material was recrystallized several times from low-boiling petroleum ether and then melted at 120.5–121°.

Anal. Calcd. for $C_{14}H_{20}O$: C, 82.46; H, 9.27. Found: C, 82.43; H, 9.47.

The remainder of the crude product was transferred to a distilling flask and distilled from freshly fused potassium acid sulfate. The fraction boiling at 120–130° (4–5 mm.) was collected, wt. 54 g. (70%). The analytical sample boiled at 89–90° (0.7 mm.), n^{26}D 1.5495.

Anal. Calcd. for $C_{14}H_{18}$: C, 90.27; H, 9.73. Found: C, 90.21; H, 9.58.

2-Isopropyl-4,5-dimethylindan.—A solution of 8.9 g. of the above indene in 70 ml. of ethanol was reduced with 5% palladium–charcoal at 2–3 atmospheres until hydrogen uptake ceased. Removal of solvent followed by fractional distillation *in vacuo* yielded 6.3 g. of the indan, b.p. 102–105° (3 mm.). The analytical sample boiled at 95–96° (1.5 mm.), n^{24}D 1.5180.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.25; H, 10.96.

4,5-Dimethylazulene.—Reaction of 36 g. of 4,5-dimethylindan with seven 8-g. portions of ethyl diazoacetate in the manner previously described[9] resulted in recovery of 19 g. of the crude indan and isolation of 37 g. of highly colored ester, b.p. 130–180° (2 mm.). This was saponified by refluxing with 140 ml. of ethanol, 30 ml. of water and 20 g. of potassium hydroxide. From the acid fraction was obtained 12.5 g. of green viscous material, b.p. 165–185° (2.5 mm.) which was dehydrogenated and decarboxylated by mixing with 2 g. of 10% palladium-on-charcoal and distilling over an open flame. The blue product was fractionated at reduced pressure, about 1.5 ml. of material boiling in the range 110–160° (1.7 mm.) being collected. The forerun and the residue were combined and dehydrogenated once more. This resulted in an additional 0.6 ml. of the crude azulene. The azulene was dissolved in 25 ml. of ethanol and mixed with a solution of 2 g. of trinitrobenzene in 75 ml. of warm ethanol. On cooling 1.25 g. of complex separated. Chromatography over alumina, eluent cyclohexane–benzene (3:1), resulted in 0.29 g. of blue dimethylazulene, b.p. 105–120° (1.5 mm.).

The trinitrobenzene complex, violet-black needles from ethanol, was recrystallized twice and melted at 157.5°.

Anal. Calcd. for $C_{18}H_{15}N_3O_6$: C, 58.54; H, 4.09. Found: C, 59.25; H, 4.39.

2,4,5-Trimethylazulene.—In a similar way, 42 g. of 2,4,5-trimethylindan, after treatment with seven 8-g. portions of diazoacetic ester, yielded 32 g. of deeply colored ester, b.p. 130–180° (1.5 mm.), and 24 g. of crude starting material. On saponification there was obtained 13.2 g. of greenish viscous acid, b.p. 150–175° (1.5 mm.) which, when subjected to two treatments with 10% palladium-on-charcoal, afforded 5.3 ml. of a crude azulene, b.p. 105–160° (2.5 mm.). This was dissolved in 50 ml. of ethanol and treated with a solution of 3 g. of trinitrobenzene in 100 ml. of warm ethanol. The complex, wt. 1.95 g., was decomposed by chromatography in the usual way. The violet-blue trimethylazulene, wt. 0.78 g., boiled at 110–120° (1.3 mm.).

The trinitrobenzoate, violet-black needles, was recrystallized twice from ethanol and melted at 160.5–161.5°.

Anal. Calcd. for $C_{19}H_{17}N_3O_6$: C, 59.53; H, 4.47. Found: C, 60.12; H, 4.66.

The trinitrotoluene complex, violet-black needles from ethanol, melted at 86–87°.

Anal. Calcd. for $C_{20}H_{19}N_3O_6$: C, 60.45; H, 4.82. Found: C, 60.52; H, 4.89.

2-Isopropyl-4,5-dimethylazulene.—Treatment of 50 g. of 2-isopropyl-4,5-dimethylindan with seven 10-g. portions of diazoacetic ester yielded 49.5 g. of crude product, b.p. 125–170° (1.5 mm.) and 19 g. of recovered material. The yield of acid, b.p. 170–190° (2 mm.), after saponification with 25 g. of potassium hydroxide and 200 ml. of 80% ethanol was 20 g. On treatment with 3 g. of palladium–charcoal there was obtained 8.8 ml. of distillate, b.p. 100–160° (1.5 mm.), which was dissolved in 50 ml. of ethanol and added to a solution of 3 g. of trinitrobenzene in 100 ml. of warm ethanol. Decomposition of the complex, wt. 3.3 g., by chromatography over alumina followed by distillation gave 1.13 g. of violet-blue azulene, b.p. 115–125° (1 mm.).

The trinitrobenzene complex, violet-black needles, was recrystallized several times from ethanol and then melted at 136.5–137°.

Anal. Calcd. for $C_{21}H_{21}N_3O_6$: C, 61.34; H, 5.14; N, 10.24. Found: C, 61.50; H, 5.41; N, 9.90.

The picrate, black needles, was recrystallized from ethanol and melted at 117–118°.

Anal. Calcd. for $C_{21}H_{21}N_3O_7$: C, 59.00; H, 4.96. Found: C, 59.13; H, 5.02.

The trinitrotoluene complex was recrystallized from ethanol, m.p. 59.5–61°.

Anal. Calcd. for $C_{22}H_{23}N_3O_6$: C, 62.11; H, 5.45. Found: C, 62.25; H, 5.47.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, BLOCKSON CHEMICAL COMPANY]

Direct Reduction of Aldoses and Ketoses by Raney Nickel

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Aldoses and ketoses can be effectively reduced to the corresponding polyhydric alcohols by refluxing with Raney nickel aqueous alcohol. This affords a convenient laboratory preparative method for the polyols.

In connection with reductive desulfurization of thiazolidine derivatives[1] of aldoses and cysteine, it was found that good yields of the polyhydric alcohols corresponding to the original sugar could be obtained with Raney nickel.[2] In addition, the earlier reported reduction of aldonic acid thiolesters to the corresponding polyols by Jeger and co-workers[3] prompted us to investigate the direct conversion of aldoses and ketoses to the polyols from a preparative standpoint. Such a method would eliminate the use of pressure equipment in the customary catalytic methods and would also eliminate the troublesome removal of inorganic ions as in the sodium amalgam reduction of aldoses and ketoses. When D-mannose and D-galactose were refluxed with a large excess of Raney nickel in 70% ethanol, D-mannitol and D-galactitol were obtained in high yield and in good purity. Subsequent quantitative investigation of this reaction, by measurement of loss in reducing power using "aged" Raney nickel, indicated that the rate of conversion varied somewhat with different types of carbohydrates.

It is obvious that the above described method offers certain advantages in the reduction of radio-

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[1] See M. P. Schubert, *J. Biol. Chem.*, **130**, 601 (1939); G. Ägren, *Enzymologia*, **9**, 321 (1941).

[2] These data were reported by Irene Vadopalaite and J. V. Karabinos at the Illinois Academy of Sciences Meeting, Macomb, Illinois, May 9, 1953.

[3] O. Jeger, J. Norymberski, S. Szpilfogel and V. Prelog, *Helv. Chim. Acta*, **29**, 684 (1946).

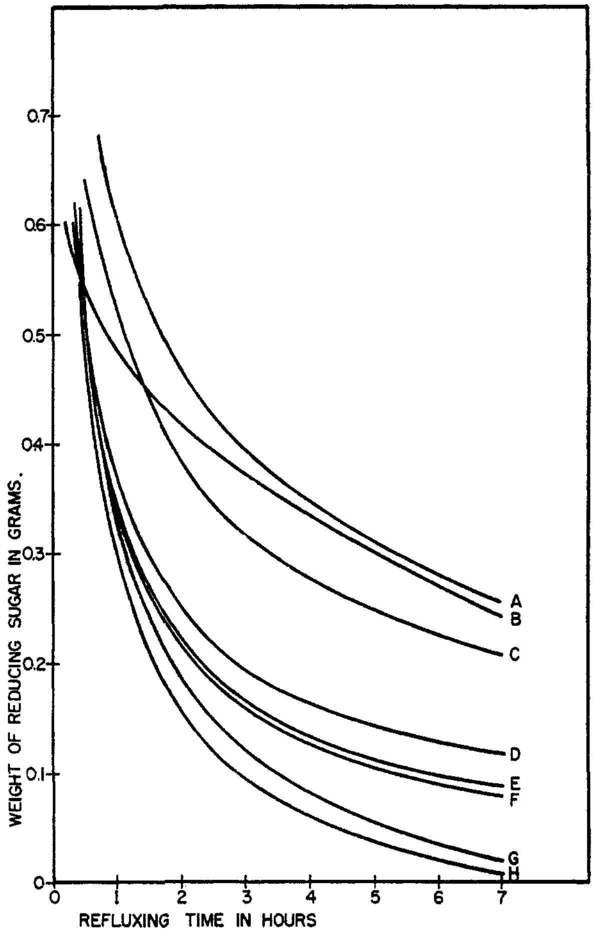

Fig. 1.—Reduction of one gram of A, maltose; B, lactose; C, D-xylose; D, D-mannose; E, D-glucose; F, D-fructose; G, D-galactose; H, D-manno-D-*gala*-heptose by refluxing with excess "aged" Raney nickel in aqueous alcohol.

active aldoses to the corresponding polyols[4] in that contamination of high pressure equipment is obviated.

Experimental

Reduction of Various Sugars with Raney Nickel.—The sugars indicated in Fig. 1 were obtained commercially except for D-manno-D-*gala*-heptose which was conveniently prepared from D-mannose and nitromethane according to the directions of Sowden and Schaffer.[5] One gram of each sugar and approximately 10 g. of Raney nickel catalyst,[6] which had been aged for six months, were diluted to 100 ml. with 70% aqueous ethanol (7 volumes of absolute ethanol to 3 volumes of distilled water). A 1-ml. sample was removed for analysis of reducing sugar by the Hagedorn–Jensen micromethod[7] before and at various intervals up to seven hours while refluxing the mixture. From the reducing values obtained, the extent of hydrogenation of the sugars to the polyhydric alcohols was ascertained and is depicted in Fig. 1. It would seem that hexoses, especially those with a *gala* configuration, are effectively hydrogenated while disaccharides are somewhat more difficult to convert to their polyols. A freshly prepared sample of Raney nickel gave approximately 90% reduction of D-xylose and D-mannose after refluxing for 15 minutes and complete reduction within 1.5 hours.

Reduction of D-Mannose to D-Mannitol.—A 1-g. sample of D-mannose was refluxed with freshly prepared Raney nickel in 70% ethanol for 1.5 hours as described above. The nickel was removed by filtration and the filtrate was concentrated to a thin sirup *in vacuo*. Twenty ml. of 95% ethanol was added to this sirup and upon standing in a refrigerator, 0.8 g. (79%) of D-mannitol of m.p. 164–166° and $[\alpha]^{27}\mathrm{D}$ −0.5° (*c* 2 in water) was obtained in crystalline condition. The recorded physical constants of D-mannitol[8] are m.p. 166° and $[\alpha]^{25}\mathrm{D}$ −0.21° (water). A preparation in which aged Raney nickel (six months) was used with a seven-hour reflux time gave similar results.

Anal. Calcd. for $C_6H_{14}O_6$: C, 39.56; H, 7.75. Found: C, 39.65; H, 8.05.

Reduction of D-Galactose to D-Galactitol.—A 1-g. sample of D-galactose was refluxed with Raney nickel, aged for six months, by the above described procedure. D-Galactitol (dulcitol) crystallized slowly after addition of ethanol to the sirupy reaction product, and it weighed 0.75 g. (74%). It gave m.p. of 185–186° and showed no optical rotation. D-Galactitol has a reported melting point of 188.5° and is optically inactive.[9]

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(4) For example, the reduction of D-mannose-1-C^{14} to D-mannitol-1 and 6-C^{14} as described by H. S. Isbell and J. V. Karabinos, *J. Research Natl. Bur. Standards*, **48**, 438 (1952).

(5) J. C. Sowden and R. Schaffer, This Journal, **73**, 4662 (1951).

(6) L. Covert and H. Adkins, *ibid.*, **54**, 4116 (1932).

(7) F. J. Bates, "Polarimetry, Saccharimetry and the Sugars," Superintendent of Documents, Washington, D. C., 1942, pp. 198 604.

(8) W. Pigman and R. Goepp, Jr., "Chemistry of the Carbohydrates," Academic Press, Inc., New York, N. Y., 1948, p. 238.

(9) R. Lohmar and R. M. Goepp, Jr., *Advances in Carbohydrate Chem.*, **4**, 219 (1949).