of II, m.p. 105–112°, which dissolved in 12 ml. of ethanol and left during 24 hr., without stirring or scratching, gave crystals, m.p. 113–115°, $[\alpha]^{26.5}D$ −23.3° (*c* 0.27, water); yield 3.7%.

Anal. (for a sample dried at 100° and 2 mm.). Calcd. for $C_{16}H_{30}O_{12}N_2 \cdot H_2O$: C, 41.73; H, 6.95; N, 6.08. Found: C, 41.91; H, 6.88; N, 6.02.

Anal. (for a sample dried at 120° 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, 6.79; N, 6.02.

Octa-O-acetyl-N,N′-diacetylcellobiosylidenediamine (III).—Fifty milligrams of II was dissolved in a boiling suspension of 1 ml. of acetic anhydride and 40 mg. of anhydrous sodium acetate. The mixture was warmed for 0.5 hr. on a boiling water bath. It was then cooled and poured into a mixture of ice and water. After 24 hr. the solution was extracted with five 20-ml. portions of chloroform. The chloroform extracts were washed with a saturated solution of hydrogen sodium carbonate and then with water, dried over anhydrous sodium sulfate, and evaporated. Thus was obtained 90 mg. of crude material (71%) which when recrystallized from water gave 60 mg., m.p. 195–196° (softens at 140°); $[\alpha]^{21}D$ +6.6° (*c* 0.18, chloroform). Recrystallizations from ethanol gave a product which melts at 140°, affording a sirup which shrinks at 195°.

Anal. Calcd. for $C_{32}H_{46}O_2N_2$: C, 49.35; H, 5.91; N, 3.59. Found: C, 48.70; H, 6.29; N, 3.69.

Ammonolysis of Octa-O-acetyl-N,N′-diacetylcellobisylidenediamine.—Three hundred milligrams of III was dissolved in 9 ml. of methanolic ammonia. After 24 hr. at room temperature and subsequent evaporation, the residue was extracted with five 3-ml. portions of ethyl acetate and then dried. By dissolution in 10 ml. of absolute ethanol and spontaneous evaporation at room temperature, 130 mg. of needles, m.p. 111–115°, were obtained, which after two recrystallizations from absolute ethanol gave m.p. and m.m.p. with II 113–115°, $[\alpha]^{25}D$ −23.0° (*c* 0.26, water).

(c) **Acetylation of the Residual Sirup. Isolation of Hepta-O-acetyl-N-acetyl-α-cellobiosylamine.**—The solution obtained after isolation of II, was evaporated to dryness and the residual powder (450 mg.) was dissolved in 12 ml. of a 1:1 mixture of pyridine and acetic anhydride, at room temperature. The solution was left to stand for 24 hr. and then left 40 min. in a boiling water bath. The cooled mixture was poured into ice–water and a solid (285 mg.) was filtered; from the filtrate, by extraction with chloroform, washing the chloroform extracts in the usual way, and evaporating, 90 mg. of III was obtained, which recrystallized from water gave m.p. 195–196° (softens at 140°) $[\alpha]^{27}D$ +6.1° (*c* 0.2, chloroform).

The solid was recrystallized from ethanol giving 250 mg. of needles, m.p. 230–233°, which were dissolved in a mixture of chloroform (7 ml.) and benzene (5 ml.). This solution was chromatographed in a column of talc–Celite 503 (5:1 by wt., 30 mm. by 220 mm.). Elution with 110 ml. of a mixture of benzene–absolute ethanol (100:0.25 v./v.) afforded 115 mg. of α-octa-O-acetylcellobiose, m.p. and m.m.p. 224–225°, $[\alpha]^{24}D$ +42.6° (*c* 0.51, chloroform). Then a benzene–absolute ethanol solution (100:1 v./v., 100 ml.) was used, which on solvent removal, did not give any residue. Finally, 300 ml. of benzene–absolute ethanol (100:3 v./v.) were used, which by evaporation and recrystallization of the residue from ethanol gave 100 mg. of hepta-O-acetyl-N-acetyl-α-cellobiosylamine (IV), m.p. 242–243°, $[\alpha]^{27}D$ +54.09 (*c* 0.28, chloroform).

Anal. Calcd. for $C_{28}H_{39}O_{18}N$: C, 49.61; H, 5.80; N, 2.07. Found: C, 49.58; H, 5.80; N, 2.37.

Ammonolysis of Hepta-O-acetyl-N-acetyl-α-cellobiosylamine.—One hundred and seventy five milligrams of IV was dissolved in 5 ml. of methanolic ammonia and left at room temperature 24 hr. The solution was evaporated to dryness and extracted with four 3-ml. portions of ethyl acetate. The residual sirup did not crystallize from ethanol, absolute ethanol or isopropyl alcohol and from mixtures of these solvents with ethyl ether. Chromatography in solvent (A) and spraying with silver nitrate–sodium methoxide reagent[15] showed only one spot R_x 0.95 at 25°. With the picric acid–sodium methoxide reagent[15] no spots were detected. This result points out the nonreducing character of the N-acetylcellobiosylamine (I) formed by the elimination of O-acetyls.

The Reaction of Ammonia with Acylated Disaccharides. II. Acetyl Derivatives of Lactose

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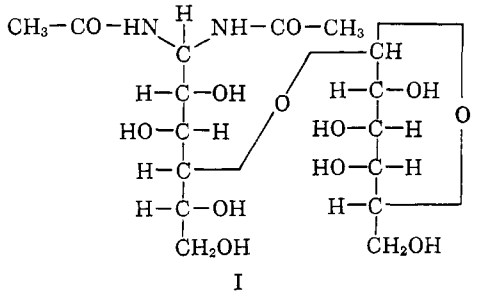
The reaction between ammonia and β-octa-O-acetyllactose was studied. As reaction products, N,N′-diacetyllactosylidenediamine and N-acetyl-α-lactosylamine were isolated and characterized *via* the corresponding acetyl derivatives.

In the first paper of this series[1] we have reported on the products obtained by the reaction of methanolic ammonia on octa-O-acetylcellobiose. This reaction follows the pattern already shown for acetylated and benzoylated derivatives of monosaccharides, by Brigl, Mühlschlegel, and Schinle,[2] Deulofeu, and Deferrari,[3] and other authors,[4] who have isolated "aldosediamides" and "aldosemonoamides" (N,N′-diacylaldosylidenediamines and N-acylaldosylamines, respectively).

However, certain differences appear in the case of disaccharides, the most evident being the lowering of the yields on the "aldobiose-diamides" (N,N′-diacylaldobiosylidenediamines) (I). Whereas the usual yields in the case of monosaccharides vary between 20 and 80%, in the disaccharides these values diminish to about 4%.



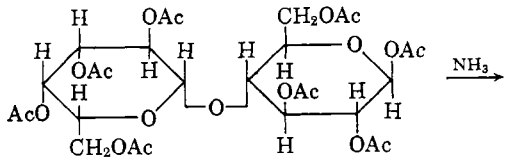
I

In the first instance, this variation can be attributed to the bulky moiety attached glycosidically to the monosaccharide unit which undergoes the transformation leading to the N,N′-diacyl derivatives. The mechanism for the formation of these derivatives was postulated by Isbell and Frush[5] for acylated monosaccharides. The intramolecularity of this mechanism

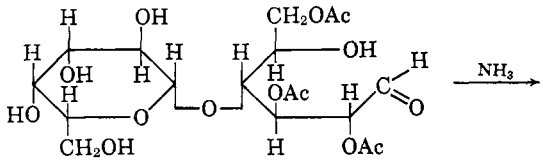
(1) J. O. Deferrari and R. A. Cadenas, *J. Org. Chem.*, **28**, 1070 (1963).
(2) P. Brigl, H. Mühlschlegel, and R. Schinle, *Ber.*, **64**, 2921 (1931).
(3) V. Deulofeu and J. O. Deferrari, *J. Org. Chem.*, **17**, 1087 (1952); **17**, 1093 (1952); **17**, 1097 (1952); **22**, 802 (1957).
(4) R. C. Hockett and L. R. Chandler, *J. Am. Chem. Soc.*, **66**, 957 (1944).
(5) H. S. Isbell and H. L. Frush, *ibid.*, **71**, 1579 (1949).

was demonstrated by Hockett, Deulofeu, and Deferrari.[6]

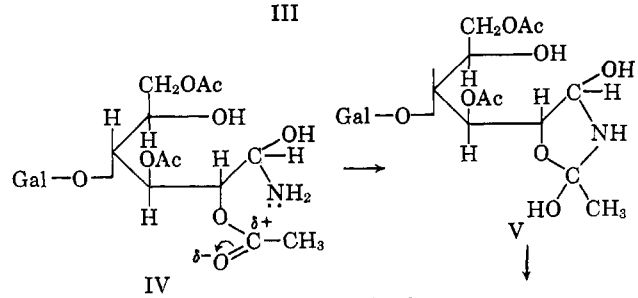
Applied to the case of β-octa-O-acetyllactose (II), this mechanism involves the formation of a free aldehydic group (III) formed through ammonolysis of the acetyl group of the carbon atom 1. This first stage is followed by the formation of an intermediate (IV) which would form the cyclic ortho ester V, in which the neighboring acetoxy group participates. This cyclization is favored by the polarization of the carbonyl group of the acetoxy group rendering the carbonilic carbon atom electrophylic. The rearrangement of this ortho ester leads to the formation of an N-acetyl derivative (VI). The reaction can stop at this stage, with cyclization to a N-acetyllactosylamine, but most of the molecules having structure VI would react with ammonia to give an intermediate, nitrogenated in the acetoxy group of carbon 3 (VII), which would pass to the cyclic labil ortho ester (VIII) form, affording finally the N,N′-diacetyl derivative in the carbon atom 1 (I).



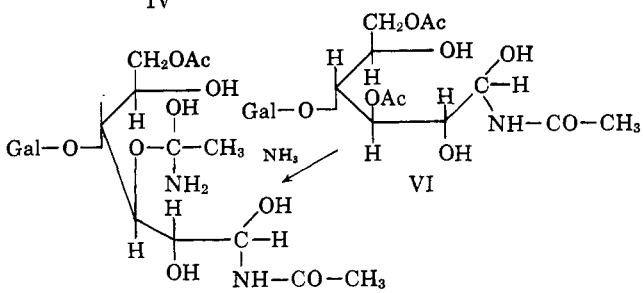
II



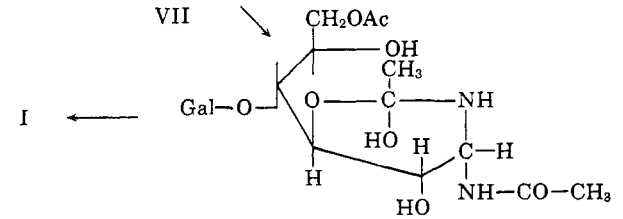
III



IV V



VI VII



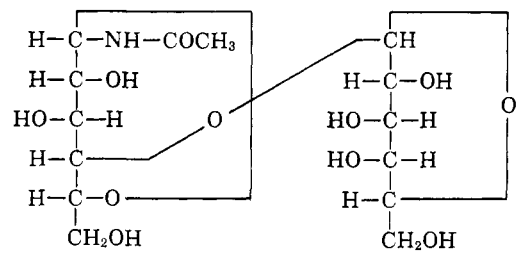
I VIII

During this ortho ester mechanism, another competitive mechanism occurs by which the remaining acyl groups are split off. This is the known mechanism for the ammonolysis of esters and also occurs with the original β-octa-O-acetyllactose (II), affording free lactose. In the field of acetylated disaccharides the latter mechanism is the principal one, leading to high yields of free sugar.

The participation of acetoxy groups in this mechanism is not particular to those on carbon atoms 2 and 3. In the case of penta-O-benzoylglucoses labelled with carbonyl-C^{14} benzoyl groups, succesively in different carbon atoms, it was demonstrated,[7] that all benzoyl groups (except that of carbon 1) contribute to a greater or lesser degree to the formation of N,N′-dibenzoyl derivative on C-1; the most important participation was of the C-3 benzoyl group, with 0.76 mole and of the C-4 benzoyl group with 0.82 mole.

However, it can not be concluded from these data that the benzoyl contributions are actually from carbon atoms 3 and 4 because the probability exists of an intermediate migration by which the migrating acyl group would be transposed to another hydroxyl, prior its attachment to carbon 1 through the nitrogen atom. Moreover, the special importance of the group attached to carbon atom 4 is evident from the results of the ammonolysis of 1,2,3,6-tetra-O-benzoyl-D-glucose, which gave only traces of the "glucose-dibenzamide" and from the ammonolysis of 1,2,3-tri-O-benzoyl-D-glucose, which did not give any detectable product.

In the present study, we describe the reaction of methanolic ammonia with β-octa-O-acetyllactose. This leads to the isolation of lactose in high yield, jointly with a low percentage of N,N′-diacetyllactosylidenediamine (I) and α-acetyllactosylamine (IX).



IX

We assigned to the N,N′-diacetyllactosylidenediamine the formula I, with an open chain in the nitrogenated moiety; this structure agrees with the results of our analysis for this substance and its acetate and receives support from the studies performed with monosaccharides,[2,3,7,8] in which an open chain was postulated.

This substance, by acetylation affords an acetate (octa - O - acetyl - N,N′ - diacetyllactosylidenediamine) which, upon treatment with methanolic ammonia gave the original N,N′-diacetyllactosylidenediamine in good yield.

The possible presence of N-acetyllactosylamine (IX), was investigated by means of acetylation of the residual

(6) R. C. Hockett, V. Deulofeu, and J. O. Deferrari, *J. Am. Chem. Soc.*, **72**, 1840 (1950); V. Deulofeu and J. O. Deferrari, *Anales Asoc. Quim. Arg.*, **38**, 241 (1950).

(7) E. Gros, M. A. Ondetti, J. F. Sproviero, V. Deulofeu, and J. O. Deferrari, *J. Org. Chem.*, **27**, 924 (1962).

(8) J. O. Deferrari, M. A. Ondetti, and V. Deulofeu, *ibid.*, **24**, 183 (1959); J. O. Deferrari, V. Deulofeu, and E. Recondo, *Anales Asoc. Quim. Arg.*, **46**, 137 (1958).

sirup obtained after isolation of lactose and N,N′-diacetyllactosylidenediamine.

The acetate crystallized after chromatographic purification to give a hepta-O-acetyl-N-acetyllactosylamine (m.p. 181°; $[\alpha]^{27}D$ +68, 1°, chloroform). The N-acetyllactosylamine (m.p. 162°; $[\alpha]^{24}D$ +71, 5°, water) was obtained in another experiment, by chromatography of the original sirup on charcoal–Celite.[9]

Kuhn and Krüger[10] obtained an N-acetyllactosylamine (m.p. 246–248°; $[\alpha]^{25}D$ +1.5°, water) by action of ketene upon 1-aminolactose. The product was designed as 1-desoxi-1-acetamino-β-lactose. The same product was obtained by the same authors by acetylation of lactosylamine and ammonolyzing this acetate with methanolic ammonia. This 1-desoxi-1-acetamino-β-lactose gives an acetate of m.p. 142–146°; $[\alpha]^{25}D$ +2, 7° (chloroform).

According to these findings, we consider that our substances have an alpha anomeric configuration, possesing the structure shown in IX for an N-acetyl-α-lactosylamine.

Experimental

A 16% methanolic solution of ammonia was employed. Paper chromatography was performed on Whatman no. 1 paper, employing ethyl acetate–pyridine–water (10:4:3 v./v.) as eluting solvent, by the descending technique. Evaporations were carried out at reduced pressure and below 60°. Melting points are not corrected.

Reaction of β-Octa-O-acetyllactose with Methanolic Ammonia. A. Isolation of Lactose.—Twenty grams of octa-O-acetyllactose[11] was suspended in 500 ml. of methanolic ammonia and shaken at room temperature for 5 min., until a clear solution was obtained. After 24 hr. the solution was concentrated to a volume of 150 ml. The concentrate on standing for 48 hr. at +5°, deposited 4.710 g. of lactose (m.p. 210–212°), which was recrystallized by solubilization in water and addition of ethanol to turbidity; by cooling, 4.120 g. of pure lactose was obtained (m.p. 222–224°, $[\alpha]^{27}D$ +52.8°; *c*, 1.38 water). By evaporation at room temperature, the mother liquors of the reaction gave a further 546 mg. of lactose.

The filtrate was evaporated to dryness and the sirup was extracted with six 20-ml. portions of warm ethyl acetate to remove acetamide. The sirup was dried and dissolved in 30 ml. of methanol; 150 mg. of lactose precipitated, which was filtered off. The filtrate, diluted with 70 ml. of water was passed through a column containing 500 ml. of Amberlite IR-C50 resin.

This passage allowed a partial elimination of substances of basic character, whose structures are yet unknown and which hinder the precipitation of the remaining lactose.

To elute the neutral sugars, the column was washed with 3 l. of distilled water and upon evaporation of the eluate to dryness, a sirup was obtained which was dried to a powder in a dessicator.

A solution of this solid in 20 ml. of methanol, deposited 1.230 g. of lactose, m.p. 222–224°. The filtrate was evaporated, dried, and extracted with 60 ml. of ethyl acetate. The residue, well dried, gave a further amount of 500 mg. of lactose. The total amount of lactose was 7.1 g.; yield 71%.

B. Isolation of N,N′-Diacetyllactosylidenediamine (I).—After the separation of practically all the lactose produced in the reaction as described above, a residual sirup was obtained from which I could be isolated after total elimination of the remaining basic substances already mentioned under A. This was achieved by dissolving the residual sirup in 200 ml. of water and passing the solution through a liter of Amberlite IR-120 resin. The resin was washed with 6 l. of distilled water, the eluate was evaporated and the sirup obtained was dried to a powder in a dessicator. The solid material was dissolved in methanol (8 ml.) and the solution was evaporated at room temperature. On inducing crystallization by mechanical means, 643 mg. of I was obtained (m.p. 110–116°). After filtration of this solid the filtrate was treated as described in C and D.

The solid material was purified by recrystallization from 6 ml. of absolute methanol. Insoluble lactose (37 mg.) was filtered off and the filtrate was evaporated to dryness. The residue was dissolved in 35 ml. of ethanol and allowed to stand 24 hr. at 5.° From this solution 560 mg. of needles of m.p. 112° was obtained. After two recrystallizations from ethanol the m.p. rose to 114–116; $[\alpha]^{111}D$ −14.8° (*c* 0.27, water); yield of I, 4.6%.

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, 43.05; H, 7.04; N, 6.37.

Octa-O-acetyl-N,N′-diacetyllactosylidenediamine (X).—Two hundred and fifty milligrams of I was slowly added to a suspension of sodium acetate (200 mg.) in acetic anhydride (3 ml.). The mixture was boiled for 3 min. and, after 30 min. in a boiling water bath was poured into 80 ml. of ice–water. The mixture was allowed to stand for 24 hr. at room temperature, and the transparent liquid was extracted with ten 15-ml. portions of chloroform. The combined chloroform extracts were washed with water, with a saturated sodium hydrogen carbonate solution and with water, then were dried with anhydrous sodium sulfate and evaporated to dryness. The residual sirup, after 24 hr. in a dessicator, weighed 460 mg. (yield 83.3%). On recrystallization from 15 ml. of benzene, 350 mg. of compound X was obtained, m.p. 223–225°. Recrystallizations from ethanol and from water gave long prismatic crystals of X, m.p. 223–225°; $[\alpha]^{27}D$ −3.94° (*c*, 0.25: chloroform).

Anal. For a sample dried at 120° and 2 mm. Calcd. for $C_{32}H_{46}O_{20}N_2$: C, 49.35; H, 5.91; N, 3.59. Found: C, 49.18; H, 5.98; N, 3.71.

Ammonolysis of Octa-O-acetyl-N,N′-diacetyllactosylidenediamine.—Octa-O-acetyl-N,N′-diacetyllactosylidenediamine (400 mg.) was dissolved in 10 ml. of methanolic ammonia. The solution was allowed to stand for 24 hr. at room temperature, than was evaporated to a sirup and the sirup was extracted with ethyl acetate to remove acetamide. The residual sirup, well dried in a dessicator, was dissolved in 15 ml. of warm absolute ethanol. On standing at room temperature and scratching, the solution deposited 210 mg. of hexagonal prisms (yield 87.5%). These on recrystallization from ethanol, gave a material melting at 115–116°. M.m.p. with N,N′-diacetyl lactosylidenediamine, 115–116°, $[\alpha]^{27}D$ −14° (*c*, 0.27; water). Paper chromatography of the substance and development of the chromatogram with picric acid and sodium methoxide[12] confirmed its nonreducing character.

C. Isolation of N-Acetyl-α-lactosylamine (IX).—The sirup obtained on removal of N,N′-diacetyllactosylidenediamine was separated into its components by chromatography on a column (200 by 30 mm.) of a mixture of charcoal Darco G-60 (5 parts) and Celite 503 (1 part). A solution of the sirup in 8 ml. of water was added to the column. To elute the material, the following solvents or mixtures were used: water (fractions 1–20, total 2 l.), ethanol 3% (fractions 21–40, total 2 l.), ethanol 5% (fractions 41–60, total 2 l.), ethanol 10% (fractions 61–80, total 2 l.), ethanol 30% (fractions 81–100, total 2 l.), and finally 2 l. of ethanol 96%. Fractions of 100 ml. were collected.

Fractions 1–41 gave 35 mg. of an amorphous and hygroscopic powder which did not crystallize. Fraction 42–61 gave 90 mg. of a hygroscopic powder which on reprecipitation from methanol with ethanol gave 50 mg. of lactose.

Fractions 62 to 65 gave 145 mg. of a sirupy material which on dissolving in 1 ml. of methanol and adding ethanol to turbidity gave after 24 hr., 85 mg. of crystalline N-acetyl-α-lactosylamine. After two recrystallizations from ethanol, 45 mg. of prismatic crystals, m.p. 162–163°, were obtained; $[\alpha]^{24}D$ +71.5° (*c*, 0.11, water).

Paper chromatography of this substance and development of the chromatogram with silver nitrate–sodium methoxide reagent,[12] shows only one spot (Rg 0.96; glucose as standard). Development with picric acid and sodium methoxide[12] and aniline hydrogen phthalate,[13] both reagents for reducing sugars, did not show any spots, pointing out the nonreducing character of this substance.

Anal. (for a sample dried at 120° and 2 mm.). Calcd. for $C_{14}H_{25}O_{11}N \cdot 2H_2O$: C, 40.09; H, 6.79; N, 3.35. Found: C, 40.64; H, 6.85; N, 3.10.

(9) R. L. Whistler and D. F. Durso, *J. Am. Chem. Soc.*, **72**, 677 (1950).
(10) R. Kuhn and G. Krüger, *Chem. Ber.*, **87**, 1544 (1954).
(11) C. S. Hudson and J. Johnson, *J. Am. Chem. Soc.*, **37**, 1270 (1915).
(12) R. A. Cadenas and J. O. Deferrari, *Analyst*, **86**, 132 (1961).
(13) L. Hough, J. K. Jones, and W. H. Wadman, *J. Chem. Soc.*, 1702 (1950).

Fraction 66 and subsequent fractions gave 100 mg. of an amorphous sirup which did not afford crystalline products.

Preparation of Hepta-O-acetyl-N-acetyl-α-lactosylamine.—Twenty five milligrams of IX was dissolved in 1.2 ml. of a 1:1 pyridine–acetic anhydride mixture, the solution was boiled for a few minutes, and allowed to stand for 24 hr. at room temperature. On removing the excess of reagents in a vacuum dessicator, the residue was dissolved in water. The solution on standing at +5° deposited 20 mg. of a solid material, m.p. 181–183°; $[\alpha]^{27}D$ +66.6° (*c*, 0.06; $CHCl_3$.)

D. Isolation of Hepta-O-acetyl-N-acetyl-α-lactosylamine from the Residual Sirup.—The mother liquors from which the N,N′-diacetyllactosylidenediamine was obtained, as described under B, were evaporated and the residue was exhaustively dried weighing 300 mg.; then it was dissolved in 7 ml. of a 1:1 mixture of pyridine–acetic anhydride. After 24 hr. at room temperature and warming for 30 min. in a boiling water bath, the solution was poured into ice–water. Practically all of the product was soluble. The aqueous solution was extracted with seven 20-ml. portions of chloroform, the combined chloroform extracts were washed with 2 *N* sulfuric acid, saturated sodium hydrogen carbonate solution, and water; then they were evaporated to dryness. On removing the chloroform by distillation, an amorphous solid was obtained, which did not crystallize from different solvents; consequently it was chromatographed on a column of talcum powder (5 parts) Celite 503 (1 part), 170 mm. by 30 mm. The substance was applied to the column in a solution of 3 ml. of benzene and 4 ml. of chloroform. The elution was performed with mixtures of benzene–absolute ethanol in the following way.

Fraction	Benzene:abs. ethanol	Volume, ml.
I	100:0,1	120
II	100:0,5	150
III	100:1	300
IV	100:1,5	150

The ratio benzene–absolute ethanol was gradually raised to 100:5, and the column was washed finally with acetone.

Fraction IV gave 120 mg. of material melting at 175°. After two recrystallizations from water, rhombic crystals of hepta-O-acetyl-N-acetyl-α-lactosylamine were obtained, m.p. 181–183°. A mixture of this compound and the hepta-O-acetyl-N-acetyllactosylamine obtained by direct acetylation of IX described under C, showed no melting point depression; $[\alpha]^{27}D$ +68,1° (*c*, 0.21; chloroform).

Anal. (for a sample dried at 120° and 2 mm.) Calcd. for $C_{28}H_{39}O_{18}N$: C, 49.61; H, 5.80; N, 2.07. Found: C, 49.62; H, 5.71; N, 2.07.

Abnormal Reaction of Benzoin with Thionyl Chloride

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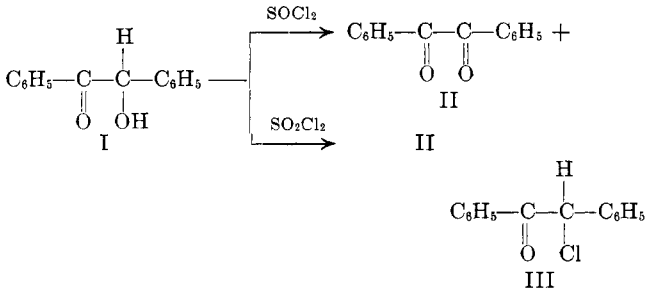
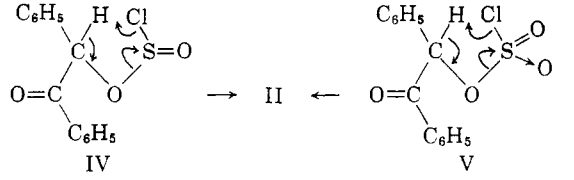
Received March 16, 1962

The formation of benzil (II) from benzoin (I) in the reaction with thionyl chloride at room temperature was proved to proceed *via cis*-stilbene-α,α′-diol sulfite (VI) by the fact that 2,2′,4,4′,6,6′-hexamethylstilbene-α,α′-diol sulfite (XIII) afforded mesitil (XI) and sulfur monoxide in pyrolysis, and that mesitoin (VIII) did not afford mesitil in the reaction with thionyl chloride. Ultraviolet spectra of the enediol sulfite (XIII) and its related compounds suggested that the enediol sulfite system could be regarded as a chromophore with an absorption maximum at 260 mμ.

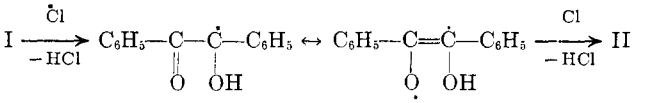
In the previous paper,[1b] it was reported that benzoin (I) reacted with thionyl chloride at room temperature and gave a mixture of benzil (II) and desyl chloride (III) containing a small amount of sulfur, and that sulfuryl chloride converted benzoin into benzil in almost quantitative yield.



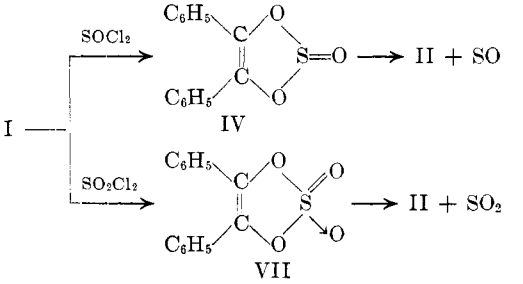
The formation of benzil from benzoin could be accounted for by postulating three different reaction paths. (1) The chlorine atom of the chlorosulfite (IV) or the chlorosulfate (V) could abstract the α-hydrogen.



(2) The reaction (especially with sulfuryl chloride) could proceed through a process involving a semiquinone-type free radical like that in the oxidation of benzoin in alkaline alcoholic solution.[2]



(3) The reaction could proceed through *cis*-stilbene-α,α′-diol sulfite (VI) or sulfate (VII) as its intermediate.



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