tion of pentyne-2 (b. p. 55.9 ± 0.05° at 760 mm., n^{20}_{D} 1.4040, d^{20}_{4} 0.7115) were hydrogenated in an alcohol-water solution in the presence of colloidal palladium. Slightly less than the theoretical quantity of hydrogen was used. The pentene with alcohol distilled from the mixture through a Vigreux column at 34–36°. The hydrocarbon (78.5% yield) freed from alcohol had a refractive index n^{20}_{D} 1.3824. One fractionation through Fenske column A gave (1) 5% boiling at 36.8–37.0° and (2) 90% boiling at 37.0 ± 0.05°; the refractive indices of these fractions were, respectively, n^{20}_{D} 1.3824 and 1.3822, that of the residue was n^{20}_{D} 1.3840. In a second fractionation of (2) the entire distillate (98%) boiled constantly at 37.0 ± 0.05°, had a refractive index n^{20}_{D} 1.3822 and a density d^{20}_{4} 0.6562. The refractive index of the residue was n^{20}_{D} 1.3826.

THE CHEMICAL LABORATORY OF
MOUNT HOLYOKE COLLEGE
SOUTH HADLEY, MASS.
RECEIVED AUGUST 1, 1938

The Specific Heat of "Lucite" (Methyl Methacrylate Polymer)

BY FRANK T. GUCKER, JR., AND WILLIAM L. FORD

We have found the polymerized methyl methacrylate plastic now made by the du Pont Company under the trade name of "Lucite" a useful insulating material in our calorimetric work. Many of its physical properties have been tabulated.[1] For our purposes, the specific heat was important and, since we could not find it listed, we determined it as follows.

Fifteen disks each 3 mm. thick were cut from a Lucite rod, $^3/_8$ inch (9 mm.) in diameter. A small hole was drilled in the center of each. The disks were then threaded on pieces of fine copper wire and suspended from the thermel tubes in one calorimeter of the apparatus developed in this Laboratory[2] for measuring heat capacities of aqueous solutions. The disks were spaced apart to allow free circulation of water, with which the calorimeter was filled to the standard height. The resistance ratio required to balance this calorimeter against the tare was then measured in the usual way, with an accuracy of about 0.01%. The heat capacity of the Lucite was calculated from this ratio and the known heat capacities of the water, the calorimeter and the copper wire. Since the heat capacity of the 3 g. of Lucite was only about 0.3% of that of the whole system, the uncertainty in its value is about 3%. The results of two independent experiments actually agreed somewhat better than that, yielding 0.342 and 0.344, and we may take as the probable value of the specific heat 0.343 (±0.005) cal. deg.$^{-1}$ g.$^{-1}$.

Although its specific heat is larger than that of Pyrex glass, its density is only half as great, and the heat capacity *per unit volume* is only 82% of that of glass. This factor, in combination with a thermal conductance less than half that of glass, equal transparency, great mechanical strength and easy machining, makes Lucite a useful substitute for glass as an insulating material in calorimetric work.

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RECEIVED JULY 5, 1938

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[1] "Methacrylate Resins," *Ind. Eng. Chem.*, **28**, 1160 (1936).

[2] Gucker, Ayres and Rubin, THIS JOURNAL, **58**, 2118 (1936).

The Methylation of Sugars

BY B. CLIFFORD HENDRICKS AND ROBERT E. RUNDLE

The importance of fully methylated sugars as reference compounds in carbohydrate chemistry has led to many attempts to find more satisfactory methods for their synthesis. Irvine and Purdie[1,2] used methyl iodide and silver oxide in their preparation. A more generally used method[3] is that of Haworth in which dimethyl sulfate and sodium hydroxide are the reagents used. More recently West and Holden[4] have modified the method of Haworth by using carbon tetrachloride as a solvent, a more concentrated alkali and a different method of hexoside hydrolysis to obtain the free methylated sugar.

The authors found that the concentrated alkali, used by West and Holden for the last step in the methylation, produced sugar decomposition. Their first steps, however, were satisfactory for partial methylation.

Muskat[5] has shown that methylation may be accomplished by using free alkali metal and methyl iodide on a hexoside in liquid ammonia. He used potassium which is expensive and prepared only small amounts of the sugars. If sodium metal is substituted for the potassium the cost is reduced but for larger quantities of reactants the insolubility of the tetrasodium salts

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[1] Irvine and Purdie, *J. Chem. Soc.*, **83**, 1021 (1903).

[2] Irvine and Purdie, *ibid.*, **85**, 1052 (1904).

[3] Haworth, *ibid.*, **107**, 11 (1915).

[4] West and Holden, THIS JOURNAL, **56**, 930 (1934).

[5] Muskat, *ibid.*, **56**, 695 (1934).

of the hexosides makes it difficult to methylate more than one or two carbons of the sugar. For that reason the procedure here reported uses liquid ammonia only for completing methylation started by the West and Holden process.

Experimental

Forty grams of hexoside with 25 ml. of water was put into a flask equipped with a heavy stirrer, separatory or dropping funnel and attached to a condenser. This mixture was then warmed to 50° by a water-bath. A mixture of 108 ml. of dimethyl sulfate in 150 ml. of carbon tetrachloride was then added and the resulting mixture vigorously stirred. A solution of 92 g. of sodium hydroxide in 130 ml. of water was introduced into the flask by means of the separatory funnel at the rate of one drop in two seconds. This rate was increased in such manner that heat resulting barely raised the reaction mixture to the boiling point of the carbon tetrachloride. After the first half of the alkali solution was used the remainder was added more rapidly and the stirring continued for thirty minutes after the last addition.

The contents of the flask were then treated as directed by West and Holden[4] except the partially methylated sirup was dried thoroughly in preparation for the ammonia methylation. To accomplish this it was dissolved in ethyl ether, this solution dried by calcium chloride and after filtering the ether evaporated under reduced pressure.

The liquid ammonia methylation was done in two unsilvered Dewar flasks of about 750 ml. capacity. Flask number one equipped with separatory funnel, an outlet tube and protected from moisture by some desiccant such as calcium oxide was to contain the sirup. The other flask was connected to the first by a glass tube which extended to the bottom of the second. This second flask also had an outlet tube closed by a clamp by means of which liquid ammonia could be forced into flask one by closing the clamp.

Into the first flask 500 ml. of liquid ammonia was passed direct from the tank. A piece of metallic sodium was added to dry the ammonia, after which the sirup was added. The 150 ml. of liquid in the second Dewar received the shavings of metallic sodium (3–4 g.). The sodium salt of the methylated hexoside was then prepared by forcing small portions of the sodium–ammonia solution into the first flask, containing the sirup, as described above. As the hexoside reacts with the sodium the blue color of the solution clears. Successive additions of the sodium were continued until the blue color persisted for an hour after the last addition. At that point 12 ml. of methyl iodide was added dropwise through the separatory funnel. Less of the iodide was used if less than the prepared amount of sodium–ammonia solution had been previously consumed. The liquid ammonia was then permitted to vaporize off and the residue neutralized by 2 *N* hydrochloric acid. After neutralization 400 ml. more of 2 *N* hydrochloric acid was added and the mixture steam hydrolyzed.[4] The product of this hydrolysis was isolated and crystallized as described by West and Holden.

The authors successfully prepared the following tetramethylhexoses by this combination method.

Tetramethyl- M. p., °C.			α-*d*-Glucose 92.5–93.5	α-*d*-Mannose 49–50	α-*d*-Galactose 70.5–71.5
Specific rotation	Init.	$[\alpha]^{0}\text{D}$	+104.0	+11.5	+146.0
		$[\alpha]^{25}\text{D}$	+104.0	+ 6.3	+150.5
	Final	$[\alpha]^{0}\text{D}$	+ 80.4	+ 2.5	+112.1
		$[\alpha]^{25}\text{D}$	+ 84.8	− 0.2	+119.9

The yield for the tetramethyl α-*d*-glucose was 20–25 g.; for the other two somewhat less. Those two sugars were rather difficult to crystallize[6] though the quantity of sirup in each case was as great as for the glucose.

In this combination method of methylation the amounts of methylating agents used were but slightly more than the theoretical, making the cost comparatively small. The time required was more than for the procedure of West and Holden but much less than that by Haworth's method. The quantities of sugars processed were larger than those used by Muskat.

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[6] Accomplished by aid of seed crystals generously furnished by Dr. M. L. Wolfrom of The Ohio State University.

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The Ineffectiveness of β-Aminopyridine in Blacktongue

BY F. M. STRONG, R. J. MADDEN AND C. A. ELVEHJEM

Subbarow, Dann, and Meilman[1] recently reported that β-aminopyridine was highly active in the treatment of blacktongue in dogs. Our attempts to demonstrate the activity of this compound have given uniformly negative results.

The compound was prepared by a Hoffman degradation of nicotinamide according to Pollak,[2] and after being purified by distillation (b. p. 132–134° at 20 mm.) and crystallization from Skelly solve "B," formed glittering, colorless plates, m. p. 61–63°. *Anal.* Calcd. for $C_5H_6N_2$: C, 63.82; H, 6.43. Found: C, 63.80; H, 6.35.

The picrate was prepared in dilute alcohol solution, and after being crystallized from alcohol melted at 200–201°. The chloroaurate precipitated instantly on mixing aqueous solutions of the reactants and was crystallized from 1–1 hydrochloric acid as red-brown needles, m. p. 237–239° (dec.). *Anal.* Calcd. for $C_5H_6N_2{\cdot}HAuCl_4$: Au, 45.4. Found: Au, 44.8, 44.8.

The dihydrochloride which was obtained from the free base and concentrated hydrochloric acid was recrystallized twice from concentrated hydrochloric acid and then from absolute alcohol. Colorless, granular crystals of m. p. 170–173°

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[1] Subbarow, Dann and Meilman, THIS JOURNAL, **60**, 1510 (1938).

[2] Pollak, *Monatsh.*, **16**, 54 (1895).