Table I

Methylation of Sugar Anilides

Partially methylated sugar	Anilide, m.p., °C.	Solvent used in methylation	Fully methylated product Name	M.p., °C.	[α]^{15}D (initial value)	Solvent
D-Galactose						
2,3,4-trimethyl-	167[7]	Acetone	2,3,4,6-Tetramethyl-D-galactose anilide[11]	192	−141°	(pyridine)
2,4,6-trimethyl-	170[8]	Acetone	2,3,4,6-Tetramethyl-D-galactose anilide[11]	192	−141°	(pyridine)
2,4-dimethyl-	216[9]	Methanol	2,3,4,6-Tetramethyl-D-galactose anilide[11]	192	−141°	(pyridine)
D-Glucose						
2,3,6-trimethyl-	Sirup	None Some aniline probably present	2,3,4,6-Tetramethyl-D-glucose anilide[12]	138	+235	(acetone)
D-Mannose						
2,3,6-trimethyl	134[5]	None	2,3,4,6-Tetramethyl-D-mannose anilide[11]	144	−150	(methanol)
2,3-dimethyl-	Sirup[6]	None	2,3,4,6-Tetramethyl-D mannose anilide[11]	144	−150	(methanol)
D-Xylose						
2,3-dimethyl-	145[a]	None	2,3,4-Trimethyl-D-xylose anilide[13]	98	− 97	(methanol)

[a] Recent preparations of 2,3-dimethyl-D-xylose anilide have provided an isomorphous form m.p. 126°. Both crystalline modifications (m.p. 126 and 145°) show the same specific rotation of [α]^{25}D +180° in ethyl acetate.[10]

reducing sugar; the latter was then treated with aniline to provide the characteristic crystalline anilide of the fully methylated sugar. The experiments recorded herein show that in many cases and especially those in which only small amounts of material are available, the rather lengthy procedure formerly used may well be dispensed with by adopting the one-stage process of directly converting the anilide of the unknown partially methylated sugar into the anilide of a known fully methylated sugar.

Experimental

One experiment will suffice to illustrate the method. A solution of 25 mg. of the anilide of 2,3,4-trimethyl-D-galactose in a mixture of acetone (2.5 ml.) and methyl iodide (2.5 ml.) was boiled under reflux for ten hours in the presence of silver oxide (0.2 g.). Isolation of the product in the usual way by means of acetone afforded 2,3,4,6-tetramethyl-D-galactose anilide, m.p. mixed m.p. 190°, [α]^{25}D −141° (*c* 1.0) in pyridine (after crystallization from ethanol). Other typical results are given in Table I.

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Styrene Sulfide

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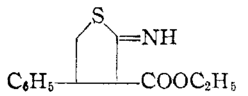
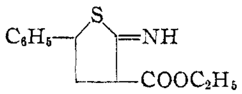
Styrene sulfide was prepared, as herein described, by a modification of the procedure of Culvenor and co-workers,[2] who reported that "attempts to make styrene sulfide gave merely high-molecular material." The reaction between potassium thiocyanate and styrene oxide, in 50% aqueous dioxane solution, gave a 59% yield of the easily-polymerized unpleasant-smelling olefin sulfide. Apparently the use of dioxane was an important modification.

The reaction of styrene sulfide with the sodium derivative of ethyl cyanoacetate[3] gave a product believed to be 2-imino-3-carbethoxy-4(or 5)-phenylthiophane (I or II). However, the structure



I



II

of this product was not determined. The water-soluble hydrochloride of this derivative was obtained as an oil which could not be crystallized. The product also formed a solid acetyl derivative.

The attempted reaction of styrene sulfide with piperidine and morpholine[4] gave only sulfur-free products.

Repeated exposure of the skin to liquid styrene sulfide may result in irritation.

Experimental[5]

Apparatus.—All apparatus was thoroughly cleaned, rinsed with ammonium hydroxide solution and dried before use.

Starting Materials.—Commercial styrene oxide (Dow Chemical Co.) was distilled before use. Analytical grade potassium thiocyanate was used. Commercial dioxane was purified by the method of Fieser.[6]

Styrene Sulfide.—A mixture of 30 g. (0.25 mole) of styrene oxide, 25 g. (0.26 mole) of potassium thiocyanate, 50 ml. of dioxane and 50 ml. of water was stirred at 60 ± 1° for one hour. This reaction mixture was then poured into a mixture of 100 g. of ice and 200 ml. of water. The product was extracted with three 50-ml. portions of purified ether. These combined ether extracts were washed with two 100-ml. portions of water, and the ether solution was then dried over anhydrous potassium carbonate for 24 hours. The ether was removed by evaporation under reduced pressure at, or below, room temperature. The crude product was filtered through a sintered glass filter, and unreacted styrene oxide was removed by distillation through a 5-inch helices-packed column at 1 mm. pressure. When the vapor temperature had reached 50°, the product was transferred to a short-path distillation apparatus and distilled at 25–28° (0.01 mm.) d^{25}_{4} 1.1044; n^{20}D 1.6015. The yield of pure styrene sulfide was 16 g. (47%). Yields of styrene sulfide up to 59% were obtained by this procedure. Styrene sulfide was also distilled at 87–88° (4 mm.), but at

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[3] H. R. Snyder and W. Alexander, This Journal, **70**, 217 (1948).

[4] H. R. Snyder, J. M. Stewart and J. B. Ziegler, *ibid.*, **69**, 2672 (1947).

[5] All temperature measurements are uncorrected.

[6] Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 369.

the higher temperature decomposition into styrene and sulfur occasionally occurred.

Pure styrene sulfide in a clean glass container can be stored for at least as long as two days at room temperature, and for ten days at 5–10° under anhydrous conditions, without its showing noticeable signs of polymerization.

Anal. Calcd. for C_8H_8S: C, 70,54; H, 5.92; S, 23.55; mol. wt., 136. Found: C, 70.15; H, 6.22; S, 23.55; mol. wt. (cryoscopic in benzene), 132.

2-Imino-3-carbethoxy-4(or 5)-phenylthiophane.—One-tenth mole (13.6 g.) of styrene sulfide was reacted with the sodium salt of ethyl cyanoacetate by the method described by Snyder and Alexander.[3] The crude product (20 g.) contained much polymeric material. The product was recrystallized from xylene–heptane solution to a constant melting point of 94–95°.

Anal. Calcd. for $C_{13}H_{15}NO_2S$: C, 62.62; H, 6.06; N, 5.62. Found: C, 62.46; H, 5.88; N, 5.30.

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The Exchange of Hydrogen Gas with Lithium and Sodium Borohydrides

BY W. G. BROWN, L. KAPLAN AND K. E. WILZBACH

The alkali metal borohydrides are effective reducing agents for a variety of organic compounds;[1,2] in some cases[3,4] they are preferred to lithium aluminum hydride because of their greater selectivity. The isotopically-labeled borohydrides would, therefore, be useful reagents for the introduction of deuterium or tritium into organic compounds. Although labeled borohydrides may be prepared[5] from the corresponding hydrides,[6,7] or from labeled diborane,[8] the direct exchange of the solid borohydrides with hydrogen gas has been found to provide a more simple route to the isotopic compounds. Exchange, leading to approximately statistical isotopic distribution, occurs at a convenient rate with lithium borohydride at 200° and with sodium borohydride at 350°. Thermal decomposition is negligible in both cases.

TABLE I

EXCHANGE OF HYDROGEN WITH ALKALI METAL BOROHYDRIDES

	Metal borohydride			Hydrogen				
Run	Mg. atoms H	Microcuries tritium Init.	Final	Mg. atoms H	Microcuries tritium Init.	Final	T, °C.	t, hr.
			Lithium borohydride					
3	16.36	0	0[a]	1.309	28.9	28.7	95	89
4	16.36	0	26.0	1.222	27.6	1.77	200	120
1	10.46	0	8.4	1.238	28.1	19.7	200	3
2	10.46	8.4	32.5	1.252	28.2	4.14	200	16
9	16.36	23.1	21.7	1.377	0	1.35	200	66
			Sodium borohydride					
10	20.46	0	4.6	1.143	23.9	19.3	300	16
11	20.46	4.6	9.3	0.778	17.3	12.6	300	64
12	12.73	0	10.8	0.649	12.3	1.51	325	92
13	14.44	0	9.1	0.661	14.5	5.44	350	8
14	22.27	0	12.3	0.619	13.1	0.76	375	3.5

[a] Within experimental error.

The results of a number of exchange experiments, traced with tritium, are shown in Table I. The amount of tritium in the solid was calculated from the change in tritium content, measured by ion current, of the gas. The calculated values agreed well with the isotopic composition of benzyl alcohol obtained by reduction of benzaldehyde with lithium borohydride in one case and with that of hydrogen from the hydrolysis of sodium borohydride in another.

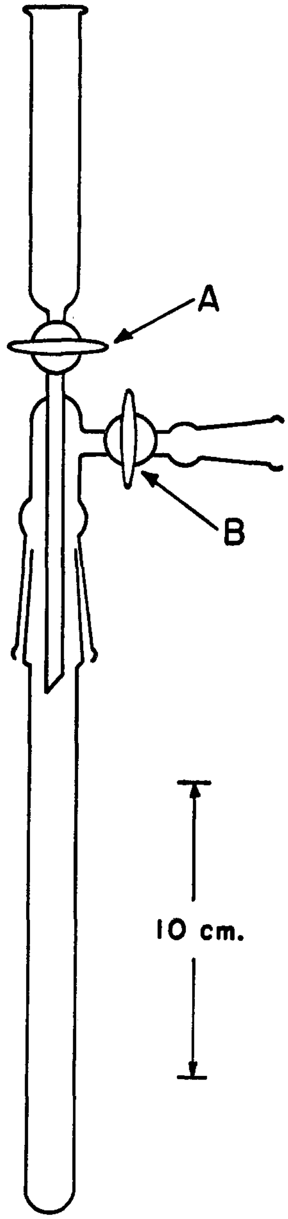

Fig. 1.—Apparatus for borohydride reactions.

Experimental

Exchange Reaction.—A sample of lithium or sodium borohydride, purified[9] by recrystallization, was transferred in a dry-box to a Pyrex tube of 25 cc. capacity (Fig. 1). A nickel foil liner was used in experiments with sodium borohydride to prevent decomposition of the borohydride by glass. The sample was heated with tank hydrogen for one hour at the temperature of the subsequent exchange experiment. The reaction vessel was evacuated through stopcock B, filled with a measured volume of a stock hydrogen–tritium mixture, and heated under the conditions shown in Table I. The quantity of gas remained essentially unchanged during the exchange reaction although a small increase had been observed during the preheating. The gas was then transferred to an evacuated Borkowski-type[10] ion chamber and diluted to atmospheric pressure with tank hydrogen. The ion current collected at 500 volts was measured with a dynamic condenser electrometer. A factor of 2.1×10^{-17} coulomb per disintegration was used to convert ion currents into disintegration rates.

Reduction of Benzaldehyde with Lithium Borohydride.—A solution of the lithium borohydride from Run 2, Table I, was prepared by adding 5 ml. of tetrahydrofuran through stopcock A. The solution was maintained at 20° by cooling while 1.3 g. of benzaldehyde in 5 cc. of tetrahydrofuran was added gradually to the still partially evacuated vessel. Solvent and excess benzaldehyde were removed by evacuation and the residue was hydrolyzed with dilute sodium hydroxide. The product was extracted with

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