Anal. Calcd. for $C_{11}H_{14}N_2OS_2$: C, 51.93; H, 5.55; N, 11.01 Found: C, 52.11; H, 5.57; N, 11.30.

B.—A solution of 0.18 g. (0.50 mmoles) of VII (R = *p*-$CH_3OC_6H_4$; R′ = CH_3) and 1.0 mmole of carbon disulfide in 2.0 ml. of acetonitrile was heated in a sealed tube at 80° for 12 hr. Crystallization of the product from carbon disulfide–methanol yielded 0.21 g. of colorless crystals, m.p. 88–90°.

Anal. Found: C, 52.04; H, 5.65; N, 11.00.

2-(*p*-Chlorophenyl)-3,4-dimethyl-1,3,4-thiadiazolidine-5-thione (XV).—From 0.73 g. (2.0 mmoles) of VII (R = *p*-ClC_6H_4; R′ = CH_3) and 4.0 mmoles of carbon disulfide in 5 ml. of acetonitrile heated in a sealed tube at 80° for 15 hr., a yield of 0.995 g. of material with m.p. 75–78° was obtained. Recrystallization from methanol yielded glistening plates, m.p. 86–86.5°.

Anal. Calcd. for $C_{10}H_{11}ClN_2S_2$: C, 46.41; H, 4.28; N, 10.83. Found: C, 46.86; H, 4.16; N, 10.83.

Treatment of XV with VII (R = *p*-ClC_6H_4; R′ = CH_3) in refluxing acetonitrile yielded no bis adduct; the components were recovered unchanged.

2-(*p*-Nitrophenyl)-3,4-dimethyl-1,3,4-thiadiazolidine-5-thione (XVI).—The analogous reaction of 1.0 mmole of VII (R = *p*-$NO_2C_6H_4$; R′ = CH_3) with 15 ml. of carbon disulfide at 120° for 100 hr. was carried out yielding 0.45 g., m.p. 129–130°. Recrystallization from methanol–carbon disulfide yielded yellow crystals of m.p. 130–131°, infrared (KBr) C=S 9.08 μ.

Anal. Calcd. for $C_{10}H_{11}N_3O_2S_2$: C, 44.60; H, 4.12; N, 15.60. Found: C, 44.73; H, 4.43; N, 15.11.

2,3,4-Triphenyl-1,3,4-thiadiazolidine-5-thione (XVII).—A solution of 0.27 g. (0.5 mmole) of VII (R = R′ = C_6H_5) in 5.0 ml. of carbon disulfide was heated at 130° for 100 hr. in a sealed tube. Upon cooling in the refrigerator, 0.170 g. of crystalline material was obtained, which was recrystallized from chloroform–methanol and had m.p. 160–161°.

Anal. Calcd. for $C_{20}H_{16}N_2S_2$: C, 68.93; H, 4.63; N, 8.04. Found: C, 68.83; H, 4.63; N, 8.29.

3,4-Dimethyl-,13,4-thiadiazolidine-2,5-dithione (XXII).—Carbon disulfide, 3.0 ml., was added slowly to 0.30 g. of 1,2-dimethylhydrazine (5.0 mmoles). Evolution of a gas was clearly observed as the reaction proceeded. After a few minutes the colorless crystalline product was collected, 0.63 g. (71%), m.p. 159–162°. The analytical sample was prepared by recrystallization from chloroform and had m.p. 163–164°, lit.[19] 168–169°.

Anal. Calcd. for $C_4H_6N_2S_3$: C, 26.94; H, 3.39; N, 15.71. Found: C, 27.04; H, 3.42; N, 15.69.

3,4-Diethyl-1,3,4-thiadiazolidine-2,5-dithione (XXIII).—This compound was prepared under conditions analogous to those used above by the interaction of 1,2-diethylhydrazine and carbon disulfide. Recrystallization from methanol yielded colorless material of m.p. 113–114°.

Anal. Calcd. for $C_6H_{10}N_2S_3$: C, 34.91; H, 4.88; N, 13.57. Found: C, 35.08; H, 4.90; N, 13.30.

The Correlation of D-*arabino*-L-*galacto*- and D-*lyxo*-D-*manno*-Nononic 1,4-Lactones

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Repetition of the cyanohydrin synthesis from D-*erythro*-L-*manno*-octose (I) has yielded the products described by Fischer and Hagenbach rather than those described by Fischer and Passmore. Direct comparisons have shown the identity of our nononic lactone and phenylhydrazide with those of Fischer and Hagenbach and also with those of Sowden and Strobach, who applied the nitromethane synthesis to the octose. The borohydride reduction of our D-*arabino*-L-*galacto*-nononic 1,4-lactone (II, whose origin was D-mannose) and of D-*lyxo*-D-*manno*-nononic lactone (V, whose origin was D-galactose) to the same nonitol (III, D-*arabino*-L-*galacto*-nonitol = D-*lyxo*-D-*manno*-nonitol) correlates the configurations assigned to these two C_9-sugar series and verifies the configurations assigned to all the related intermediate seven- and eight-carbon sugars and their derivatives. This procedure is a variation of what Hudson has termed Emil Fischer's method of obtaining conclusive proof of configuration by way of an identical active alcohol from two different aldoses. Some infrared data on aldonic lactones and phenylhydrazides are included in the Experimental section.

Many years ago Fischer and Passmore[2] described the addition of hydrogen cyanide to "*d*-mannooctose" and the isolation of a "*d*-mannononononolactone"; the lactone, upon reduction with sodium amalgam, yielded a crystalline "*d*-mannononose" that was fermented readily by fresh brewers' yeast. Subsequently, Fischer[3] wrote that Dr. R. Hagenbach had attempted a repetition of that synthesis; the result, as Hudson[4] was able to reveal through a study of Hagenbach's notebook, was the isolation of a different lactone and of an amorphous nonose that was not fermentable by yeast. The structure of Fischer and Passmore's "*d*-mannooctose" was established later as that of D-*erythro*-L-*manno*-octose (I) by Peirce[5] and confirmed by Hann, Maclay, Knauf, and Hudson.[6] While the structure of Fischer and Passmore's "*d*-mannononose" still remains a mystery, the structure of Fischer and Hagenbach's nonose was deemed to be probably that of D-*arabino*-L-*galacto*-nonose by Sowden and Strobach.[7] Those authors added nitromethane to D-*erythro*-L-*manno*-octose (I), separated the epimeric 1-deoxy-1-nitrononitols, and then by means of the Nef reaction obtained two amorphous nonoses. To one of these they assigned the D-*arabino*-L-*galacto*-nonose configuration by application of certain rules of optical rotation. The melting points and rotations (when obtainable) of this nonose and its phenylhydrazone, as well as of the corresponding nononic lactone and phenylhydrazide, were in quite good agreement with the data found in Hagenbach's notebook.[4] Furthermore, the nonose was not fermentable.

Hudson,[8] meanwhile, had added hydrogen cyanide to D-*erythro*-L-*manno*-octose (I) and isolated a crystalline nononic acid. This substance has now been found

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(1) University of Illinois.

(2) E. Fischer and F. Passmore, *Ber.*, **23**, 2226 (1890).

(3) E. Fischer, "Untersuchungen über Kohlenhydrate und Fermente (1884–1908)," Springer-Verlag, Berlin, 1909, p. 582.

(4) C. S. Hudson, *Advan. Carbohydrate Chem.*, **1**, 1 (1945).

(5) G. Peirce, *J. Biol. Chem.*, **23**, 327 (1915).

(6) R. M. Hann, W. D. Maclay, A. E. Knauf, and C. S. Hudson, *J. Am. Chem. Soc.*, **61**, 1268 (1939).

(7) J. C. Sowden and D. R. Strobach, *ibid.*, **82**, 956 (1960).

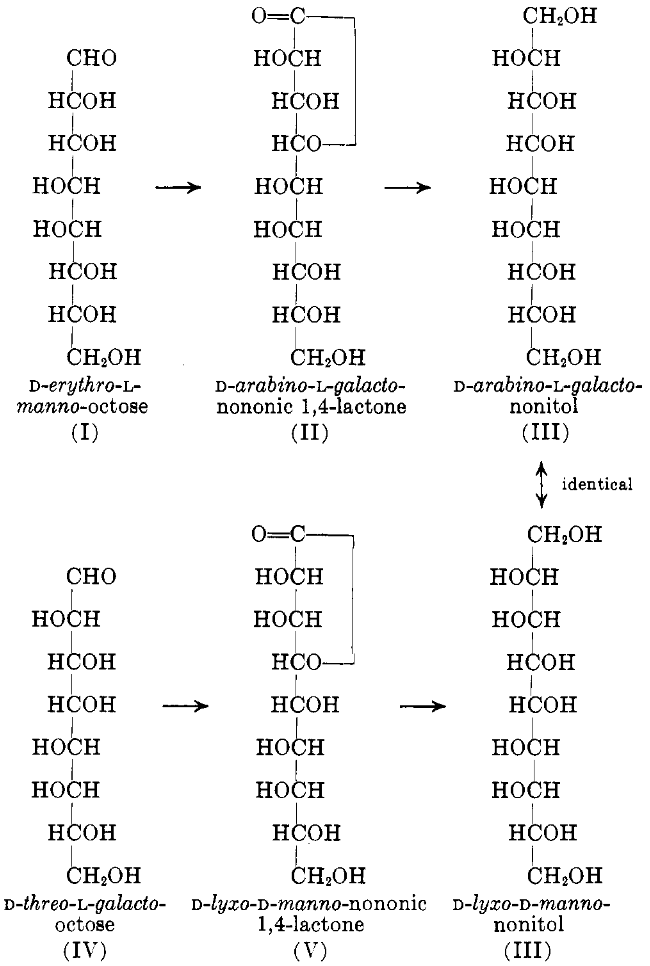
(8) C. S. Hudson's laboratory notebook for 1950; see Experimental section.

by direct comparison to be identical with the D-*arabino*-L-*galacto*-nononic acid described by Sowden and Strobach.[7] Similarly, the derived lactone (II) and phenylhydrazide were found to be identical with those obtained through the nitromethane synthesis.[7]

Finally, through the cooperation of Professor Clinton E. Ballou we were able to obtain samples of the nononic lactone and nononic phenylhydrazide of Fischer and Hagenbach (a note says that the work was done in 1901–1902). Infrared spectra showed the identity of these substances with the corresponding compounds prepared by Sowden and Strobach and with those prepared from Hudson's nononic acid.

Hann, Merrill, and Hudson[9] have attributed to Emil Fischer three methods of obtaining conclusive proof of the configuration of sugars: (1) proof by way of a *meso* derivative; (2) proof of epimerism by way of osazone identity; and (3) proof by way of an identical active alcohol from two different aldoses. In this paper we present a slight variation of method 3 as applied for the first time in the nonose series. When D-*arabino*-L-*galacto*-nononic 1,4-lactone (II)[7] was reduced with borohydride it yielded the corresponding D-*arabino*-L-*galacto*-nonitol (III), which was characterized through its crystalline nonaacetate. Inspection of formula III showed that this nonitol should be obtainable also by reduction of one of the epimeric nonoses (or nononic lactones) derivable by a cyanohydrin or nitromethane synthesis from the known D-*threo*-L-*galacto*-octose (IV).[10] Maclay and Hudson[11] had already added hydrogen cyanide to that octose (IV) and obtained a crystalline nononic lactone. Starting with this sample of lactone we first prepared a benzimidazole; its levorotation, by application of the "benzimidazole rule,"[12] indicated that the hydroxyl group at C-2 was on the left when written in the Fischer projection formula, and the compound must be D-*lyxo*-D-*manno*-nononic 1,4-lactone (V) rather than its epimer. Reduction of this lactone (V) with borohydride yielded the crystalline D-*lyxo*-D-*manno*-nonitol (III) whose crystalline nonaacetate was identical with that derived from reduction of the nononic lactone II.

Thus, a conclusive proof of configuration has been obtained for all of the substances in the two series of seven-, eight-, and nine-carbon sugars derived from D-mannose on the one hand and from D-galactose on the other. Only if these compounds had the assigned structures could the same nonitol (III) be formed from each of the nononic lactones II and V.


D-*erythro*-L-*manno*-octose (I)

D-*arabino*-L-*galacto*-nononic 1,4-lactone (II)

D-*arabino*-L-*galacto*-nonitol (III)

D-*threo*-L-*galacto*-octose (IV)

D-*lyxo*-D-*manno*-nononic 1,4-lactone (V)

D-*lyxo*-D-*manno*-nonitol (III)

Experimental

D-*arabino*-L-*galacto*-Nononic Acid from the Addition of Hydrogen Cyanide to D-*erythro*-L-*manno*-Octose (I).—Dr. Hudson's notebook records that in 1950 he dissolved 12 g. of the octose[6] in 100 ml. of water, added 5 ml. of liquid hydrogen cyanide, and kept the mixture in the refrigerator at 5° for 12 days. Considerable crystallization began after a couple of days. The pale yellow solution was diluted with 75 ml. of water and boiled for 0.5 hr.; the precipitate (amide?) was dissolved. About 15 g. of barium hydroxide octahydrate in 500 ml. of water was added and the solution was diluted further with water to bring the total volume to 2 l. The mixture was boiled, presumably until the evolution of ammonia had ceased, and with 2-octanol added to control foaming; a very voluminous precipitate of basic barium nononate separated. Dr. Hudson carried out two such experiments. In the first one, at this point he bubbled in carbon dioxide until the solution was no longer basic to phenolphthalein. The mixture was then boiled, cooled, and filtered on a Büchner funnel; the residue was washed with water. The filtrate and washings were decationized by passage through a column of Amberlite IR-100 ion-exchange resin and the eluate was concentrated on the steam bath in a current of air to give 1.7 g. of "lactone." The washed residue of barium salt was digested with 400 ml. of warm, 10% aqueous acetic acid to dissolve any barium carbonate, and again filtered and washed with water. This new residue was boiled with 7 g. of potassium carbonate in 200 ml. of water for 1 hr. The appearance of the solid phase changed and, after filtration, the mixture of soluble potassium salts was passed through a column of Amberlite IR-100 (H^+) ion-exchange resin; concentration of the eluate soon gave crystals to raise the total yield of "lactone" to 5.5 g. In the second experiment, at the point noted above, Dr. Hudson added enough dilute aqueous sulfuric acid to convert all the barium ions into barium sulfate; the mixture was heated on the steam bath for 2 hr. and the precipitate was allowed to settle overnight at room temperature. The resulting clear supernatant solution gave a very faint test for sulfate ion. The light yellow color was removed by the addition of 10 g. of decolorizing carbon and, after filtration, the 3 l. of clear, colorless solution was concentrated on the steam bath in a current of air. Crystals had begun to separate when the volume had been reduced to 300 ml.

From one or the other of Dr. Hudson's experiments there remained 1.8 g. of material labeled "D-manno-L-*gala*-nononic lactone." Upon recrystallization from hot water it separated in rather insoluble, fine needles that had the composition of the free acid rather than of the lactone.

Anal. Calcd. for $C_9H_{18}O_{10}$: C, 37.77; H, 6.34; mol. wt., 286. Found: C, 38.28; H, 6.22; mol. wt. (by titration with sodium hydroxide), 290.

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(9) R. M. Hann, A. T. Merrill, and C. S. Hudson, *J. Am. Chem. Soc.*, **66**, 1912 (1944).

(10) E. Fischer, *Ann.*, **288**, 139 (1895); W. D. Maclay, R. M. Hann, and C. S. Hudson, *J. Am. Chem. Soc.*, **60**, 1035 (1938).

(11) Dr. W. Dayton Maclay's laboratory notebook for 1937.

(12) N. K. Richtmyer and C. S. Hudson, *J. Am. Chem. Soc.*, **64**, 1612 (1942).

Its melting point depended upon the rate of heating; when the product was heated slowly it melted at 200° with the evolution of gas, but when the capillary was put into the bath at 215° and heated fairly rapidly the melting point was 225–226° dec. Sowden and Strobach[7] reported that their D-*arabino*-L-*galacto*-nononic acid melted at 223°, and the melting point of a mixture of Hudson's acid with an authentic sample of Sowden and Strobach's acid was not depressed. The infrared spectra of the two acids in Nujol mulls confirmed their identity. The principal absorption bands were located at 3280, 3180 (sh), 1740 (C═O), 1316, 1263, 1220, 1133, 1092, 1073, 1058, 1032, 954, 887, 768, and 732 (broad band) cm.$^{-1}$.

Conversion of D-*arabino*-L-*galacto*-Nononic Acid into D-*arabino*-L-*galacto*-Nononic 1,4-Lactone (II) and Its Phenylhydrazide.—A sample of Hudson's nononic acid was lactonized by refluxing in 2-methoxyethanol for about 12 hr. and then concentrating the solution to a small volume by heating on a hot plate. Upon cooling, granular prisms of the lactone (II) separated; the product, washed with methanol and dried at room temperature, showed some decomposition on heating, but a sample put into the bath at 197° melted at 205–206° in accord with the m.p. 205–206° reported by Sowden and Strobach.[7] The melting point of a mixture of the two lactones was not depressed. Those authors found $[\alpha]^{20}\text{D}$ +58.5°, we found +56.0°, and Hagenbach[4] reported +60° for his best sample, all in water. Hagenbach quoted melting points between 192 and 202° dec. with 199.5° (cor.) for his best product. We recrystallized a sample of Hagenbach's lactone from 2-methoxyethanol and found that when put into the bath at 197° it also melted at 205–207° followed by the evolution of gas and subsequent darkening. The melting point of a mixture of our product with his showed no depression. Complete identity of the three lactone samples (Nujol mulls) was confirmed by their infrared spectra which showed the principal absorption bands at 3410, 3270, 1774 (γ-lactone C═O), 1303, 1178, 1157, 1100, 1055, 1003, and 893 cm.$^{-1}$.

Another sample of Hudson's nononic acid (120 mg.) was suspended in 25 ml. of water and heated with 120 mg. of phenylhydrazine for 8 hr. on the steam bath. The acid went into solution slowly and then, as the solution became more concentrated, it deposited clusters of tiny, plate-like needles. The yellowish product was filtered and washed with water and ethyl ether, 94 mg. After recrystallization from hot water the tiny grains of D-*arabino*-L-*galacto*-nononic phenylhydrazide melted to a black liquid with the evolution of much gas at about 242°; Sowden and Strobach[7] reported 251°, and the melting point of a mixture of the two samples was not depressed. Hagenbach[4] reported m.p. 254°; his sample showed the same melting point behavior as ours. A comparison of the infrared spectra of the three phenylhydrazide samples in Nujol mulls confirmed their identity. The principal absorption bands of the D-*arabino*-L-*galacto*-nononic phenylhydrazide were located at 3300, 3200, 1667 (C═O), 1303, 1090, 1075, 1045, 1027, 956, 895, 732 (broad band), and 692 cm.$^{-1}$. Because we have been unable to find any recorded spectra for aldonic phenylhydrazides we have obtained two for comparison. Thus, D-*glycero*-D-*manno*-heptonic phenylhydrazide[13] showed a strong carbonyl absorption band at 1665 cm.$^{-1}$ and another band of almost equal intensity at 1644 cm.$^{-1}$; other prominent bands were located at 3280, 1320, 1294, 1094, 1057, 1032, 1021, 974, 767, 753, 734 (broad), and 693 cm.$^{-1}$. In the spectrum of D-*erythro*-D-*galacto*-octonic phenylhydrazide[14] the principal absorption bands were located at 3350, 3240, 1700, 1669 (C═O), 1604 1497, 1297, 1270, 1101, 1078, 1058, 1030, 1019, 750, 730 (broad), and 695 cm.$^{-1}$. The phenylhydrazide of acetic acid has its carbonyl absorption band[15] at 1664 cm.$^{-1}$.

D-*arabino*-L-*galacto*-Nonitol Nonaacetate (D-*lyxo*-D-*manno*-Nonitol Nonaacetate; III Nonaacetate) from D-*arabino*-L-*galacto*-Nononic 1,4-Lactone (II).—The lactone was a portion of that prepared by Sowden and Strobach[7,16]; its infrared spectrum showed a strong band at 1770 cm.$^{-1}$ in confirmation of its earlier designation as a γ-lactone.[17] For its reduction, a solution containing 43 mg. of it in 3 ml. of water was added dropwise to a solution of 50 mg. of potassium borohydride in 3 ml. of water. After 2 hr. the excess of borohydride was destroyed with acetic acid and the solution was passed through Amberlite IR-120 (H^+) ion-exchange resin to remove potassium ions. After concentration of the effluent to dryness, the residue was acetylated for 0.5 hr. on the steam bath with 4 ml. of acetic anhydride containing a trace of sulfuric acid. The mixture was poured into cold water and extracted with chloroform. The chloroform extracts were dried over sodium sulfate and concentrated to a small volume. Slow addition of pentane, with scratching (glass rod), produced crystals, 78 mg., m.p. 143–145°. Recrystallization by dissolution in the minimum amount of hot ethanol, addition of water to turbidity, and cooling produced the pure product as needle-shaped crystals, m.p. 146.5–147.5° (hot stage), $[\alpha]^{20}\text{D}$ +27.8° (*c* 2, chloroform).

Anal. Calcd. for $C_{27}H_{38}O_{18}$: C, 49.85; H, 5.89. Found: C, 49.70; H, 5.84.

D-*lyxo*-D-*manno*-Nononic 1,4-Lactone (V).—Dr. Maclay's notebook records that in 1937 he dissolved 50 g. of "*d*-α,α-galaoctose" (D-*threo*-L-*galacto*-octose, IV) monohydrate[10] in 90 ml. of water, cooled the solution to 0°, added 0.5 ml. of concentrated ammonium hydroxide and 15 ml. of liquid hydrogen cyanide, and left the mixture for 2 days in the refrigerator. The mixture of liquid and crystals was diluted with 125 ml. of water and heated for 9 hr. at 60–70°. The clear, dark brown solution was boiled with 50 g. of barium hydroxide octahydrate in a total volume of 750 ml. for 6 hr. to complete the saponification. The barium salt appeared to be quite insoluble, and was decomposed by the addition of 50 ml. of 6.7 *N* sulfuric acid. The barium sulfate was removed by filtration and the slight excess of sulfuric acid was removed from the filtrate by the (then) usual procedure of balancing out with aqueous barium hydroxide. After the final filtration, the solution containing the nononic acids was concentrated *in vacuo* to 200 ml., at which point crystallization began. The mixture was refrigerated overnight and a first crop of 28.7 g. of material was obtained. Further concentration and dilution with ethanol gave four more crops for a total yield of 47.3 g. The first crop appeared, from its titration and from its mutarotation, to be a mixture of lactone and acid. A 5-g. portion of the first crop of material was lactonized by dissolving it in 25 ml. of water, boiling the solution 45 min. under a reflux condenser, concentrating to dryness, and recrystallizing the residue from 15 ml. of hot water. After two further recrystallizations from 50% ethanol, the D-*lyxo*-D-*manno*-nononic 1,4-lactone melted at 226° dec. and showed $[\alpha]^{20}\text{D}$ +42.9° (*c* 1, water).

Anal. Calcd. for $C_9H_{16}O_9$: C, 40.30; H, 6.01; mol. wt., 268. Found: C, 40.16; H, 5.88; mol. wt. (by titration with sodium hydroxide), 268.

Dr. Maclay prepared a phenylhydrazide, m.p. 255°, and an amide, m.p. 228° dec., but reported that they were too insoluble in water for him to determine their rotations; he apparently obtained no analytical data for these substances.

We have found Dr. Maclay's recrystallized first-crop lactone to show a single spot on paper chromatograms developed in ethyl acetate–acetic acid–formic acid–water (18:3:1:4) and visualized with a silver nitrate reagent. The other samples remaining from his researches showed two or three spots; these samples we recrystallized from water, as chunky prisms, until paper chromatography showed them to be homogeneous. Our best product showed signs of sintering at 215°, it sintered strongly at 221°, and melted at 223–225° with the evolution of gas, $[\alpha]^{20}\text{D}$ +43.3° (*c* 1, water). The infrared spectrum showed a strong band at 1790 cm.$^{-1}$ indicative of a γ-lactone of an aldonic acid[17]; other principal absorption bands were located at 3545, 1330, 1305, 1250, 1218, 1190, 1145, 1070, 1035, 1010, 990, 978, 926, 895, 785, and 682 cm.$^{-1}$.

2-(D-*lyxo*-D-*manno*-Octahydroxyoctyl)benzimidazole.—A mixture of 0.3 g. of the nononic lactone (V), 0.22 g. of *o*-phenylenediamine dihydrochloride, 6 ml. of water, and 4 drops of concentrated hydrochloric acid was heated in an oil bath at 135–140° for 2 hr. The brown solution was treated with decolorizing carbon and filtered, the carbon was washed with water, and the filtrate was made alkaline with a few drops of ammonium hydroxide. The precipitated benzimidazole was filtered, washed with water,

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[13] D. A. Rosenfeld, N. K. Richtmyer, and C. S. Hudson, *J. Am. Chem. Soc.* **73**, 4907 (1951).

[14] A. J. Charlson and N. K. Richtmyer, *ibid.*, **82**, 3428 (1960).

[15] National Research Council–National Bureau of Standards Compound Card No. 595.

[16] Dr. Strobach (personal communication to N. K. R.) recalls that while working in Dr. Sowden's laboratory he prepared a benzimidazole (m.p. 301–302°) from this lactone; it was too insoluble in 1 *N* hydrochloric acid and in 5% citric acid for him to determine its rotation, and no analytical data were obtained.

[17] S. A. Barker, E. J. Bourne, R. M. Pinkard, and D. H. Whiffen [*Chem. Ind.* (London), 658 (1958)] found that, in general, γ-lactones of aldonic acids show carbonyl absorption at 1765–1790 cm.$^{-1}$ while the δ-lactones of aldonic acids show carbonyl absorption at 1726–1760 cm.$^{-1}$.

and dried, 0.2 g. It was recrystallized three times from 400 parts of hot water from which it separated on cooling as microscopic crystals with m.p. 263–264° dec. and $[\alpha]^{20}D$ −10.3° (*c* 1, *N* hydrochloric acid).

Anal. Calcd. for $C_{15}H_{22}N_2O_8$: C, 50.27; H, 6.19; N, 7.82. Found: C, 50.24; H, 6.10; N, 7.54.

D-*lyxo*-D-*manno*-**Nonitol** (D-*arabino*-L-*galacto*-**Nonitol, III) from** D-*lyxo*-D-*manno*-**Nononic 1,4-Lactone** (V).—To a stirred solution of 1 g. of sodium borohydride in 40 ml. of water was added a solution of 1 g. of lactone in 30 ml. of water, dropwise over a period of 1.5 hr. After an additional 1.5 hr. of stirring, 10 ml. of acetone was added dropwise to destroy the excess of borohydride. Sodium ions were removed by passage of the solution through a column of Amberlite IR-120 ion-exchange resin and the eluate was concentrated *in vacuo*. The crystalline residue was digested with hot methanol to extract the boric acid; the nearly insoluble nonitol, filtered and dried, weighed 0.80 g. and an additional 0.05 g. was recovered by a similar concentration of the methanolic filtrate (total yield 85%). The D-*lyxo*-D-*manno*-nonitol (III) was recrystallized twice from 50 parts of hot water, from which it separated as needles with m.p. 250–255°.

Anal. Calcd. for $C_9H_{20}O_9$: C, 39.70; H, 7.41. Found: C, 39.72; H, 7.35.

D-*lyxo*-D-*manno*-**Nonitol Nonaacetate (III Nonaacetate)**.—A 220-mg. portion of the crystalline nonitol (III) derived from the lactone V was acetylated by heating with 150 ml. of acetic anhydride and 1 drop of concentrated sulfuric acid for 1 hr. on the steam bath. When poured onto ice the mixture yielded an oil that crystallized when kept overnight in the refrigerator. The product, filtered and washed with cold water and ethanol, weighed 343 mg.; an additional 55 mg. was obtained by concentration of the filtrate (total yield 76%). The nonaacetate, upon recrystallization from aqueous ethanol, gave prismatic needles of m.p. 149–150° (capillary) and $[\alpha]^{20}D$ +27.3° (*c* 2, chloroform). The melting point of a mixture of this nonaacetate with the one of m.p. 146.5–147.5° (hot stage) and $[\alpha]^{20}D$ +27.8° (*c* 2, chloroform) obtained from D-*arabino*-L-*galacto*-nononic 1,4-lactone, and a comparison of their infrared spectra showed the identity of the two nonitol nonaacetates. The very strong ester carbonyl absorption band appeared at 1755 cm.$^{-1}$.

Anal. Calcd. for $C_{27}H_{38}O_{18}$: C, 49.85; H, 5.89; CH_3CO, 59.5. Found: C, 49.84; H, 6.03; CH_3CO, 59.4.

Acknowledgment.—The authors wish to thank Dr. William C. Alford and his associates of the Section on Microanalytical Services and Instrumentation, Laboratory of Chemistry, National Institute of Arthritis and Metabolic Diseases, for obtaining the infrared spectra and microanalyses; Professor David Lipkin of the Department of Chemistry, Washington University, St. Louis, Missouri, for furnishing us with additional samples from the collection of the late Professor John C. Sowden; and Professor Clinton E. Ballou of the Department of Biochemistry, University of California, Berkeley, California, for the samples of nononic lactone and phenylhydrazide prepared by Dr. Hagenbach.

Catalytic Carbanionic Addition of Butadiene to Alkyl Aromatic Hydrocarbons

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Conditions and procedures are given for a catalytic 1:1 addition of butadiene to alkyl aromatic hydrocarbons using high-surface potassium or sodium metal on a calcium oxide support. The resulting product is the corresponding terminally substituted 2-pentene. These olefins can be cyclodehydrogenated to a number of specific substituted aromatic hydrocarbons.

The sodium-initiated polymerization of butadiene has been known for a long time.[1,2] It has also been found that a similar reaction may be run in an autoclave using excess alkylbenzenes and various dienes (*e.g.*, butadiene) yielding a 1:1 adduct,[3] and more recently the reaction has been extended to nitrogen-containing aromatics[4] (*e.g.*, picoline). The work of Ziegler[5,6] has shown that the mechanism of this reaction involves organosodium intermediates. It was further shown that well-defined organometallic compounds such as 2-phenyl-2-propylpotassium or benzylsodium can add butadiene in a stepwise fashion. More recently Robertson and Marion[7] found that the sodium-initiated polymerization of butadiene in toluene leads to the formation of telomers of toluene and butadiene. These results were explained by a transmetalation reaction occurring from the growing polybutadiene chain (reaction 3) to toluene, with the formation of benzylsodium, which again is able to initiate a butadiene polymerization. The present work describes conditions under which a catalytic 1:1 addition of butadiene to alkyl aromatic hydrocarbons can be achieved at high yields. The resulting aromatic olefins are intermediates in the synthesis of specific methyl-substituted naphthalenes *via* a cyclodehydrogenation reaction.

Metalation

$$2Ph{-}CH_3 + NaCH_2{-}CH{=}CH{-}CH_2Na \longrightarrow 2Ph{-}CH_2Na + CH_3{-}CH{=}CH{-}CH_3 \quad (1)$$

Equations 2 and 3 constitute the catalytic cycle.

Butadiene Addition

$$Ph{-}CH_2Na + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow Ph{-}CH_2CH_2{-}CH{=}CH{-}CH_2Na \quad (2)$$

Transmetalation

$$Ph{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2Na + Ph{-}CH_3 \longrightarrow Ph{-}CH_2CH_2{-}CH{=}CH{-}CH_3 + Ph{-}CH_2Na \quad (3)$$

Discussions and Results

The reaction with potassium metal as catalyst is suggested to involve analogous sequences; only the initial metalation of the alkylaromatic hydrocarbon can occur directly. The uncontrolled addition of butadiene

$$Ph{-}CH_3 + K \longrightarrow Ph{-}CH_2K + (1/2H_2) \quad (4)$$

leads to its polymerization and telomerization, which suggests that reaction 2 is faster than the chain-transfer step 3. Then, an excess of the alkyl aromatic reactant

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