(developing solvent benzene, elution solvent chloroform), was 11%.[4]

1,2,3,4,4a,9a-Hexahydro-1,4,4-trimethyl-9H-indeno[2,1-*b*]-pyridine Perchlorate (VIII).—Methanol (40 ml), 0.5 g of V, and 12.5 mg of platinum oxide absorbed 1 molar equiv of hydrogen in 15 min. The resultant VIII (0.5 g) melted at 59–64° to a glass which charred above 145°; needles from methanol.

Anal. Calcd for $C_{15}H_{22}ClNO_4$: C, 57.1; H, 7.0. Found: C, 57.1; H, 6.9.

The **methiodide**, prepared from an ethereal solution of the base (retention time 5 min),[4] crystallized from acetone–ethyl acetate as pale yellow prisms, mp 252–253°.

Anal. Calcd for $C_{16}H_{24}IN$: C, 53.8; H, 6.8. Found: C, 53.7; H, 7.0.

3-(1,1-Dimethyl-3-dimethylaminopropyl)indene (IX).—The above methiodide (0.2 g), 0.2 g of KOH, and 3 ml of water were refluxed for 4 hr. The resultant IX was isolated from ether and distilled at 100–110° (0.1 mm), giving 72 mg (57%) of IX: λ_{max}^{EtOH} 224, 246, 249, 263, 280, 290 mμ (ε 7872, 8409, 8766, 5093, 822).

Anal. Calcd for $C_{16}H_{23}N$: C, 83.8; H, 10.1. Found: C, 83.5; H, 10.3.

1,2,3,4,4a,9a-Hexahydro-1,4,4a-trimethyl-9H-indeno[2,1-*b*]-pyridine (VI) Methiodide.—Methanol (80 ml), 0.6 g of IV perchlorate, and 15 mg of platinum oxide absorbed 1 molar equiv of hydrogen during 48 hr to yield VI as its oily perchlorate. This was converted (*via* the base) in ethanol to the VI picrate (0.8 g, 94%), which recrystallized from acetone as yellow prisms, mp 234–235° dec. The methiodide of VI was prepared in ether solution from the base (which had been purified through the picrate). It crystallized from methanol as short needles, mp 282–284° dec.

Anal. Calcd for $C_{16}H_{24}IN$: C, 53.8; H, 6.8. Found: C, 53.5; H, 6.8.

1-(3-Dimethylamino-1-methylpropyl)-1-methylindene (VII).—To a suspension of 0.15 g of the methiodide corresponding to VI in 5 ml of water was added 0.1 *M* thallous hydroxide until precipitation ceased. The suspension was digested under reflux for 20 min and filtered. The filtrate was evaporated to dryness *in vacuo*. Distillation of the residue at 100° (0.2 mm) gave 66 mg (70%) of VII: λ_{max}^{EtOH} 259, 283, 294 mμ (ε 7084, 894, 371); δ = 1.0, 0.87 (*J* = 7 cps, equivalent to three protons), 1.23, 1.18 (*J* = 1.5 cps, also equivalent to three protons), and 2.1 ppm equivalent to six protons [$-N(CH_3)_2$].

The **hydrochloride** was prepared in ethereal solution, giving colorless needles from ethanol, mp 161–162°.

Anal. Calcd for $C_{16}H_{24}ClN$: C, 72.3; H, 9.1. Found: C, 72.35; H, 9.1.

Dehydration of II.—Thionyl chloride (25 ml) and 0.5 ml of pyridine were mixed and added cautiously with stirring to 2.6 g of II cooled to 0°. Reaction was vigorously exothermic. The solution was kept at 40° for 2 hr, concentrated to one-half volume *in vacuo*, poured onto 200 g of ice, and made basic with concentrated NH_4OH. The mixture was extracted with four 50-ml portions of ether. Evaporation of the dried ether extracts left an amber oil which could be resolved into two major and two minor fractions by vpc and tlc. Evaporative distillation of this oil at 140–160° (0.1 mm) gave 2.1 g of colorless distillate consisting of five products. It was acidified with ethereal HCl to give an oily hydrochloride of III[2] which crystallized from ethanol–ether in a yield of 0.8 g of needles, mp 254–255°.

Anal. Calcd for $C_{15}H_{20}ClN$: C, 72.1; H, 8.1. Found: C, 72.4; H, 7.8.

The mother liquors from the hydrochloride of III were basified with 12% NH_4OH and extracted four times with ether. The residue from the dried, evaporated extracts were dissolved in 5 ml of petroleum ether (bp 60–75°) and put onto a column containing 25 g of Woelm grade III alumina. Elution with 200 ml of petroleum ether gave an oil which yielded an unidentified perchlorate (48 mg), mp 184–195°; benzene (5%) in petroleum ether (100 ml) gave an oil whose perchlorate (0.15 g), mp 192–193° after recrystallization from methanol–ethyl acetate, was identical in all respects with the IV obtained from I. Further elution with 250 ml of 30:55 benzene–petroleum ether gave additional III isolated as the perchlorate[2] (0.43 g); the total yield of III perchlorate was 41%, mp 218–220° alone or in mixture with authentic material.

Acknowledgment.—We are indebted to Dr. H. M. Fales for determination and interpretation of the mass spectra and to Dr. Arthur Jacobson for valuable discussions.

The Wohl Reaction Applied to Some Benzoylated Aldononitriles

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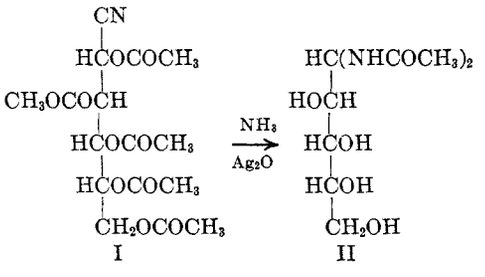
Hexa-*O*-benozyl-D-*glycero*-D-*gulo*-heptononitrile (III), hexa-*O*-benzoyl-D-*glycero*-L-*manno*-heptononitrile (IV), D-*glycero*-D-*galacto*-heptose oxime (V), and, from this last compound, hexa-*O*-benzoyl-D-*glycero*-D-*galacto*-heptononitrile (VI) were prepared; these nitriles were treated with methanolic ammonia. From III, 1,1-bis(benzamido)-1-deoxy-D-glucitol, *N*-benzoyl-β-D-glucopyranosylamine, and D-glucose were obtained. From IV, 1,1-bis(benzamido)-1-deoxy-D-galactitol, *N*-benzoyl-β-D-galactopyranosylamine, and D-galactose were obtained. From VI, 1,1-bis(benzamido)-1-deoxy-D-mannitol, *N*-benzoyl-β-D-mannopyranosylamine, and D-mannose were obtained.

The aldose degradation reaction *via* acylated aldononitriles was discovered by Wohl[1] in 1893. With the purpose of obtaining an aldose having one carbon atom less than the original one, Wohl prepared the oxime and, by acetylation and dehydration, obtained the acetylated aldononitrile. By eliminating the acetyl and cyano groups with aqueous ammonia and a trace of silver oxide, he expected to isolate the lower aldose.

He treated penta-*O*-acetyl-D-gluconononitrile (I) in this way, but, instead of the D-arabinose expected, he obtained a nitrogen-containing substance which he called "arabinose diacetamide," now known as 1,1-bis(acetamido)-1-deoxy-D-arabinitol (II). The structure of this compound may be considered as deriving formally from the condensation of the free aldehyde group of a molecule of the D-arabinose originated in the reaction with two molecules of acetamide arising from



I II

(1) A. Wohl, *Ber.*, **26**, 730 (1893).

the ammonolytic elimination of the acetyl groups of the penta-*O*-acetyl-D-gluconononitrile.

Several authors[2–10] extended the Wohl reaction to other acetylated aldononitriles, and found that, in all cases, the corresponding 1,1-bis(acetamido)-1-deoxyalditols were formed, with the exception of the hexa-*O*-acetyl-D-*glycero*-D-*gulo*-heptononitrile studied by Hockett and Chandler[10] that gave *N*-acetyl-D-glucofuranosylamine.

Brigl, Mühlschlegel, and Schinle[9] were the first to apply the Wohl reaction to a benzoylated aldononitrile; they treated hexa-*O*-benzoyl-D-*glycero*-D-*galacto*-heptononitrile with methanolic ammonia in the presence of silver oxide and obtained 1,1-bis(benzamido)-1-deoxy-D-mannitol plus a small proportion of *N*-benzoyl-β-D-mannopyranosylamine. They suggested that the latter was a secondary product of the reaction derived from the 1,1-bis(benzamido)-1-deoxy-D-mannitol. However, Deferrari and Deulofeu[11] proved that *N*-benzoyl-β-D-mannopyranosylamine is a primary product of the reaction, because, when 1,1-bis(benzamido)-2,3,4,5,6-penta-*O*-benzoyl-1-deoxy-D-mannitol is debenzoylated by treatment with methanolic ammonia, 1,1-bis(benzamido)-1-deoxy-D-mannitol is obtained in almost quantitative yield.

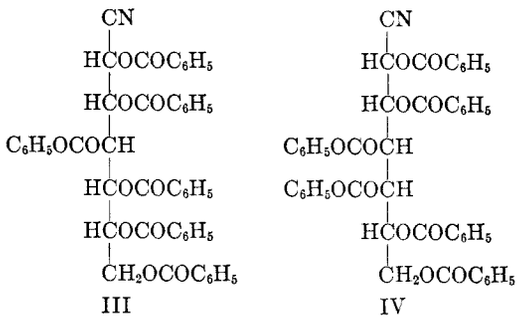
Restelli de Labriola and Deulofeu[12] applied this to other benzoylated nitriles; they degraded penta-*O*-benzoyl-D-gluconononitrile, penta-*O*-benzoyl-D-galactononitrile, penta-*O*-benzoyl-D-mannononitrile, and tetra-*O*-benzoyl-L-rhamnononitrile with methanolic ammonia. Under their experimental conditions, they found that, when the nitriles have a benzoyl group esterifying a primary hydroxyl group, the corresponding 1,1-bis(benzamido)-1-deoxyalditols retain the benzoyl group at this hydroxyl group. In the case of tetra-*O*-benzoyl-L-rhamnononitrile, a deoxy derivative at the primary carbon atom, they obtained the normal product of the Wohl degradation, namely, 1,1-bis(benzamido)-1,5-dideoxy-L-arabinitol.

Deferrari, Ondetti, and Deulofeu[13] degraded tetra-*O*-benzoyl-D-xylononitrile and tetra-*O*-benzoyl-L-arabinononitrile with methanolic ammonia, and obtained 1,1-bis(benzamido)-1-deoxy-D-threitol and 1,1-bis(benzamido)-1-deoxy-L-erythritol, respectively.

We have prepared some benzoylated aldononitriles, not yet described in the literature, and have applied the Wohl reaction to them. Hexa-*O*-benzoyl-D-*glycero*-D-*gulo*-heptononitrile and hexa-*O*-benzoyl-D-*glycero*-L-*manno*-heptononitrile, treated with methanolic ammonia, gave the corresponding free sugars besides the corresponding 1,1-bis(benzamido)-1-deoxyalditols and *N*-benzoylglycosylamines.

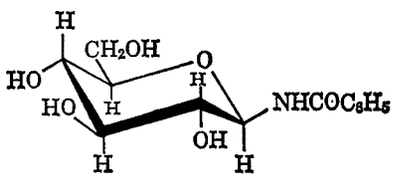
We have confirmed that 1,1-bis(benzamido)-1-deoxy-D-mannitol and *N*-benzoyl-β-D-mannopyranosylamine are obtained from hexa-*O*-benzoyl-D-*glycero*-D-*galacto*-heptononitrile and methanolic ammonia; the results are the same as those described[9] in the presence of silver oxide.

We have prepared hexa-*O*-benzoyl-D-*glycero*-D-*gulo*-heptononitrile (III) and hexa-*O*-benzoyl-D-*glycero*-L-*manno*-heptononitrile (IV) from the corresponding oximes by treatment with benzoyl chloride and pyridine.



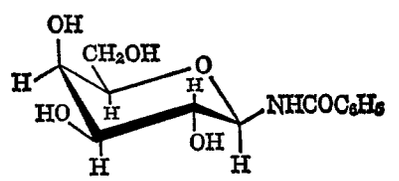
We have also prepared D-*glycero*-D-*galacto*-heptose oxime (V) from D-*glycero*-D-*galacto*-heptose and hydroxylamine. By treatment of this compound with benzoyl chloride and pyridine, we obtained hexa-*O*-benzoyl-D-*glycero*-D-*galacto*-heptononitrile (VI). Its physical constants are the same as those of the compound obtained[9] by benzoylation of D-*glycero*-D-*galacto*-heptononitrile.

By ammonolysis of hexa-*O*-benzoyl-D-*glycero*-D-*gulo*-heptononitrile with methanolic ammonia, 30% of 1,1-bis(benzamido)-1-deoxy-D-glucitol (VII) was obtained; from the mother liquor, 8% of *N*-benzoyl-D-glucosylamine (VIII) was isolated by chromatography on a cellulose column, together with 4.6% of D-glucose, identified by paper chromatography and by preparation of its *p*-nitrophenyl hydrazone. Our *N*-benzoyl-D-glucosylamine was identical with the *N*-benzoyl-β-D-glucopyranosylamine prepared by Delpy and Cerezo.[14]



VIII

By treatment of hexa-*O*-benzoyl-D-*glycero*-L-*manno*-heptononitrile with methanolic ammonia, we obtained 37% of 1,1-bis(benzamido)-1-deoxy-D-galactitol (IX); from the mother liquor, we isolated (by cellulose column chromatography) *N*-benzoyl-D-galactosylamine (X), that was identical with the *N*-benzoyl-β-D-galactopyranosylamine prepared by Delpy and Cerezo,[14]



X

(2) E. Fischer, *Ber.*, **29**, 1377 (1896).
(3) A. Wohl and E. List, *ibid.*, **30**, 3101 (1896).
(4) A. Wohl, *ibid.*, **32**, 3666 (1899).
(5) L. Maquenne, *Compt. Rend.*, **130**, 1402 (1900).
(6) R. C. Hockett, *J. Am. Chem. Soc.*, **57**, 2265 (1935).
(7) V. Deulofeu, *ibid.*, **51**, 2458 (1929).
(8) E. Votoček, *Ber.*, **50**, 35 (1917).
(9) P. Brigl, H. Mühlschlegel, and R. Schinle, *ibid.*, **64**, 2921 (1931).
(10) R. C. Hockett and R. L. Chandler, *J. Am. Chem. Soc.*, **66**, 957 (1944).
(11) J. O. Deferrari and V. Deulofeu, *J. Org. Chem.*, **17**, 1093 (1952).
(12) E. Restelli de Labriola and V. Deulofeu, *ibid.*, **12**, 726 (1947).
(13) J. O. Deferrari, M. A. Ondetti, and V. Deulofeu, *ibid.*, **24**, 183 (1959).
(14) S. Delpy, Thesis, Facultad de Ciencias Exactas, Universidad de Buenos Aires, 1962; A. Cerezo, personal communication.

and 3.4% of D-galactose, identified by paper chromatography and preparation of its *p*-nitrophenylhydrazone.

By ammonolysis of hexa-*O*-benzoyl-D-*glycero*-D-*galacto*-heptononitrile with methanolic ammonia, we obtained 22% of 1,1-bis(benzamido)-1-deoxy-D-mannitol (XI), 4.4% of *N*-benzoyl-β-D-mannopyranosylamine (XII), and D-mannose, identified by paper chromatography and preparation of its *p*-nitrophenylhydrazone.

It is noteworthy that, in the aforesaid cases, not only 1,1-bis(benzamido)-1-deoxyalditols were produced, but also free sugars and *N*-benzoylglycosylamines. This indicates that these compounds are the normal products of this acyl-migration reaction.

N-Benzoyl-β-D-glucopyranosylamine and *N*-benzoyl-β-D-galactopyranosylamine were not obtained in the ammonolysis of penta-*O*-benzoyl-D-glucopyranose and penta-*O*-benzoyl-D-galactopyranose. This could be due to the fact that these substances were either not produced during the reaction or were formed in quantities too small to be isolated by the classical techniques of crystallization. On the other hand, these compounds were isolated by application of chromatographic techniques after the ammonolysis of the benzoylated aldoheptononitriles. The second supposition is supported by the determination of the solubilities in ethanol at 20° of *N*-benzoyl-β-D-glucopyranosylamine and *N*-benzoyl-β-D-galactopyranosylamine that were found to be, respectively, 17 and 8 times higher than that of *N*-benzoyl-β-D-mannopyranosylamine.

The yields of 1,1-bis(benzamido)-1-deoxyalditols in the examples studied by us are similar to those recorded in the literature[11,15,16] for the ammonolysis of benzoylated derivatives of cyclic aldoses.

In the ammonolysis of acylated nitriles, the first step in the formation of 1,1-bis(benzamido)-1-deoxyalditols and *N*-acylglycosylamines would be the loss of the nitrile group as ammonium cyanide, and the formation of an aldehyde function at C-2 of the aldononitrile. The reaction would then proceed as in the ammonolysis of an acylated, acyclic aldose.[17,18] This would explain why hexa-*O*-acetyl-D-*glycero*-D-*gulo*-heptononitrile and hexa-*O*-acetyl-D-*glycero*-D-*ido*-heptononitrile give the same *N*-acetyl-D-glucofuranosylamine as is obtained by ammonolysis of penta-*O*-acetyl-*aldehydo*-D-glucose and penta-*O*-acetyl-β-D-glucopyranose.[19]

In the cases we have studied, and in the ammonolysis of acylated, cyclic aldose derivatives, the yield of 1,1-bis(acylamido)-1-deoxyalditols and *N*-acylglycosylamines is lower than for the acyclic derivatives. As the aldehyde group is not preformed, the participation of the acyl groups in the migration reaction that leads to this type of compound would be smaller, because of their competitive elimination by ammonolysis and transesterification with the methanol[20] present.

Experimental Section

Chromatography was performed on Whatman No. 1 paper and cellulose, employing 1-butanol–ethanol–water (2:1:1 v/v) as the eluent (system A) and detecting with silver nitrate–sodium methoxide reagent[21] (reagent B). A 16% solution of ammonia in methanol was employed; 96% ethanol was used. Melting points are not corrected.

Hexa-*O*-benzoyl-D-*glycero*-D-*gulo*-heptononitrile (III).—D-*glycero*-D-*gulo*-Heptose oxime, prepared by the procedure of Restelli de Labriola and Deulofeu,[22] was added to 62 ml of 1:1 solution of benzoyl chloride in pyridine. The reaction was exothermic, and the temperature was kept at 100° by occasional cooling. After 24 hr at room temperature, the mixture was poured into 200 ml of cold water, and the resulting gummy material was washed several times with cold water until it became friable. It was filtered and recrystallized from acetone–ethanol (1:3); there resulted 13.75 g (67%) of III as tetrahedra of mp 166–167°, $[\alpha]^{17}D$ +30.5° (*c* 0.85, chloroform).

Anal. Calcd for $C_{49}H_{37}NO_{12}$: C, 70.39; H, 4.45; N, 1.68. Found: C, 70.18; H, 4.61; N, 1.63.

Ammonolysis of III. A. Isolation of 1,1-Bis(benzamido)-1-deoxy-D-glucitol (VII).—III (4 g) was suspended in 100 ml of methanolic ammonia and was dissolved by shaking for 50 min. After 24 hr at room temperature, the solution was evaporated, and the residual solid was dissolved in 20 ml of boiling ethanol; on cooling and scratching, 760 mg of needles, mp 190–192°, was obtained. Recrystallizations from ethanol gave 700 mg (37%) of VII, mp 200–201°, $[\alpha]^{30}D$ +1.8° (*c* 1.1, pyridine). [Deulofeu and Deferrari[15] gave mp 201–202°, $[\alpha]D$ +1.3° (pyridine).]

B. Isolation of *N*-Benzoyl-β-D-glucopyranosylamine (VIII) and D-Glucose.—The mother liquor from A was evaporated, and the resulting syrup was extracted with four 40-ml portions of boiling ethyl acetate to remove the benzamide. The residual material was dried and chromatographed on a cellulose column (430 × 17 mm); elution was carried out with system A, 100 22-ml fractions being collected. Evaporation of fractions 4 and 5 afforded 180 mg of needles, mp 207–210°. Recrystallization from ethanol gave 110 mg (8%) of VIII, mp 236°, $[\alpha]^{30}D$ −12.5° (*c* 0.5, water) [lit.[14] mp 232–233°, $[\alpha]D$ −12.2° (water)]; it gave no depression of melting point when mixed with an authentic sample of *N*-benzoyl-β-D-glucopyranosylamine; paper chromatography in system A, detected with reagent B, gave only one spot, of the same R_f as that of an authentic sample of *N*-benzoyl-β-D-glucopyranosylamine. Solubility of VIII was 1.111% (w/v) in ethanol at 20°. Fractions 7–14 gave 20 mg more of VII. Fractions 21–46 gave 40 mg (4.6%) of a syrup which, by paper chromatography run in system A and detected with reagent B, gave only one spot of the same R_f as that of D-glucose. By treatment of this syrup with *p*-nitrophenylhydrazine, a *p*-nitrophenylhydrazone was obtained which, by paper chromatography run with system A, gave only one spot, of the same R_f as an authentic sample of D-glucose *p*-nitrophenylhydrazone.

Hexa-*O*-benzoyl-D-*glycero*-L-*manno*-heptononitrile (IV).—D-*glycero*-L-*manno*-Heptose oxime (3.92 g) was added to 48 ml of a 1:1 solution of benzoyl chloride in pyridine. The reaction was exothermic, and the temperature was kept at 100° by occasional cooling. After 24 hr at room temperature, the mixture was poured into 400 ml of cold water, and the resulting syrup was washed several times with cold water until it became friable. It was filtered and recrystallized from acetone–ethanol (1:3); there resulted 9.45 g (65.6%) of tetrahedra, mp 190–191°. After being recrystallized three times from the same solvent, IV, mp 190–191°, $[\alpha]^{23}D$ +19.5° (*c* 0.7, chloroform), was obtained.

Anal. Calcd for $C_{49}H_{37}NO_{12}$: C, 70.39; H, 4.45; N, 1.68. Found: C, 70.63; H, 4.56; N, 1.77.

Ammonolysis of IV. A. Isolation of 1,1-Bis(benzamido)-1-deoxy-D-galactitol (IX).—IV (4 g) was suspended in 100 ml of methanolic ammonia and was dissolved by shaking for 60 min. After 24 hr at room temperature, the solution was evaporated, and the residual solid was dissolved in 20 ml of boiling ethanol on cooling and scratching, 770 mg of needles, mp 194° was obtained. Recrystallization from ethanol gave 700 mg (37%) of IX, mp 203–204°, $[\alpha]^{27}D$ −5.8° (*c* 0.85, pyridine) [lit.[16] mp 207°, $[\alpha]D$ −6.2° (pyridine)].

B. Isolation of *N*-Benzoyl-β-D-galactopyranosylamine (X) and D-Galactose.—The mother liquor from A was evaporated, and the resulting syrup was extracted with four 40-ml portions of boiling ethyl acetate to remove the benzamide. The residual material

(15) V. Deulofeu and J. O. Deferrari, *J. Org. Chem.*, **17**, 1087 (1952).
(16) J. O. Deferrari and V. Deulofeu, *ibid.*, **17**, 1097 (1952).
(17) H. S. Isbell and H. L. Frush, *J. Am. Chem. Soc.*, **71**, 1579 (1949).
(18) E. Gros, M. A. Ondetti, J. Sproviero, V. Deulofeu, and J. O. Deferrari, *J. Org. Chem.*, **27**, 924 (1962).
(19) C. Niemman and J. T. Hays, *J. Am. Chem. Soc.*, **62**, 2960 (1960).
(20) J. O. Deferrari and R. A. Cadenas, *J. Org. Chem.*, **28**, 2613 (1963).
(21) R. A. Cadenas and J. O. Deferrari, *Analyst*, **86**, 132 (1961).
(22) E. Restelli, de Labriola, and V. Deulofeu, *J. Am. Chem. Soc.*, **62**, 1613 (1940).

was dried and chromatographed on a cellulose column (500 × 25 mm); elution was carried out with system A, 45 20-ml fractions being collected. Evaporation of fractions 4 and 5 gave 60 mg (4.4%) of needles; purification from ethanol gave X, mp 179–181°, $[\alpha]^{30}D$ +21.5° (*c* 0.5, water) [lit.[14] mp 180–181°, $[\alpha]D$ +21.8° (water)]; it gave no depression of the melting point when mixed with an authentic sample of *N*-benzoyl-β-D-galactopyranosylamine. Paper chromatography run in system A (and detected with reagent B) gave only one spot, of the same R_f as that of an authentic sample of *N*-benzoyl-β-D-galactopyranosylamine. Solubility of X was 0.536% (w/v) in ethanol at 20°. Fractions 8 and 9 gave 50 mg more of IX, mp 195–196°; recrystallization from ethanol gave mp 203–204°. Fractions 12–19 gave 30 mg (3.4%) of a syrup which, by paper chromatography run in system A and detected with reagent B, gave only one spot, of the same R_f as D-galactose. By treatment of this syrup with *p*-nitrophenylhydrazine a *p*-nitrophenylhydrazone was obtained which, by paper chromatography run in system A, gave only one spot, of the same R_f as an authentic sample of D-galactose *p*-nitrophenylhydrazone.

D-*glycero*-D-*galacto*-Heptose Oxime (V).—D-*glycero*-D-*galacto*-Heptose[23] (2.45 g) was added to a solution of 1.233 g of hydroxylamine hydrochloride in 0.7 ml of water to which had been added 0.400 g of sodium dissolved in 10 ml of methanol. The mixture was warmed for 10 min at 60°, and the oxime crystallized spontaneously. After 12 hr at room temperature, the mixture was cooled to 0° and filtered; 2.47 g (91%) of prisms, mp 170°, was obtained. After three recrystallizations from ethanol, V, mp 171–172°, $[\alpha]^{30}D$ + 136.5° → + 101.2° (*c* 0.5, water), was obtained.

Anal. Calcd for $C_7H_{15}NO_7$: C, 37.33; H, 6.66; N, 6.22. Found: C, 37.58; H, 6.95; N, 5.82.

Hexa-*O*-benzoyl-D-*glycero*-D-*galacto*-heptononitrile (VI).—V (1.84 g) was added to 24 ml of 1:1 solution of benzoyl chloride in pyridine. The reaction was exothermic, and the temperature was kept at 100° by occasional cooling. After 24 hr at room temperature, the mixture was poured into 100 ml of cold water, and the resulting gummy material was washed several times with cold water until it became friable. It was filtered and recrystallized from acetone–ethanol (1:3); there resulted 5.10 g (75%) of rectangular plates, mp 159–160°. Recrystallization from the same solvent gave VI, mp 159–160°, $[\alpha]^{25}D$ +29.4° (*c* 0.9, chloroform) [lit.[9] mp 161–163°, $[\alpha]D$ +30° (chloroform)].

Ammonolysis of VI. A. Isolation of 1,1-Bis(benzamido)-1-deoxy-D-mannitol (XI).—VI (4 g) was dissolved, by shaking, in 100 ml of methanolic ammonia. After 24 hr at room temperature, the solution was evaporated, and the residual syrup was dissolved in 20 ml of boiling ethanol; by cooling and scratching, 600 mg of needles, mp 180°, was obtained. Recrystallization from ethanol gave 480 mg (22%) of XI, mp 227°, $[\alpha]^{32}D$ +4.8° (*c* 1.6, pyridine) [lit. mp 226°,[9] 225–226°;[17] $[\alpha]D$ 3.6°,[9] +2.8°[17]].

B. Isolation of *N*-Benzoyl-β-D-mannopyranosylamine (XII) and D-Mannose.—The mother liquor was evaporated, and the resulting solid was dissolved in 5 ml of boiling ethanol; by cooling, 60 mg (4.4%) of XII, mp 246–247°, was obtained. After recrystallization from ethanol, the product melted at 254°, $[\alpha]^{30}D$ +6.1° (*c* 1.4, pyridine) [lit. mp 254°,[9] 253–254°[17]; $[\alpha]D$ +6.4°[17]]; it gave no depression of the melting point when mixed with an authentic sample of *N*-benzoyl-β-D-mannopyranosylamine. Paper chromatography run in system A (and detected with reagent B) gave only one spot, of the same R_f as that of an authentic sample of *N*-benzoyl-β-D-mannopyranosylamine. Solubility of XII was 0.066% (w/v) in ethanol at 20°.

The mother liquor was evaporated, and the resulting syrup was extracted with four 40-ml portions of boiling ethyl acetate to remove the benzamide and dried; it gave 35 mg (3.5%) of a syrup which, by paper chromatography run with system A (and detected with reagent B) gave only one spot, of the same R_f as D-mannose. By treatment of this syrup with *p*-nitrophenylhydrazine, a *p*-nitrophenylhydrazone was obtained which, by paper chromatography run in system A, gave only one spot, of the same R_f as that of an authentic sample of D-mannose *p*-nitrophenylhydrazone.

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Reaction of Trialkylaluminums with Halohydrocarbons[1a]

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In the presence of ether, triethylaluminum smoothly effects replacement of benzylic halogens by ethyl groups (alkylation). Thus, benzyl chloride, (1-bromoethyl)benzene, trityl chloride, and benzal chloride yield 65–75% alkylation products. Reduction (up to 20% yield), which usually accompanies alkylation, becomes more important for benzotrichloride, which yielded 26% 3-ethyl-3-phenylpentane and 39% 3-phenylpentane. Primary, secondary, and tertiary haloalkanes show increasing reactivity toward triethylaluminum in the sequence given; the degree of dehydrohalogenation which accompanies alkylation and reduction increases in the same direction. Neopentyl and neophyl chlorides give only rearranged products. Trialkylaluminums and propargyl chloride give in 35–60% yield the corresponding alkylallene. Mechanisms are considered for the various reactions, and the behaviors of trialkylaluminums, alkyl Grignards, and alkyllithiums toward halohydrocarbons are compared.

Alkylaluminums show a formal similarity to such organometallics as alkyl Grignards and alkyllithiums. Speculations[2] that alkylaluminums, too, may react with organic halides as shown in eq 1 (alkylation)

$$Rm + R'X \longrightarrow RR' + mX \qquad (1)$$

m = a metal atom and one valency

were therefore not unexpected. However, previous studies of the reactions of alkylaluminums with organic halides are fragmentary and inconclusive. In the presence of alkylaluminum halides or alkylaluminum halide–titanium halide mixtures, haloalkanes are variously reported to undergo dehydrohalogenation[2a,3,4] and alkylation.[5] Alkylation of organic halides having special reactivity is less ambiguous. α-Halo ethers[6–8] and allyl chloride[9] are alkylated by alkylaluminums, and 3-halopropylaluminum gives cyclopropane,[10] but, on the other hand, possible alkylation products of 2-chloropropane and triethylaluminum were not de-

(1) (a) Much of this work was presented at the 20th Southwest Regional Meeting of the American Chemical Society, Shreveport, La., Dec 1964. (b) Polymer Sciences Department, Stanford Research Institute, Menlo Park, Calif.

(2) (a) K. Weyer, Ph.D. Thesis, Technischen Hochschule, Aachen, 1956; (b) H. Hoberg, *Ann.*, **656**, 1 (1962); (c) J. B. Rose, "The Chemistry of Cationic Polymerization," P. H. Plesch, Ed., The Macmillan Co., New York, N. Y., 1963, p 435; (d) D. B. Miller, *Tetrahedron Letters*, 989 (1964).

(3) The observed products may be olefins and an alkane generated by cleavage of the alkyl–aluminum bond by the hydrogen halide.

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