ml. The solution was allowed to warm to room temperature and was stirred for 5 hr. before it was carbonated. The carbonation mixture was hydrolyzed, and the layers were separated. The organic layer was washed with 5% aqueous sodium hydroxide. The combined aqueous solution was boiled to remove any dissolved organic solvent, acidified with concd. hydrochloric acid, and filtered while hot to give 0.74 g. (39.1%) of dibenzofuran-4-carboxylic acid, m.p. 195–205°. Recrystallization from ethanol-water gave 0.51 g. (27%) of product, m.p. 203–207° (mixed melting point).

The results of this and other metalation experiments are listed in Table I.

Table I

Metalations of Dibenzofuran

RLi	Solvent	Time, Hr.	Acid, %[a] Crude	Pure
$PhCH_2Li$[b]	THF	5	39.1	27.0
			31.8	24.0
$PhCH_2Li$[b]	THF	46	41.3	34.7
$PhCH(CH_3)Li$[c]	THF	5	46.0	38.8
$PhCH_2Li$[b]	THP	5	10.9	8.0
			6.0	...

[a] The acid isolated was dibenzofuran-4-carboxylic acid. [b] The benzyllithium was prepared from dibenzyl ether. See ref. 14. [c] The α-methylbenzyllithium was prepared from bis(α-methylbenzyl) ether. See ref. 14.

Reaction of Benzyllithium with Benzophenone.—To 95 ml. of a 0.156 *N* solution of benzyllithium prepared from dibenzyl ether in THF there was added dropwise, at the temperature of an ice bath, a solution of 2.95 g. (0.016 mole) of benzophenone in 40 ml. of diethyl ether. The resulting blue solution gave a negative Color Test I[15] within 10 min. after the addition was complete. The solution was hydrolyzed and then extracted with diethyl ether. The combined organic solution was dried and evaporated to leave a yellow residue which was distilled under reduced pressure to give 0.89 g. of benzyl alcohol, b.p. 60–62.5° at 2.5 mm., n^{20}_D 1.5442. The distillation residue was rinsed from the flask with boiling petroleum ether (b.p. 60–70°) and filtered while hot to liberate 0.88 g. (25%) of 1,1,2-triphenylethanol, m.p. 84–89.5°. Recrystallization from benzene-petroleum ether gave 0.80 g. (22.9%) of pure product, m.p. 91–92° (mixed melting point).

The filtrate from the above separation was poured onto a column of dry alumina. Elution with petroleum ether (b.p. 60–70°) afforded 0.33 g. (26.6%) of bibenzyl, m.p. 50–54° (mixed melting point). Elution with benzene led to the isolation of an additional 0.75 g. (21.5%) of 1,1,2-triphenylethanol, m.p. 90–91° (mixed melting point) giving a total of 1.63 g. (46.5%) of this product. Continued washing of the alumina column with benzene gave a cloudy oil which was subsequently distilled under reduced pressure to yield 0.31 g. (10.5%) of recovered benzophenone, m.p. 47–50° (mixed melting point).

In a second experiment using benzyllithium prepared from benzyl methyl ether there was isolated 23.1% of bibenzyl, mixed m.p. 52–54°, and 54.2% of 1,1,2-triphenylethanol, m.p. 91–93° (mixed melting point).

Reaction of Benzyllithium with Pyridine. To 220 ml. of a 0.15 *N* solution of benzyllithium prepared from dibenzyl ether in tetrahydrofuran (THF) there was added rapidly with vigorous stirring 3.30 g. (0.041 mole, 10% excess) of dry pyridine in 25 ml. of THF at room temperature. Color Test I was negative after 1 hr. although the solution remained reddish brown. After stirring overnight under reflux, the solution was poured slowly upon crushed ice. The separated water layer was extracted with diethyl ether, and the combined organic solvent was dried and distilled under reduced pressure giving an almost colorless liquid boiling over the range 100–145° at 15 mm. A second distillation of the product afforded 1.11 g. (17.5%) of 4-benzylpyridine, boiling over the range 146–153°/14 mm.

The picrate of the 4-benzylpyridine melted at 142–143.5° after crystallization from ethanol. A mixture melting point with the picrate prepared from an authentic sample of 4-benzylpyridine (K and K Laboratories, Inc., Lot No. 6696) also was 142–143.5° A mixture melting point with the picrate from an authentic sample of 2-benzylpyridine (K and K Laboratories, Inc., Lot No. 6695) was depressed to 119–125°. This is almost identical with the melting point range observed for a mixture of the picrates prepared from the authentic samples of 2- and 4-benzylpyridine.

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[15] H. Gilman and F. Schultz, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

Synthesis of 1,2,6-Tris(2-cyanoethoxy)hexane

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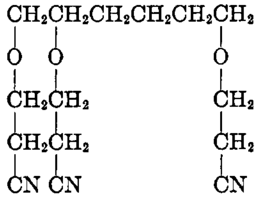
In connection with the use of extremely sensitive ionization detectors in gas chromotography, a polar liquid phase having a very low vapor pressure was required. To fill this need 1,2,6-tris(2-cyanoethoxy)hexane (I) was prepared from acrylonitrile and 1,2,6-hexanetriol by the method of Bruson and Riener.[1,2]

Acrylonitrile condenses readily with the labile hydrogen atoms of the polyalcohol with the formation of a molecule containing three very polar cyanoethyl groups as shown in I.



$$\begin{array}{cccccc} CH_2 & CH_2 & CH_2 & CH_2 & CH_2 & CH_2 \\ | & | & & & & | \\ O & O & & & & O \\ | & | & & & & | \\ CH_2 & CH_2 & & & & CH_2 \\ | & | & & & & | \\ CH_2 & CH_2 & & & & CH_2 \\ | & | & & & & | \\ CN & CN & & & & CN \end{array}$$

I

The compound is easily purified by molecular distillation, provided the alkaline condensing agent is first destroyed by acidification in order to prevent the β-alkoxynitrile to the corresponding β-alkoxypropionic acid.[3]

Experimental

Preparation of 1,2,6-Tris(2-cyanoethoxy)hexane (I).—Three moles (159.2 g.) of acrylonitrile was gradually added to a mixture of 1 mole (134.2 g.) of 1,2,6-hexanetriol and 9.4 g. (7% by weight) of 40% aqueous potassium hydroxide solution. The mixture was stirred and maintained at a temperature of 15–20° during the addition of the acrylonitrile. Subsequently, the mixture was stirred overnight while being allowed to warm to room temperature. After this time, the mixture was diluted with 200 ml. of distilled water and made acid to litmus with hydrochloric acid. The

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[1] H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **65**, 23 (1943).

[2] H. A. Bruson, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, 1945, p. 79.

[3] J. H. MacGregor and C. Pugh, *J. Chem. Soc.*, 535 (1945).

acidified solution was saturated with sodium chloride and extracted repeatedly with 25-ml. portions of distilled ethylene dichloride until the extracts were colorless. The ethylene dichloride extracts were dried over anhydrous calcium sulfate, filtered, and the volatile materials removed under vacuum at room temperature. A total of 214.2 g. (73.5% yield) of crude I was recovered. This material was distilled at 1–3 μ of mercury and at temperatures of 168–191° using an ASCO molecular still.[4] The distillates of the second and third pass, having indices of refraction of 1.4654 and 1.4653, respectively, were combined. The combined distillates were then percolated through an activated silica gel column, using 5 l. of distilled isopropyl alcohol as eluent. After evaporating the eluent, a total of 158.1 g. of I was recovered.

Anal. Calcd. for $C_{15}H_{23}O_3N_3$:N, 14.2; mol. wt. 293. Found: N(Kjeldahl), 13.8; mol. wt. (ebullioscopic), 292; d^{25}_4 1.0667; n^{20}_D 1.4650; $\eta(25°)$, 24.41 cp.

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[4] ASCO "50" molecular still manufactured by Arthur F. Smith Co., Rochester, N. Y.

Crystalline D-*glycero*-D-*gulo*-Octulose

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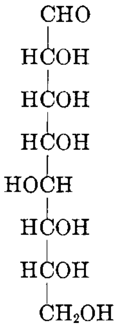
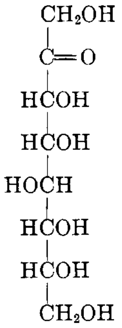
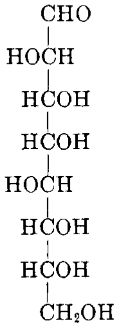
D-*erythro*-L-*talo*-Octose (I) was crystallized first by Merrill, Hann, and Hudson[1] in this laboratory. The sirupy mother liquor from one of their preparations, which had been kept in a Pyrex flask for nearly twenty years, was examined recently by paper chromatography. An ammoniacal silver nitrate spray showed the presence of at least seven components; one of these was suspected of being an octulose because when sprayed with orcinol–hydrochloric acid it gave a color characteristic of this class of compounds. Through cellulose column chromatography we were able to isolate and crystallize this octulose; it melted about 125°, showed $[\alpha]^{20}_D$ +34.6° in water (final), and was proved to be D-*glycero*-D-*gulo*-octulose (II)[2a] because it gave a phenylosazone identical with the one derived from D-*erythro*-L-*talo*-octose (I)[1] and D-*erythro*-L-*galacto*-octose (III).[3] We have also prepared the same crystalline octulose deliberately through rearrangement of D-*erythro*-L-*galacto*-octose (III) in boiling pyridine.


I


II


III

Experimental

D-*glycero*-D-*gulo*-Octulose (II) from D-*erythro*-L-*talo*-octose Mother Liquors.—About 1942, Drs. Raymond M. Hann and Alice T. Merrill, in this laboratory, reduced several batches of D-*erythro*-L-*talo* octonic lactone in the usual manner with sodium amalgam, precipitated most of the sodium salts with methanol, concentrated the filtrate to a sirup, and from that sirup isolated crystalline D-*erythro*-L-*talo*-octose (I)[1] in about a 50% yield. Some of the mother liquors were combined, concentrated, and the sirup kept in a Pyrex distilling flask at room temperature until June, 1961. At that time we dissolved the sirup in water, deionized the solution with Amberlite IR-120 and Duolite A-4 ion-exchange resins, and concentrated to a sirup that weighed 53 g. Paper chromatograms developed in 1-butanol–pyridine–water (6:4:3) and sprayed with ammoniacal silver nitrate showed at least seven spots. Comparison with known substances that might be expected among the reduction products of D-*erythro*-L-*talo*-octonic lactone after nearly 20 years under slightly alkaline conditions (glass or residual sodium salts), indicated that the slowest moving spot was D-*erythro*-L-*galacto*-octose (visualized also with aniline hydrogen phthalate). The second spot had the same mobility as D-*erythro*-L-*talo*-octitol. The third was not identified but the fourth was undoubtedly D-*erythro*-L-*talo*-octose (visualized also with aniline hydrogen phthalate). The fifth and largest spot could be visualized readily with the orcinol-hydrochloric acid spray, with which it gave, when heated at 110°, a crimson color that faded rapidly to gray; this behavior is characteristic of the octuloses.[2c] The resulting spot gave a bluish-white fluorescence under the ultraviolet lamp, as do octuloses and nonuloses but not the lower carbon ketoses. The sixth, and smallest, spot appeared to be a second octulose, and its mobility in three solvent systems was the same as D-*glycero*-D-*ido*-octulose,[4] the epimeric octulose that might be expected from the further action of alkali on D-*glycero*-D-*gulo*-octulose.[5] The seventh and fastest moving spot, as will be mentioned again later, appeared to be an octosaccharinic lactone.

In order to isolate the octulose the 53 g. of sirup was placed on top of a cellulose column 90 cm. long and 4.8 cm. in diameter and the column was eluted with 1-butanol half-saturated with water, 250 ml. of eluate being collected in each fraction. When the fractions were concentrated and dissolved in small amounts of methanol, fraction 32 deposited crystals spontaneously, and fractions 25–37 deposited additional amounts of the same material on seeding. The yield of crystals so far is 4 g. The product was recrystallized from methanol from which it separates as chunky

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[1] A. T. Merrill, R. M. Hann, and C. S. Hudson, *J. Am. Chem. Soc.*, **65**, 994 (1943); R. M. Hann, A. T. Merrill, and C. S. Hudson, *J. Am. Chem. Soc.*, **66**, 1912 (1944).

[2] (a) M. L. Wolfrom and A. Thompson [*J. Am. Chem. Soc.*, **68**, 1453 (1946)] obtained this octulose earlier as a sirup through the diazomethane synthesis starting with D-*glycero*-D-*gulo*-heptonic acid; (b) Similarly, M. L. Wolfrom and P. W. Cooper [*J. Am. Chem. Soc.*, **71**, 2668 (1949)] prepared sirupy D-*glycero*-L-*gluco*-octulose, D-*glycero*-L-*manno*-octulose, and [*J. Am. Chem. Soc.*, **72**, 1345 (1950)] D-*glycero*-D-*galacto*-octulose; (c) A. J. Charlson and N. K. Richtmyer [*J. Am. Chem. Soc.*, **81**, 1512 (1959); **82**, 3428 (1960)] isolated D-*glycero*-D-*manno*-octulose as a sirup from the avocado and from *Sedum* species; (d) J. K. N. Jones and H. H. Sephton [*Can. J. Chem.*, **38**, 753 (1960)] synthesized four sirupy octuloses enzymically, namely, D-*glycero*-D-*altro*-octulose, L-*glycero*-L-*galacto*-octulose, D-*glycero*-L-*gluco*-octulose (see also ref. 2b), and D-*glycero*-L-*galacto*-octulose.

[3] E. Fischer, *Ann.*, **270**, 64 (1892).

[4] H. H. Sephton and N. K. Richtmyer, unpublished results from this laboratory.

[5] *Cf.*, E. M. Montgomery and C. S. Hudson [*J. Am. Chem. Soc.*, **61**, 1654 (1939)] for the alkaline rearrangement of D-*glycero*-D-*galacto*-heptose to both D-*manno*-heptulose and D-*gluco*-heptulose.