the solution while the container was immersed in an ice-bath. The solution became dark red in color but no precipitate was formed. Dry, low boiling ligroin (30–60°) was added dropwise to the solution and a chocolate brown crystalline material was precipitated. These crystals were collected on a filter by means of suction and washed with a small amount of warm benzene. The crystals which remained were slightly pink in color.

Anal. Calcd. for $C_{16}H_{17}NCl_2$: Cl, 24.12. Found: Cl, 24.03, 23.93.

The compound is the dihydrochloride of 1-phenyl-4-anilidobutadiene.

In order to determine the ionizable chlorine, the compound was dissolved in alcohol. An equal volume of water was added to precipitate the organic residue, and immediately filtered to avoid the hydrolysis of any loosely bound organic chlorine. The chloride ion was determined in the filtrate.

Anal. Calcd. for one ionizable chlorine in $C_{16}H_{17}NCl_2$: Cl, 12.06. Found: Cl, 12.58.

The compound is then the hydrogen chloride salt of the monohydrochloride addition product of 1-phenyl-4-anilidobutadiene.

These crystals melted at 124° and were hydrolyzed in contact with the atmosphere, but not as readily as was the hydrogen chloride salt of 1-phenyl-4-anilidobutadiene. The crystals are soluble in alcohol, acetone, chloroform, and to quite an appreciable extent in hot benzene.

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[6] Muskat and Huggins, THIS JOURNAL, **51**, 2496 (1929).

This dihydrogen chloride derivative of 1-phenyl-4-anilidobutadiene was dissolved in chloroform and a current of ozonized oxygen passed into the solution for about twenty-four hours. The chloroform was removed by means of suction and the residual ozonide decomposed with water. It was possible to isolate benzoic acid from the ozonization products. The benzoic acid was identified by its melting point and by the melting point of a mixture with known benzoic acid. The hydrogen chloride has therefore been absorbed in the 3,4-positions of the 1-phenyl-4-anilidobutadiene. We did not determine the orientation of the hydrogen chloride in the 3,4-double bond but due to its reactions and also upon theoretical grounds we favor the formula 1-phenyl-3-chloro-4-anilido-Δ^1-butene. In what follows, we shall use this formula although its structure was not proved.

The 1-phenyl-3-chloro-4-anilido-Δ^1-butene hydrochloride was dissolved in chloroform, and a current of chlorine was passed into the solution until no more was absorbed. The chloroform was removed by means of suction. There remained a residue of slightly yellow crystals which were washed with ether to remove the color. The pure white crystals melted at 218°.

Anal. Calcd. for $C_{16}H_{14}NCl_7$: Cl, 53.00. Found: Cl, 53.17, 53.08.

The compound is 1-phenyl-1,2,3-trichloro-4-trichloroanilidobutane hydrochloride.

Addition of Bromine.—The 1-phenyl-4-anilidobutadiene was dissolved in chloroform and exactly one mole of bromine, dissolved in chloroform, was added. After the reaction was complete, the chloroform was removed by means of suction. There remained a dark purple colored solid, which when pulverized was dark brown in color. This compound melted at 103°.

Anal. Calcd. for $C_{16}H_{15}NBr_2$: Br, 42.22. Found: Br, 42.25, 42.41.

This analysis shows the compound to be the dibromide of 1-phenyl-4-anilidobutadiene.

The dibromide was dissolved in chloroform and a current of ozonized oxygen passed into the solution for about twenty-four hours. The chloroform was removed by means of suction and the residual ozonide decomposed with water. It was possible to isolate benzoic acid from the ozonization products. The benzoic acid was identified by its melting point and by the melting point of a mixture with known benzoic acid. The compound thus proves to be 1-phenyl-3,4-dibromo-4-anilido-Δ^1-butene.

The 1-phenyl-3,4-dibromo-4-anilido-Δ^1-butene was dissolved in chloroform and exactly one mole of bromine, dissolved in carbon tetrachloride was added. When the raction was complete, the chloroform and the carbon tetrachloride were removed by means of suction and a purple crystalline residue remained.[7]

Anal. Calcd. for $C_{16}H_{15}NBr_4$: Br, 59.14. Found: Br, 58.94, 58.92.

The compound is the tetrabromide of 1-phenyl-4-anilidobutadiene.

The tetrabromide of 1-phenyl-4-anilidobutadiene was dissolved in chloroform and quite an excess of bromine, dissolved in carbon tetrachloride, added. The reaction mixture was allowed to stand at room temperature for about forty-eight hours. Large volumes of hydrogen bromide were evolved and crystals separated out. The crystals were collected on a filter by means of suction and washed with small amounts of chloroform. The pure white crystals which remained melted at 182°.

Anal. Calcd. for $C_{16}H_{13}NBr_8$: Br, 74.50. Found: Br, 74.62, 74.70.

The compound is the hydrogen bromide salt of 1-phenyl-1,2,3,4-tetrabromo-4-tribromoanilidobutane.

Addition of Chlorine.—The 1-phenyl-4-anilidobutadiene was dissolved in chloroform and exactly one mole of chlorine, dissolved in chloroform, was added. The re-

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(7) These crystals melted at 88–91°. Judging from the melting point of similar compounds described above, this melting point may be low.

action mixture was allowed to stand at room temperature for about twenty-four hours. The chloroform was removed by means of suction and the dark red viscous oil remaining was taken up in dry ether. The solution was filtered clear and the ether was removed from the filtrate by means of suction. The dark red viscous oil which remained was analyzed for chlorine.

Anal. Calcd. for $C_{16}H_{15}NCl_2$: Cl, 24.28. Found: Cl, 24.10, 24.12.

The compound is the dichloride of 1-phenyl-4-anilidobutadiene.

The dichloride of 1-phenyl-4-anilidobutadiene was dissolved in dry ether and dry hydrogen chloride was passed into the solution. The crystals which precipitated out were almost pure white. They were collected on a filter by means of suction, washed with dry ether to remove the excess hydrogen chloride and then dried in a vacuum desiccator over anhydrous calcium chloride. The crystals melted at 135°.

Anal. Calcd. for $C_{16}H_{16}NCl_3$: Cl, 32.39. Found: Cl, 32.55, 32.59.

The compound is the hydrogen chloride salt of the dichloride of 1-phenyl-4-anilidobutadiene.

These crystals were dissolved in chloroform and a current of ozonized oxygen passed into the solution. The chloroform was removed by means of suction and the residual ozonide decomposed with water. It was possible to isolate benzoic acid from the ozonization products. The benzoic acid was identified by its melting point and by the melting point of a mixture with known benzoic acid. The compound is therefore 1-phenyl-3,4-dichloro-4-anilido-Δ^1-butene hydrochloride.

1-Phenyl-4-aminobutadiene.—The 1-phenyl-4-bromobutadiene was dissolved in alcohol and gaseous ammonia passed into the solution for about three days. The reaction product was diluted with a large volume of water and then extracted with ether. The ether extract was washed free of bromide ion and of ammonia and dried, first over anhydrous sodium sulfate, and then over sodium hydroxide. Dry hydrogen chloride was passed into the solution; a slightly yellow crystalline precipitate was formed. The passage of the hydrogen chloride into the solution was not carried out too long lest the salt of any secondary amine be likewise precipitated. The crystals were collected on a filter by means of suction, washed with dry ether to remove the excess hydrogen chloride and then dried in a vacuum desiccator over phosphorus pentoxide. The crystals were slightly yellow and melted at 111°.

Anal. Calcd. for $C_{10}H_{12}NCl$: Cl, 19.53; N, 7.71. Found: Cl, 19.64, 19.70; N, 7.52, 7.61.

The compound is the hydrogen chloride salt of 1-phenyl-4-aminobutadiene.

The hydrogen chloride salt of 1-phenyl-4-aminobutadiene was dissolved in moist chloroform and a current of ozonized oxygen was passed into the solution. The chloroform was removed by means of suction and the residual ozonide decomposed with water. Benzoic acid was isolated from the ozonization products. The benzoic acid was identified by its melting point and by the melting point of a mixture with known benzoic acid.

Addition of Hydrogen Chloride.—The 1-phenyl-4-aminobutadiene was dissolved in dry benzene and dry hydrogen chloride was passed into the solution. A precipitate was not formed but the solution became dark red in color. Low boiling ligroin was added, drop by drop, to the solution and a chocolate brown crystalline mass was precipitated. The crystals were washed with small quantities of warm benzene and then dried on a porous plate. The crystals were slightly pink in color and melted at 138°.

Anal. Calcd. for $C_{10}H_{13}NCl_2$: Cl, 32.54. Found: Cl, 32.41, 32.38.

The structure of the compound is assumed to be 1-phenyl-3-chloro-4-amino-Δ^1-butene hydrochloride for the same reasons as given above for 1-phenyl-3-chloro-4-anilido-Δ^1-butene.

The 1-phenyl-4-aminobutadiene was prepared also by the following methods. (a) An ether solution of 1-phenyl-4-bromobutadiene was introduced into a bomb tube and liquid ammonia condensed upon it. The tube was sealed and allowed to stand at room temperature for two or three days. The reaction product was worked up in a manner analogous to that described above. It was found that if sufficient alcohol were added to the tube to ensure a homogenous solution, the time of the reaction was materially shortened. It was likewise found that if the 1-phenyl-4-bromobutadiene was dissolved in alcohol, concentrated ammonium hydroxide added almost to the point of precipitating out the monobromide and the solution allowed to stand for about forty-eight hours, the 1-phenyl-4-aminobutadiene was formed.

(b) 1-Phenyl-4-bromobutadiene was dissolved in ether, a suspension of finely ground sodium amide in dry ether added and the mixture stirred mechanically. The reaction mixture was allowed to stand for eight to ten hours and the excess of sodium amide destroyed with moist ether. The reaction product was then diluted with an equal volume of ether and the solution was washed free of bromide ion and dried, first over anhydrous sodium sulfate and then over sodium hydroxide. Dry hydrogen chloride was passed into the solution and the hydrogen chloride salt of 1-phenyl-4-aminobutadiene was precipitated. Dry xylene was used to replace the ether in order that the temperature might be raised. The only result apparent was an increase in the polymerization.

The 1-phenyl-4-bromobutadiene was treated with sodium amide, dissolved in liquid ammonia, and the reaction mixture worked up as before. The 1-phenyl-4-aminobutadiene hydrochloride was isolated. Potassium amide was used with similar results.

(c) 1-Phenyl-4-bromobutadiene, in alcoholic solution, was treated with an alcoholic solution of potassium phthalimide and the reaction mixture allowed to stand at room temperature for about twenty-four hours. The reaction mixture was diluted with a large quantity of water and then extracted with ether. The ether extract was washed free of bromide ion and the ether was removed by gentle warming. The resulting residue was hydrolyzed with aqueous hydrochloric acid. The solution was then made alkaline with sodium hydroxide and extracted with ether. The ether solution was washed free of chloride ion and dried, first over anhydrous sodium sulfate and then over sodium hydroxide. 1-Phenyl-4-aminobutadiene hydrochloride was isolated from this solution.

(d) Styrylacrylic acid, $C_6H_5CH{=}CH{-}CH{=}CHCOOH$, was prepared according to the method of Doebner[8] by heating for six hours a mixture of 90 g. of cinnamic aldehyde, 90 g. of malonic acid, and 70 g. of pyridine and then pouring the reaction mixture into cold dilute sulfuric acid. The acid thus formed was purified by crystallization from dilute alcohol. The acid melted at 165°. The acid chloride of styrylacrylic acid was prepared according to the method of Rupe[9] by heating, the acid for forty minutes with an excess of phosphorus trichloride in the presence of a small amount of dry benzene. However, it was not found necessary to isolate the acid chloride. The benzene solution of the acid chloride was poured off. Concentrated ammonium hydroxide was added to the benzene solution and then gaseous ammonia was passed into the solution for about thirty minutes. The reaction vessel was immersed in an ice-bath during the reaction. The solid that was formed was collected on a filter by means of suction and washed several times with concentrated ammonium hydroxide in order to remove any unchanged acid. The crystals which remained melted at 185°, the melting point of the acid amide of styrylacrylic acid. These crystals, in aqueous suspension, were treated with a freshly prepared 8% solution of sodium hypochlorite and the reaction mixture heated on the water-bath for six hours. The reaction mixture was then extracted with ether and the solution washed free of chloride ion. It was then dried, first over anhydrous sodium sulfate and then over sodium hydroxide. Dry hydrogen chloride was passed into the

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(8) Doebner, *Ber.*, **35**, 2137 (1902).

(9) Rupe, *Ann.*, **369**, 340 (1909).

dry ether solution; the hydrogen chloride salt of 1-phenyl-4-aminobutadiene was precipitated from this solution. It is apparent that the acid amide of styrylacrylic acid has undergone a rearrangement to give 1-phenyl-4-aminobutadiene.

Summary

1. The method of preparation of 1-phenyl-4-aminobutadiene and of 1-phenyl-4-anilidobutadiene is described.
2. Both of these amines absorb hydrogen chloride in the 3,4-positions.
3. 1-Phenyl-4-anilidobutadiene absorbs both chlorine and bromine in the 3,4-positions.
4. The significance of these reactions of aliphatic amino conjugated compounds to the problem of substitution in the benzene ring is indicated.

CHICAGO, ILLINOIS RECEIVED MAY 15, 1933
PUBLISHED SEPTEMBER 5, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Effects of Glucose and Fructose on the Sucrose Content in Potato Slices

BY J. M. NELSON AND R. AUCHINCLOSS

The opinion seems to be held by many[1] that desiccation of starch containing plant tissues, such as leaves and potato slices, increases the sucrose content. Schroeder and Horn[2] studying the increase in sucrose on drying tropæolum leaves as well as the changes in the amount of reducing sugar present in the leaves, reached the conclusion that starch is converted into sucrose in the desiccation of the leaves in a more direct way than through the reducing sugars as an intermediate stage. Ahrns[3] more or less repeated the work of Schroeder and his co-workers using starch bearing leaves of several plants, and also reached the conclusion that the conversion of the starch to sucrose in the desiccation of leaves is independent of the reducing sugars present.

Waterman[4] studied the phenomenon of starch to sucrose by drying potato slices at temperatures from 30 to 50°, and like the above-mentioned investigators expressed the opinion that starch is changed to sucrose during the drying process, in some direct way, probably by the aid of enzymic action. Following Waterman, de Wolff[5] studied the starch to sucrose reaction when potato slices are subjected to desiccation. He too looked upon the reaction as one independent of the reducing sugars present.

(1) M. W. Onslow, "The Principles of Plant Biochemistry," The University Press, Cambridge, 1931, p. 55; R. A. Gortner, "Outlines of Biochemistry," John Wiley and Sons, New York, 1929, p. 535.

(2) H. Schroeder and T. Horn, *Biochem. Z.*, **130**, 165 (1922); H. Schroeder and F. Herman, *ibid.*, **235**, 407 (1931).

(3) W. Ahrns, *Bot. Archiv.*, **5**, 234 (1924).

(4) H. I. Waterman, *Chem. Weekblad.*, **11**, 332 (1914).

(5) C. J. de Wolff, *Biochem. Z.*, **176**, 225 (1926); **178**, 36 (1926).