main cut, a colorless oil, was taken at 111–112°/8–10 mm.; lit. value[30] for *o*-methoxybenzyl alcohol, b.p. 104°/5 mm.

o-Methoxybenzyl alcohol-hypochlorite reaction. The total pure cut of the above distillate was dissolved in 15 ml. of methanol and this solution was diluted with 100 ml. of water. This solution was then added to 100 ml. (0.1 mole) of potassium hypochlorite solution and then diluted with 100 ml. of water. At this point the solution had *p*H 11. The system was mechanically shaken overnight at room temperature which was attained shortly after the initial exotherm (to 51°) on mixing the reactants. The organic constituents were then removed by ether extraction (to negative 2,4-dinitrophenylhydrazone test of aqueous residue) and the aldehyde removed from the combined ether portions by extraction with aqueous sodium bisulfite solution (to negative 2,4-dinitrophenylhydrazone test of ethereal layer). These combined aqueous extracts were acidified to *p*H 2 with dilute cold hydrochloric acid, then extracted with ether until no aldehyde remained in the aqueous portion (negative 2,4-dinitrophenylhydrazone test). The combined ether extracts were dried over anhydrous sodium sulfate, the ether was removed under reduced pressure, and 7 g. of water-white oil remained. Several drops of the oil were used to make derivatives: *2,4-dinitrophenylhydrazone*, dark orange crystals, m.p. 249–252° (lit.[30] m.p., 253° for this derivative of *o*-methoxybenzaldehyde); *oxime*, white needles, m.p. 89–91° (lit.[30] m.p., 92° for this derivative of *o*-methoxybenzaldehyde). The 7 g. of pure *o*-methoxybenzaldehyde obtained represented a 51.5% yield[27] (overall reaction, based on sodium saligenate). No methoxybenzoic acid was found.

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Further Application of the Hypochlorite Method of Chain Shortening in the Carbohydrate Series[1]

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Received July 15, 1960

D-Arabinose from D-mannonic acid and D-lyxose from D-galactonic acid are prepared in yields of 35.3% and 40.7%, respectively. β-Maltose monohydrate is converted to 3-*O*-α-D-glucopyranosyl-α-D-arabinose in 32.6% yield and α-lactose monohydrate is converted to 3-*O*-β-D-galactopyranosyl-α-D-arabinose in 38.1% yield. This convenient chain shortening procedure is thus, apparently, well suited to oligosaccharides. The glycosylpentoses are obtained in crystalline form and as crystalline osazones. The galactosylarabinose is also obtained as its crystalline anilide.

Recently Whistler and Schweiger[2] described the preparation of D-arabinose from D-glucose by a two-stage, but single batch, hypochlorite oxidation. D-Arabinose was obtained in 35% crystalline yield. Work is here undertaken to determine the applicability of this convenient chain shortening procedure to two hexoglyconic acids and to two reducing disaccharides.

General usefulness of the oxidation reaction to glyconic acid is indicated by application to D-mannonic acid and D-galactonic acid with the production of D-arabinose and D-lyxose in crystalline yields of 35.3% and 40.7%, respectively. The yields thus approximate those obtained through use of the Ruff degradation.[3]

A very useful extension of the procedure appears to be to the reducing oligosaccharides where other chain shortening procedures are cumbrous or lead to low over-all yields. The hypochlorite procedure when applied to β-maltose monohydrate produces 3-*O*-α-D-glucopyranosyl-α-D-arabinose in a yield of 32.6%, and when applied to α-lactose monohydrate produces 3-*O*-β-D-galactopyranosyl-α-D-arabinose in 38.1% yield. Both disaccharides are obtained crystalline and as the crystalline phenylosazones. The second disaccharide is also obtained as the crystalline anilide, *N*-phenyl-(3-*O*-β-D-galactopyranosyl) - D - arabinosylamine monohydrate.

EXPERIMENTAL

Oxidation of maltose. Ten grams of β-maltose monohydrate were dissolved in 200 ml. of water and the *p*H was adjusted to 11 with sodium hydroxide. To this was added 500 ml. of 0.334*N* sodium hypochlorite (3 moles of oxidant per mole of maltose) which was adjusted to *p*H 11 with sodium hydroxide and sodium carbonate. The mixture was kept at 25° in the dark and the *p*H was frequently checked and corrected by addition of sodium hydroxide solution. In 22 hr. when about 2.4 moles of sodium hypochlorite per mole of maltose were consumed, the solution was brought to *p*H 5.0 by the addition of hydrochloric acid. To this was added 300 ml. of 0.266*N* sodium hypochlorite: 1.4 moles per mole of original maltose. The mixture was kept at 25° in the dark and the *p*H was maintained at *p*H 4.5–5.0 by the addition of sodium hydroxide solution. After 12 hr. when the oxidant was consumed, the solution was neutralized and concentrated under reduced pressure until sodium chloride crystallized in large amounts. After addition of three volumes of methanol, the salt crystals were removed by filtration. The filtrate was then further desalted by passage through Amberlite IR-120(H) and IR-45(OH) exchange resins.[4] The solution was filtered through a thin layer of activated carbon[5] and concentrated to a sirup under reduced pressure.

(1) This is paper No. 8 in a series concerning "Action of Oxidants on Carbohydrates." The previous paper is R. L. Whistler and A. M. Belfort, *TAPPI*, in press. Journal Paper No. 1640 of the Purdue Agricultural Experiment Station, Lafayette, Ind.

(2) R. L. Whistler and R. Schweiger, *J. Am. Chem. Soc.*, **81**, 5190 (1959).

(3) See: H. G. Fletcher, Jr., H. W. Diehl, and C. S. Hudson, *J. Am. Chem. Soc.*, 72, 4546 (1950).

(4) Products of Rohm & Haas, Philadelphia.

(5) Darco G-60, a product of the Matheson Company, Inc., East Rutherford, N. J.

Paper chromatograms using ethyl acetate:acetic acid:formic acid:water (18:3:1:4 v./v.) as irrigant and silver nitrate[6] as spray reagent showed the presence of a principal component, $R_{glucose}$ 0.52, which gave only D-glucose and D-arabinose on hydrolysis. The sirup also contained small amounts of D-glucose and D-arabinose ($R_{glucose}$, 1.43) and a trace amount of unoxidized maltose ($R_{glucose}$, 0.36).

The amount of the disaccharide ($R_{glucose}$, 0.52) present in the sirup was determined by quantitative[7] paper chromatographic measurement of the increase in D-arabinose which was obtained on hydrolysis. The yield thus calculated was 32.7% of the theoretical amount.

Isolation and identification of 3-O-α-D-glucopyranosyl-α-D-arabinose. Ten grams of β-maltose monohydrate was treated as above except that the crude product was chromatographed on a carbon-Celite[8] column[9] (30 × 170 mm.). The 5% ethanol eluate which contained only the disaccharide was evaporated under reduced pressure to a sirup and triturated with absolute ethanol to give 2.83 g. or 32.6% yield of amorphous disaccharide, $R_{glucose}$ 0.52.

A 1.50-g. sample of this crude, amorphous disaccharide was repurified on a carbon-Celite column[9] (48 × 17 cm.) which was washed successively with 3 l. of water, 4 l. of 1.5% ethanol, 3 l. of 4% ethanol and 3 l. of 6% ethanol. Since paper chromatographic examination showed that the 1.5% and 4% ethanol effluents contained most of the disaccharide, these two were combined and evaporated under reduced pressure to dryness; yield 1.33 g. This material was dissolved in a few drops of water, 20 ml. of methanol was added, and a small amount of insoluble material removed by filtration. The filtrate was evaporated under reduced pressure to about 3 ml., seeded with an authentic sample provided by H. S. Isbell and allowed to stand at room temperature for 2 weeks. Crystals which formed were filtered, washed with methanol, and dried; m.p. 114–117°, yield 0.86 g. Two recrystallizations from 95% methanol afforded pure 3-O-α-D-glucopyranosyl-α-D-arabinose monohydrate; m.p. 119–121°, undepressed on admixture with an authentic sample, $[\alpha]_D^{25}$ +56.9° → +47.0° (constant after 15 hr.) (*c*, 1.0 in water). The observed values are in agreement with the m.p. 121° and $[\alpha]_D$ +47° (water), reported for the α-monohydrate by Moyer and Isbell,[10] but are in disagreement with the m.p. 172° and $[\alpha]_D^{20}$ +16.5° (water), reported by Gakhokidze[11] and with the optical rotation, $[\alpha]_D^{20}$ +72.0° (water), reported for the amorphous disaccharide by Zemplén.[12]

To prepare the phenylosazone, 0.4 g. of the disaccharide and 0.8 g. of phenylhydrazine hydrochloride with 1.5 g. of sodium acetate trihydrate were dissolved in 10 ml. of water and the mixture was heated on a steam bath for 60 min. On cooling and stirring, crystals separated and were recrystallized from 30% ethanol and dried at 70° in vacuum. They decomposed at 195–200°; reported[11] m.p. 195–200°.

Oxidation of lactose. Ten grams of α-lactose monohydrate were oxidized as described for maltose. Paper chromatography of the products showed the presence of a major component at $R_{glucose}$ 0.46. This substance gave D-galactose and D-arabinose on hydrolysis. The amount of the disaccharide present in the sirup as measured by quantitative chromatographic determination of the increase in D-arabinose on hydrolysis showed it present in 36.5% yield.

Another similar oxidation of 10 g. of α-lactose monohydrate gave 3.30 g. of the amorphous disaccharide; yield 38.1%.

Isolation and identification of 3-O-β-D-galactopyranosyl-α-D-arabinose. A 0.60-g. sample of the amorphous disaccharide was dissolved in 3 ml. of methanol, filtered, and the filtrate seeded with an authentic sample provided by H. S. Isbell. On standing at room temperature crystallization proceeded gradually for 2 weeks, at which time the crystals were filtered, washed with methanol, and dried; m.p. 160–163°, yield 0.25 g. Recrystallization was effected by dissolving the crude crystals in a few drops of water, adding 20 ml. of methanol, filtering the resulting solution, concentrating the filtrate to about 3 ml. under reduced pressure, and allowing the solution to stand at room temperature for a week. The pure sample of 3-O-β-D-galactopyranosyl-α-D-arabinose was obtained after two recrystallizations; m.p. 166–168°, undepressed on admixture with an authentic sample, $[\alpha]_D^{25}$ −50.2° → −63.0° (constant after 15 hr.) (*c*, 1 in water). Reported values for the disaccharide are: m.p. 166–168°,[13] 165°,[14] 165–166°,[15] and 162–169°[16]; $[\alpha]_D^{19}$ −50.3° → −63.1°,[13] $[\alpha]_D^{20}$ −55.1°,[14] $[\alpha]_D^{23}$ −54.5° → −62°[16] and $[\alpha]_D^{20}$ −62.5°,[17] in water.

For further identification, a crystalline aniline derivative of the disaccharide was prepared after Kuhn and Kirschenlohr.[16] The mother liquor separated from the crude crystals of the disaccharide was evaporated to dryness. The resulting residue weighing 0.30 g. was dissolved in 2 ml. of methanol; 0.10 g. of aniline was added, and the mixture was heated under reflux for 1.5 hr. After cooling, *N*-phenyl(3-O-β-D-galactopyranosyl)-D-arabinosylamine monohydrate was collected on a fritted glass funnel; yield 0.31 g., m.p. 169–170°. On recrystallization from 80% aqueous ethanol it melted at 170–171° and showed $[\alpha]_D^{25}$ +34.0° (*c*, 0.50 in pyridine); $[\alpha]_D^{25}$ +2.6° → 10.5° (after 1 hr.) → −44.3° (constant after 10 hr.) (*c*, 0.42 in water) and $[\alpha]_D^{25}$ +37.0° → +25.0° (after 4 days) → +16.5° (after 14 days) (*c*, 0.60 in dimethylformamide). Kuhn and Kirschenlohr[16] reported m.p. 170–171°, $[\alpha]_D^{22}$ +34.7° (pyridine), $[\alpha]_D^{22}$ −16° → −42° (after 1 hr. in water) and $[\alpha]_D^{25}$ +36° → +7.5° (after 4 days in dimethylformamide). The phenylosazone prepared as described above decomposed at 236°; reported m.p. 236–238°,[18] 242°.[19]

Oxidation of maltobionic acid. β-Maltose monohydrate was oxidized by bromine in the presence of calcium benzoate[20] and the resulting calcium maltobionate solution was deionized with Amberlite IR-120(H). After neutralization with lithium hydroxide, the solution was concentrated to a thick sirup and mixed with 2-propanol. On cooling the mixture, fine crystals of lithium maltobionate trihydrate were obtained; $[\alpha]_D^{25}$ +96.8° (*c*, 5.0 in water), reported[21] $[\alpha]_D^{20}$ +97.3° (*c*, 8.7 in water).

A 4.28-g. portion of lithium maltobionate trihydrate (0.01 mole) was dissolved in 200 ml. of water and was mixed with 200 ml. of 0.222*N* sodium hypochlorite (2 moles per mole of maltobionate) at *p*H 5. The mixture was held at 25° in the dark and the *p*H maintained at 4.5–5.0 by the addition of

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(7) R. L. Whistler, H. H. Kramer, and R. D. Smith, *Arch. Biochem. Biophys.*, 66, 374 (1957).

(8) Celite is diatomaceous silica, a product of Johns-Manville, New York.

(9) R. L. Whistler and D. F. Durso, *J. Am. Chem. Soc.*, 72, 677 (1950).

(10) J. D. Moyer and H. S. Isbell, Abstracts of Papers, 126th Meeting of the American Chemical Society, New York, N. Y., 1954, p. 24-D.

(11) A. M. Gakhokidze, *J. Gen. Chem. USSR*, 18, 60 (1948); *Chem. Abstr.*, 42, 4948 (1948).

(12) G. Zemplén, *Ber.*, 60, 1555 (1927).

(13) G. Zemplén, *Ber.*, 59, 2402 (1926); 60, 1309 (1927).

(14) A. M. Gakhokidze, *J. Gen. Chem. USSR*, 16, 1907 (1946); *Chem. Abstr.*, 41, 6208 (1947).

(15) F. Zilliken, P. N. Smith, R. M. Tomarelli, and P. György, *Arch. Biochem. Biophys.*, 54, 398 (1955).

(16) R. Kuhn and W. Kirschenlohr, *Ann.*, 600, 135 (1956).

(17) H. L. Frush and H. S. Isbell, *J. Res. Natl. Bur. Standards*, 50, 133 (1953).

(18) O. Ruff and G. Ollendorff, *Ber.*, 33, 1798 (1900).

(19) G. Zemplén, *Ber.*, 59, 2402 (1926).

(20) C. S. Hudson and H. S. Isbell, *J. Am. Chem. Soc.*, 51, 2225 (1929).

(21) H. S. Isbell and R. Schaffer, *J. Am. Chem. Soc.*, 78, 1887 (1956).

sodium hydroxide when necessary. After 28 hr. when the oxidant was consumed, the mixture was deionized by means of both cation and anion exchange resins in the manner described above and was concentrated to 100 ml. A 50-ml. aliquot was concentrated further and chromatographed on a carbon-Celite column. The first 300 ml. of aqueous effluent contained both D-glucose and D-arabinose in small amounts. The next 100 ml. contained a very small amount of D-glucose and some disaccharide. The remaining disaccharide was then removed from the column with 700 ml. of 5% ethanol. This fraction was concentrated to a sirup and triturated with absolute ethanol to give 0.260 g. (16.6% of the theoretical amount) of amorphous powder ($R_{glucose}$ 0.52) which yielded only D-glucose and D-arabinose on hydrolysis. The phenylosazone, m.p. 196–200°, showed no change in melting point on admixture with 3-*O*-α-D-glucopyranosyl-α-D-arabinose obtained by the oxidation of maltose.

Oxidation of D-*mannonic acid.* D-Mannono-γ-lactone was prepared from D-mannose by oxidation with bromine,[22] m.p. 151°. After hydrolysis of 1.78 g. (0.01 mole) of D-mannono-γ-lactone by boiling with 100 ml. of 0.1*N* sodium hydroxide solution for 10 min., the solution was adjusted to *p*H 5 with hydrochloric acid, and 100 ml. of 0.418*N* sodium hypochlorite (2 moles per mole of D-mannonic acid) at *p*H 5 were added. The solution was kept at 25° in the dark and the *p*H was maintained at 4.5–5.0 by the addition of sodium hydroxide solution. After about 30 hr. when the oxidant was consumed, the reaction mixture was deionized with ion exchange resins and found to contain D-arabinose in 48.7% of the theoretical amount when analyzed by the Willstätter-Schudel method.[23] Crystalline β-D-arabinose was obtained in the yield of 0.53 g. (35.3% of the theoretical amount); $[\alpha]_D^{25}$ −175° → −105° (*c*, 1.0 in water), m.p. 156–157°, undepressed on admixture with authentic D-arabinose.

Oxidation of D-*galactonic acid.* After hydrolysis of 1.78 g. (0.01 mole) of D-galactono-γ-lactone by boiling with 100 ml. of 0.1*N* sodium hydroxide solution for 10 min., the solution was adjusted to *p*H 5 with hydrochloric acid and mixed with 100 ml. of 0.401*N* sodium hypochlorite solution (2 moles per mole of D-galactonate) at *p*H 5. The oxidation was completed in about 24 hr. at the *p*H range of 4.0–5.0 in the dark at 25°. Determination of D-lyxose by Willstätter-Schudel titration of the deionized sirup indicated that there was present 50.1% of the theoretical amount. The yield of crystalline α-D-lyxose, $[\alpha]_D^{25}$ −14° → +5.3° (*c*, 1.0 in water) obtained from the final solution was 0.61 g. (40.7% of the theoretical amount); m.p. 103–106°, undepressed on admixture with authentic D-lyxose.

Acknowledgment. The authors gratefully acknowledge grants from the American Maize Company and from the Department of Health, Education, and Welfare which helped to support this work. Thanks are also given to Dr. Susumu Hirase for his crystallization of the two disaccharides and to Dr. H. S. Isbell for supplying nuclei for these crystallizations.

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[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Alumina: Catalyst and Support. VI.[1] Aromatization of 1,1-Dimethylcyclohexane, Methylcycloheptane, and Related Hydrocarbons over Platinum-Alumina Catalysts[2,2a]

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Received July 22, 1960

The aromatization of 1,1-dimethylcyclohexane (I), 4,4-dimethylcyclohexene (II), methylcycloheptane (III), and 5,5-dimethylcyclohexadiene (IV) over platinum-alumina catalysts has been investigated. The catalysts were prepared by impregnating aluminas of various intrinsic acidities with a solution of dinitrodiammine platinum, $Pt(NH_3.NO_2)_2$.

The relative acidities of the aluminas and the method of platinizing them were found to have a profound effect on the composition of the aromatized product. The aromatization of I and II was accompanied by isomerization and the extent of isomerization could be related to the intrinsic acidity of the alumina. The product of the isomerization was mainly *o*-xylene admixed with *m*- and *p*-xylene and in the presence of a catalyst having high intrinsic acidity, alkylcyclopentanes were also produced.

The aromatization of methylcycloheptane formed ethylbenzene and xylenes; the distribution of the various aromatic compounds depended upon the acidity of the alumina used.

Recent publications of this laboratory have stated that aluminas have intrinsic acidic properties and that the relative acidities of the aluminas depend upon the method of their preparation.[4] It was demonstrated that alumina prepared from aluminum isopropoxide is more acidic than that prepared from potassium aluminate. The relative acidities of the aluminas were determined by the ease with which they brought about the isomerization of various olefins.[4,5] Recently it has been shown

(1) For paper V of this series see: H. Pines and C. N. Pillai, *J. Am. Chem. Soc.*, 82, 2401 (1960).

(2) Paper III of the series of Aromatization of Hydrocarbons. For paper II see: H. Pines and C. T. Chen, *J. Am. Chem. Soc.*, 82, 3562 (1960).

(2a) This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said Fund.

(3) Postdoctoral Fellow, 1958–1959.

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