Anal. Found for A: C, 33.2; H, 6.55; Cl, 16.3; N, 6.30; S, 15.0. Found for B: C, 33.4; H, 6.77; Cl, 16.2; N, 6.36; S, 14.6.

Methyl 2,5-Di-*O*-methylsulfonyl-3-(dithiocarbomethoxy)amino-α-D-arabinofuranoside (XI).—A chilled (0°), stirred mixture of 5.00 g. (19.8 mmoles) of II in 80 ml. of pyridine was treated dropwise with 7.4 g. (64.7 mmoles) of methanesulfonyl chloride under standard sulfonylation conditions. After a standard work-up, utilizing extraction with dichloromethane, there was obtained 7.62 g. (94%) of a sirup; $\lambda_{\max}^{\text{film}}$ 3.03, 6.55 (NH), 7.35, 8.50 μ (sulfonate ester).

1′-*O*-Methyl-2′-*O*-methylsulfonyl-2-(methylthio)-α-D-arabinofurano-[5′,3′:4,5]-4,5-dihydro-6H,1,3-thiazine (X). A. From V.—A mixture of 1.00 g. (2.57 mmoles) of V in 10 ml. of methanol was treated with a solution of 0.150 g. (2.78 mmoles) of sodium methoxide in 10 ml. of methanol. The solution was stirred at room temperature for 5 min. and heated on the steam bath for 3 min., then chilled and treated with a large volume of water. The precipitate, 0.19 g. (24%), m.p. 101–103°, was recrystallized twice from petroleum ether (b.p. 88–99°) to give 0.13 g. (16%) of crystals, m.p. 111–113°; $[\alpha]^{24}\text{D}$ −93.9°; $\lambda_{\max}^{\text{Nujol}}$ 6.35 (C=N), 7.39, 8.43 μ (sulfonate ester); there was no OH absorption near 3.0 μ.

Anal. Calcd. for $C_9H_{15}NO_5S_3$: C, 34.5; H, 4.82; N, 4.47; S, 30.7. Found: C, 34.9; H, 4.98; N, 4.23; S, 31.0.

B. From XI.—To a stirred, chilled (−11°) solution of 4.30 g. (10.5 mmoles) of the dimethanesulfonate XI in 20 ml. of methanol was added a solution of 0.60 g. (11.1 mmoles) of sodium methoxide in 20 ml. of methanol. The solution was stirred for 10 min. then poured into about 100 ml. of water. The precipitate, 2.08 g. (64%), was recrystallized from petroleum ether to give 1.32 g. (40%) of white crystals. A second recrystallization from petroleum ether gave product with m.p. 110–112°. There was no mixture melting point depression with the product from V.

1′-*O*-Methyl-2′-*O*-methylsulfonyl-α-D-arabinofurano[5′,3′:4,5]-tetrahydro-1,3-thiazine (XII).—A chilled, stirred suspension of 3.0 g. of aluminum which had been amalgamated,[10] 1.20 g. (3.84 mmoles) of X, and 100 ml. of tetrahydrofuran was treated, dropwise, with 15 ml. of water. The mixture was heated with stirring at 50° for 18 hr. under a nitrogen atmosphere, then was cooled and filtered through Celite. The filtrate was evaporated *in vacuo*, the residue partitioned between 20 ml. of dichloromethane and 20 ml. of water, and the dichloromethane layer washed with 10 ml. of water, then dried over magnesium sulfate. Evaporation *in vacuo* left 1.20 g. (116%) of a sirup that crystallized when it was scratched. This was recrystallized from ethanol, yielding 0.45 g. (44%) of crystals, m.p. 122–125°. The analytical sample from ethanol had m.p. 125–127°; $[\alpha]^{25}\text{D}$ +80°; $\lambda_{\max}^{\text{Nujol}}$ 3.07 (NH), 7.37, 8.50 μ (sulfonate ester); there was no C=N absorption near 6.4 μ.

Anal. Calcd. for $C_8H_{15}NO_5S_2$: C, 35.7; H, 5.61; N, 5.20; S, 23.8. Found: C, 35.6; H, 5.69; N, 5.22; S, 23.9.

Methyl 3-Amino-3-deoxy-2-*O*-methylsulfonyl-5-thio-α-D-arabinofuranoside Hydrochloride (XII).—The tetrahydro-1,3-thiazine (XII), 1.59 g. (5.91 mmoles), was dissolved in 50 ml. of boiling water and to the hot solution was added an excess of saturated aqueous mercuric chloride. The mixture was heated for 45 min. and cooled yielding a white precipitate, 5.08 g., that was collected and suspended in 50 ml. of methanol. Hydrogen sulfide was bubbled through the well stirred suspension for 15–20 min., then the mixture was filtered through Celite, and the filtrate evaporated *in vacuo*. The residue was washed with ether and dried *in vacuo* to afford 1.20 g. (69% from XII) of a white, nitroprusside-positive foam, $[\alpha]^{23}\text{D}$ +71° (1% in methanol); $\lambda_{\max}^{\text{film}}$ 2.95 (OH), 4.85–5.0, 6.25, 6.69 (NH_3^+), 7.32, 8.47 μ (sulfonate ester).

Anal. Calcd. for $C_7H_{16}ClNO_6S_2$: C, 28.6; H, 5.49; Cl, 12.1; N, 4.77; S, 21.8. Found: C, 28.7; H, 5.72; Cl, 12.0; N, 4.68; S, 21.7.

Acknowledgment.—The authors wish to thank Dr. Peter Lim for interpretation of the infrared spectra and his staff for the paper chromatography and rotation data. They also are indebted to Mr. O. P. Crews and his group for the large-scale preparation of certain intermediates.

The Reaction of Ammonia with Acylated Disaccharides. III. Acetyl Derivatives of Maltose and an Interpretation

Raúl A. Cadenas and Jorge O. Deferrari

Laboratorio de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Argentina

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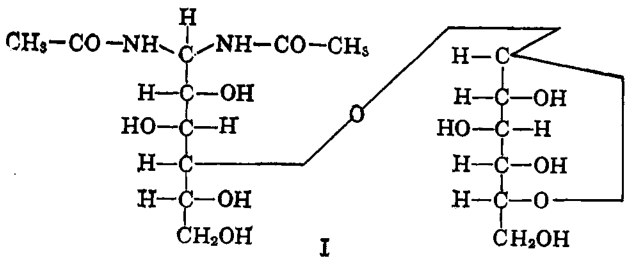
The reaction of ammonia with β-octa-O-acetylmaltose affords N,N′-diacetylmaltosylidenediamine (I), from which its acetate was prepared. A comparative study of the reaction in methanolic and in aqueous media was performed. The higher yield of I obtained in aqueous medium was qualitatively interpreted according to known kinetic studies about the reaction of ester ammonolysis, which is simultaneous and competitive with the reaction described. It is demonstrated that, in the reaction of penta-O-benzoyl-α-D-glucopyranose with methanolic ammonia, methyl benzoate is produced. Therefore, in that medium methoxide ions are formed, pointing out that, apart from the ammonolysis reaction and from the formation of "aldose-amides" by an ortho ester mechanism, a third competitive reaction takes place, by which acyl groups are split off through a transesterification mechanism.

In the previous papers of this series[1,2] it was shown that acetylated disaccharides react with methanolic ammonia affording the original free sugar in high yields and the so-called "aldobiose-diamides" (or more correctly N,N′-diacetylaldobiosylidenediamines) in yield lower than 5%, jointly with N-acetylaldobiosylamines in yields lower than 1%.

In this paper we describe the reaction of ammonia with β-octa-O-acetylmaltose. The presence of N,N′-diacetylmaltosylidenediamine (I) could be detected, in the sirup obtained in the reaction, by paper chromatography and spraying with the picric acid–sodium metaperiodate reagent.[3] It was observed that I had the same R_f of pure maltose and this coincidence persisted in different solvent systems. A charcoal column chromatography afforded crystalline maltose, but it was impossible to separate the mixture of maltose and I. The eluted fractions, which on paper chromatog-



I

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[1] J. O. Deferrari and R. A. Cadenas, *J. Org. Chem.*, **28**, 1070 (1963).

[2] R. A. Cadenas and J. O. Deferrari, *ibid.*, **28**, 1072 (1963).

[3] R. A. Cadenas and J. O. Deferrari, *Analyst*, **86**, 132 (1961).

raphy gave a pink color with the aforementioned reagent, were acetylated and thus was obtained β-octa-O-acetylmaltose and octa-O-acetyl-N,N′-diacetylmaltosylidenediamine.

In the study of the reaction of octa-O-acetyl cellobiose with methanolic ammonia,[1] we considered that the low yield of the "aldobiosyl-amides" cannot be attributed only to the steric hindrance exerted by the nonreducing moiety of the disaccharide upon the ortho ester mechanism through which these substances would be formed.[4] The solvent would exert a definite influence on the greater or lesser preponderance of that mechanism among the various competitive mechanisms which act in this reaction and lead to a mixture of different substances. This is demonstrated in this paper by performing the reaction with aqueous ammonia, in which the yield of I rose from 1% to 27%.

The two fundamental known mechanisms which compete in this reaction are (a) a mechanism of ammonolysis of esters, which led to the free sugar and (b) an intramolecular ortho ester mechanism for the formation of "aldobiose-amides". We will discuss in some detail the factors on which the rate of ammonolysis is dependent. Deserving special mention on this subject are the papers of Betts and Hammett[5] and Bunnett and Davis.[6]

Betts and Hammett studied kinetically the aminolysis of esters (ammonolysis being a particular case) and postulated a mechanism which can be formulated in the following general way.

$$\text{R—NH}_2 + \text{R—NH}_2 \rightleftarrows \text{R—NH}_3^+ + \text{R—NH}^- \qquad (1)$$

$$\text{R—NH}_2 + \text{R}'\text{—OH} \rightleftarrows \text{R—NH}_3^+ + \text{R}'\text{—O}^- \qquad (2)$$

Both equations show a pre-equilibrium of the three ions upon whose interrrelation the rate of aminolysis would depend: the ammonium ion, R-NH_3^+; the alkoxide ion, $\text{R}'\text{-O}^-$, which would come from the solvent employed; and the amide ion, R-NH^-.

The amide ion would catalyze the aminolysis reaction and consequently a "specific lyate ion catalysis" would take place. Betts and Hammett[5] likewise postulated a simultaneous noncatalyzed reaction and pointed out that the rate of aminolysis was increased by addition of alkoxide ions and was retarded by ammonium ions.

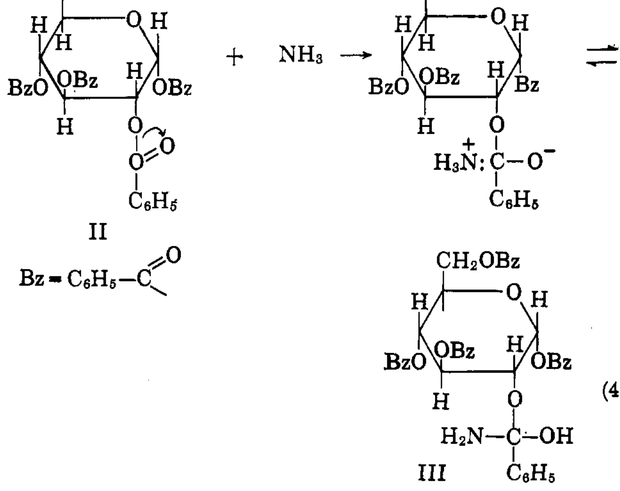
Bunnett and Davis consider that in this reaction a "general base catalysis" takes place, in the sense postulated by Hammett.[7] They performed experiments to determine the type of catalysis involved, from which the following conclusions were obtained: (a) the aminolysis is a general base-catalyzed reaction; (b) a noncatalyzed or a solvent-catalyzed reaction was not detectable; (c) the alkoxide ions and the amine catalyze the reaction—the addition of alkoxide ion (R-O^-) provokes a strong increase in the rate of aminolysis; (d) the addition of ammonium ion ($\text{R-NH}_3\text{Cl}$) has a moderate retarding effect upon the aminolysis, which could be predicted from equation 2. The addition of that ion will shift the equilibrium to the left and will lower the formation of alkoxide ion. However, if the concentration of ammonium ion is high, the rate of aminolysis increases which can be attributed to a positive saline effect.

The general conclusions from these papers could be applied qualitatively to the reaction of methanolic ammonia with carbohydrate esters. Bunnett and Davis[6] postulated, among the various possibilities, a mechanism of aminolysis of esters that more closely adheres to the experimental facts and which we shall consider for the case of penta-O-benzoyl-α-D-glucopyranose (II). This mechanism would be a general one for any acyl derivative of carbohydrates.

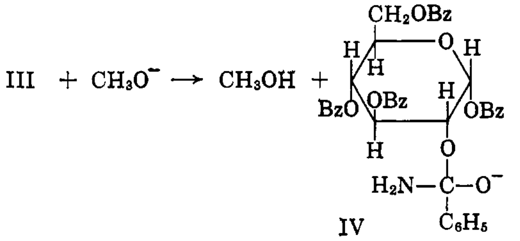
In methanolic ammonia the following pre-equilibrium takes place, equivalent to the one formulated in equation 2.

$$\text{NH}_3 + \text{CH}_3\text{OH} \rightleftarrows \text{NH}_4^+ + \text{CH}_3\text{O}^- \qquad (3)$$

Then the following reactions occur.



(4)



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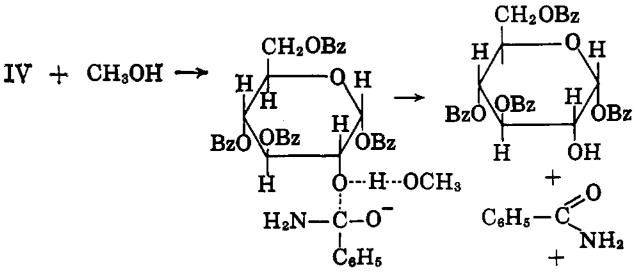

(6)

The last step, a slow one, would imply the removal of alkoxide ion through an acid catalysis from IV. This mechanism excludes the amide ion postulated by Betts and Hammett. This ion (NH_2^-) in liquid ammonia is a powerful nucleophile. However, the carboxylic esters do not react quickly in this medium to give carboxamides. It is unlikely that the amide ion would be slow to attack the esters, but is more probable that the alkoxide would be slow to depart from the tetrahedric intermediate IV through acid catalysis. In

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(4) H. S. Isbell and H. L. Frush, *J. Am. Chem. Soc.*, **71**, 1579 (1949).

(5) R. L. Betts and L. P. Hammett, *ibid.*, **59**, 1568 (1937).

(6) J. F. Bunnett and G. T. Davis, *ibid.*, **82**, 665 (1960).

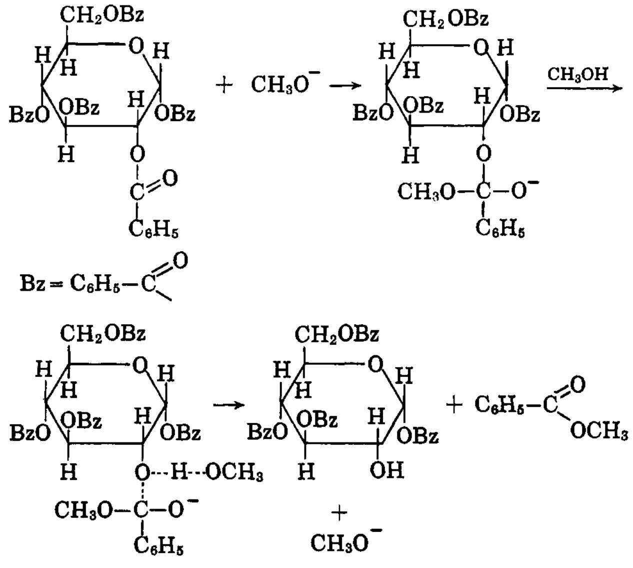
(7) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 215.

liquid ammonia containing amide ions, an acid catalysis would be very difficult.[6]

The presence of an excess of alkoxide (CH_3O^-) would increase the rate of ammonolysis, which implies that a small number of molecules of the acyl derivative would react according to the ortho ester mechanism which led to the "aldose-amides." For that reason in methanolic medium the yields of these substances are comparatively low.

The alkoxide effect in our study could be demonstrated by performing a comparative ammonolysis of penta-O-benzoyl-α-D-glucopyranose[8] in methanolic medium, with addition of sodium (0.015 mole) which allows us to raise the concentration of methoxide ion and verify its effect. This experiment was compared to another one performed without addition of sodium. In the presence of the higher concentration of methoxide, a decrease in the N,N′-dibenzoylglucosylidenediamine formed was observed. From a normal yield of 25.6% it diminished to 14%. From both experiments, methyl benzoate could be obtained in yields of 13% and 5%, respectively, for the experiments with and without addition of methoxide.

This points out that along with a general base catalysis and with an intramolecular ortho ester mechanism, another reaction occurs in which the methoxide ions from the media, formed according to equation 3, attack the ester molecule, producing a third competitive reaction, transesterification, which follows the following mechanism.



Thus it is difficult to affirm that the lowering of the yield of "aldose-amides," as the concentration of alkoxide increases, can be attributed only to an increase of the rate of ammonolysis (equations 4–6).

The total absence of methoxide ions would favor the reaction of formation of "aldose-amides" and this was demonstrated by performing the reaction of β-octa-O-acetylmaltose with aqueous ammonia, a medium in which the yield of I rose noticeably. If in equation 3 water is substituted for methanol, water being an acid comparatively weaker than methanol,[9] the equilibrium would shift to the left, and a great number of molecules in the tetrahedric intermediate state III, could follow the ortho ester mechanism already described,[2,4] giving a high yield of "aldose-amides." This explanation could be applied to the case of tetra-O-acetyl-D-xylononitrile,[10] of tetra-O-acetyl-L-xylononitrile and penta-O-acetylgalactononitrile[11] which, through a Wohl degradation in methanolic medium gave yields of 30 to 40% of "aldose-diamides," while in aqueous medium the yields rose to more than 70%.

It is clear why in liquid ammonia, Zechmeister and Toth[12] obtained practically all cellobiose monoacetamide and cellobiose diacetamide as unique derivatives of carbohydrate, not having obtained the corresponding free sugar in that medium.

The catalytic effect of the alkoxide ion can be correlated to its structure, and it is possible to expect some variation in the results of the reaction when carried out in different alcohols. Hine and Hine[9] showed that ethanol, isopropyl alcohol, and *t*-butyl alcohol are acids weaker than water, but methanol is stronger. From this it follows that in alcohols other than methanol, the equilibrium in the general equation 2 would be greatly shifted to the left, with the concomitant lowering of the alkoxide concentration and the ammonolysis rate.

This explains the fact observed by Restelli de Labriola and Deulofeu,[13] who ammonolyzed the D-gluconic, D-galactonic, and D-mannonic benzoylated nitriles in ammonia saturated ethanol, and isolated "pentose-diamides" with an O-benzoyl residue attached to the primary alcoholic group of the pentose. More recently[14] it was shown that the degree of ammonolysis of the benzoyl groups of different sugars varied with the alcohol employed in the following decreasing order: methanol > ethanol > 2-propanol > 2-butanol.

Experimental

Paper chromatography was performed on Whatman no. 1, employing the following solvents: (A) ethyl acetate–pyridine–water (10:4:3 v./v.); (B) 1-butanol–ethanol–water (5:1:4 v./v., top layer). The sprays were the previously described[3]: (C) silver nitrate–sodium methoxide; (D) picric acid–sodium methoxide; and (E) picric acid–sodium metaperiodate. The evaporations were carried out under reduced pressure and below 60°. Melting points are not corrected.

Reaction of β-Octa-O-acetylmaltose with Methanolic Ammonia. Isolation of Maltose.—Twenty grams of β-octa-O-acetylmaltose (m.p. 158°) was dissolved by shaking with 500 ml. of a 16% methanolic ammonia solution which was left to stand for 24 hr. at room temperature and then evaporated to dryness. The sirup obtained was extracted with four 40-ml. portions of cold ethyl acetate, then dried in a vacuum dessicator, and extracted again with eight 30-ml. portions of boiling ethyl acetate to remove the acetamide produced.

The aqueous solution of the residual sirup from these extractions (30 ml.) was passed through 750 ml. of an Amberlite IR-120 resin, and eluted with 6 l. of water, which was evaporated to dryness; there was obtained a sirup which on paper chromatography with solvent A and developing the chromatogram with reagent C, showed a spot of R_f 0.64 and two other superimposed spots, one of them being of nonreducing character with R_f 0.50. A pure specimen of maltose gave R_f 0.50. With reagent D, for reducing sugars, two spots R_f 0.50 and R_f 0.64 were detected. The reagent E gave only one spot of R_f 0.50 attributable to

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[8] V. Deulofeu and J. O. Deferrari, *J. Org. Chem.*, **17**, 1087 (1952).

[9] J. Hine and M. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952).

[10] L. Maquenne, *Compt. rend.*, **130**, 1402 (1900); R. C. Hockett, *J. Am. Chem. Soc.*, **57**, 2265 (1935).

[11] V. Deulofeu, *J. Chem. Soc.*, 2458 (1929); R. C. Hockett, V. Deulofeu, A. L. Sedoff, and R. J. Mendive, *J. Am. Chem. Soc.*, **60**, 278 (1938).

[12] L. Zechmeister and G. Toth, *Ann.*, **525**, 14 (1936).

[13] E. Restelli de Labriola and V. Deulofeu, *J. Org. Chem.*, **12**, 726 (1947).

[14] E. Gros, A. Lezerovich, E. F. Recondo, V. Deulofeu, and J. O. Deferrari, *Anales Asoc. Quim. Arg.*, **50**, 185 (1962).

N,N′-diacetylmaltosylidenediamine (I), since this reagent did not give any color with pure maltose.

The sirup was extracted once more with boiling ethyl acetate (50 ml.) and was chromatographed on a column of charcoal Darco G-60–Celite 503 (5:1 by weight, 270 mm. by 63 mm.). The column was eluted with water (4 l.) and with increasing concentrations of ethanol in water, as follows: 4% (2 l.), 8% (2 l.), 96% (2.5 l.). The aqueous and the 4% ethanol fractions gave 250 mg. of a sirup containing maltose, but I was not detected on a paper chromatogram treated with reagent E. The 8% ethanol and the first 800 ml. of 96% ethanol, afforded a sirup which by dissolution in methanol and addition of ethanol to turbidity, deposited 3.4 g. of maltose, m.p. 128–130°; $[\alpha]^{28}\text{D}$ +111.6° → +129.6° (*c* 0.43, water). The filtrate was evaporated and the residue weighed 1.2 g.; paper chromatography, employing solvent B and spraying with reagent E, showed the presence of I. The remaining eluate from the charcoal column (1.7 l., 96% ethanol) gave 800 mg. of a sirup which did not give any color with reagent E.

The 1.2 g. obtained from the mother liquors of the crystallization of maltose was chromatographed on a charcoal–Celite column (200 mm. by 30 mm.). The elution with increasing concentrations of ethanol in water gave fractions which were evaporated and chromatographed on paper with solvent B. The fractions which gave a pink color with the reagent E were combined and on evaporation gave a sirup which weighed 714 mg. and was treated in the following manner.

Isolation of Octa-O-acetyl-N,N′-diacetylmaltosylidenediamine.—The 714 mg. of the sirup previously obtained was dissolved in 16 ml. of a 1:1 mixture of pyridine–acetic anhyride. The solution was left to stand 24 hr. at room temperature, then half an hour in a boiling water bath and was then poured into ice–water. A solid (511 mg.) was filtered and by recrystallization from ethanol gave 182 mg. of β-octa-O-acetylmaltose, m.p. and m.m.p. 157–158°. The filtrate obtained from the separation of the 511 mg. of crude solid, was extracted with five 50-ml. portions of chloroform. The chloroform extracts were washed and dried in the usual way and evaporated to dryness. The residual sirup was dissolved in 2 ml. of boiling benzene, and by cooling at room temperature, 175 mg. of octa-O-acetyl-N,N′-diacetylmaltosylidenediamine was obtained, m.p. 95°; $[\alpha]^{23}\text{D}$ +47.4° (*c* 0.37, chloroform). Mixture melting point with octa-O-acetyl-N,N′-diacetylmaltosylidenediamine did not give a depression. These 175 mg. of acetate theoretically correspond to 108 mg. of I; therefore, the yield of I was 0.80%.

Acetylation of the other sirups obtained from the charcoal chromatographs did not afford crystalline products.

Reaction of β-Octa-O-acetylmaltose with Aqueous Ammonia.—Twenty grams of β-octa-O-acetylmaltose was dissolved in 500 ml. of a 25% aqueous solution of ammonia by shaking for 3 hr. at room temperature. The solution was evaporated to dryness and the residue extracted with six 50-ml. portions of ethyl acetate. The residue was dissolved in a small amount of water and passed through 750 ml. of Amberlite IR-120 resin. The elution was performed with 6 l. of water which was evaporated to dryness. The sirup obtained was chromatographed on a charcoal column of Darco G-60–Celite 503 (5:1 by weight, 600 mm. by 30 mm.). The sugars were eluted from the column by increasing concentrations of ethanol in water, collecting fractions of 500 ml. With 5% ethanol (4 l. total) 3.55 g. of I was obtained; m.p. 84–86°; $[\alpha]^{27}\text{D}$ +80.9° (*c* 0.27, water).

Anal. (for a sample dried at 50° and 1 mm.). Calcd. for $C_{16}H_{30}O_{12}N_2 \cdot 2H_2O$: C, 40.50; H, 6.75; N, 5.90. Found: C, 40.86; H, 7.04; N, 6.31.

Anal. (for a sample dried at 100° and 2 mm.). Calcd. for $C_{16}H_{30}O_{12}N_2$: C, 43.43; H, 6.78; N, 6.33. Found: C, 43.35; H, 7.04; N, 6.31.

The remaining fractions eluted from the column, on evaporation, gave sirups which did not crystallize; nor did their acetates.

Octa-O-acetyl-N,N′-diacetylmaltosylidenediamine.—Two hundred and fifty milligrams of I was dissolved in 5 ml. of a 1:1 mixture of pyridine–acetic anhydride and the solution was allowed to stand 24 hr. at room temperature. The solution was poured into ice–water but no precipitation appeared. The aqueous solution was extracted with five 30-ml. portions of chloroform. The combined chloroform extracts were washed and dried in the usual way and evaporated to dryness. The crude product weighed 430 mg. which on recrystallization from benzene gave prismatic crystals of m.p. 95°; $[\alpha]^{22}\text{D}$ +46.6° (*c* 0.17, chloroform).

Anal. (for a sample dried at 80° and 1 mm.). Calcd. for $C_{32}H_{46}O_{20}N_2$: C, 49.35; H, 5.91; N, 3.59. Found: C, 48.90; H, 6.00; N, 3.82.

Ammonolysis of Octa-O-acetyl-N,N′-diacetylmaltosylidenediamine.—Three hundred milligrams of octa-O-acetyl-N,N′-diacetylmaltosylidenediamine was dissolved in 7.5 ml. of 16% methanolic ammonia and the solution was allowed to stand 24 hr. at room temperature. It was then evaporated to dryness and extracted with three 4-ml. portions of ethyl acetate to remove acetamide. The residual sirup was dried in a vacuum dessicator and dissolved in 12 ml. of ethanol. By evaporation at room temperature 160 mg. of I was obtained (85.5%, m.p. 84–86°) which recrystallized from 3 ml. of ethanol to give 126 mg. of m.p. 85–86°; $[\alpha]^{27}\text{D}$ +81.1° (*c* 0.18, water). Mixture melting point with I did not give a depression. Paper chromatography with solvent B and glucose as standard gave only one spot of nonreducing character, of R_g 0.40, detected with the spraying reagents C and E.

Influence of Methoxide Ions upon the Ammonolysis of Penta-O-benzoyl-α-D-glucopyranose with Methanolic Ammonia.—Ten grams of penta-O-benzoyl-α-D-glucopyranose (m.p. 186–187°),[15] was dissolved in 350 ml. of a 16% methanolic ammonia solution, in which 125 mg. of sodium (equivalent to a 0.015 *M* concentration of CH_3O^-) was previously dissolved. The solution was left to stand 24 hr. at room temperature, and the excess of ammonia was evaporated at reduced pressure at 25°. The methanolic solution was shaken with 20 g. of an acid resin Zeo-Karb 225 until neutralization, then was filtered, washed with methanol, and concentrated to one third of its original volume. This solution gave 550 mg. of N,N′-dibenzoylglucosylidenediamine, m.p. 198°.[8] The filtrate was evaporated to dryness and the sirupy residue was dissolved in 20 ml. of ethanol. From this solution 270 mg. of N,N′-dibenzoylglucosylidenediamine of m.p. 150–160° was obtained which on recrystallization gave 200 mg. of m.p. 198°. Further recrystallization of this substance raised the m.p. to 200–201°. Mixture melting point with a pure specimen[8] did not give a depression; yield, 14%.

The mother liquors were evaporated to dryness and dried in a vacuum dessicator. The residue was repeatedly extracted with ether and the combined extracts were evaporated. The residue from ether was then extracted with 24 ml. of petroleum ether (b.p. 60–80°) and from this solution, by evaporation at room temperature and cooling at +5°, benzamide crystallized and was filtered off. Finally, by total evaporation of the filtrate, 1.252 g. of methyl benzoate was obtained; b.p. 196–198°; yield, 13%. By ammonolysis of the methyl benzoate with 3 ml. of methanolic ammonia, benzamide was obtained, m.p. and m.m.p. 129°.

Comparative Experiment without Addition of Sodium.—This experiment was performed with the same conditions previously employed, with the same reagents and solvents. The yield of N,N′-dibenzoylglucosylidenediamine was of 1.360 g. (25.6%). The amount of methyl benzoate obtained was 552 mg.; yield, 5.7%.

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(15) R. K. Ness, H. G. Fletcher, and C. S. Hudson, *J. Am. Chem. Soc.* **72**, 2200 (1950).