

TABLE I
 METHYLATION OF SUGAR ANILIDES

Partially methylated sugar	Anilide, m.p., °C.	Solvent used in methylation	Fully methylated product		
			Name	M.p., °C.	Solvent [α] ¹⁵ _D (initial value)
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	2,3,4,6-Tetramethyl-D-glucose anilide ¹²	138	+235 (acetone)
Some aniline probably present					
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 ⁵	None	2,3,4-Trimethyl-D-xylose anilide ¹³	98	-97 (methanol)

⁶ 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]²⁰_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.

(7) D. McCreath and F. Smith, *J. Chem. Soc.*, 387 (1939).

(8) E. L. Hirst and J. K. N. Jones, *ibid.*, 1482 (1939).

(9) F. Smith, *ibid.*, 1724 (1939).

(10) Cf. H. A. Hampton, W. N. Haworth and E. L. Hirst, *ibid.*, 1739 (1929); S. K. Chanda, E. L. Hirst, J. K. N. Jones and E. G. V. Percival, *ibid.*, 1289 (1950); I. Ehrenthal, Ph.D. thesis Minnesota, 1950.

(11) J. C. Irvine and D. McNicoll, *J. Chem. Soc.*, 97, 1449 (1910).

(12) J. C. Irvine and Agnes M. Moodie, *ibid.*, 93, 103 (1908).

(13) R. A. Laidlaw and E. G. V. Percival, *ibid.*, 1600 (1949).

DEPARTMENT OF AGRICULTURAL BIOCHEMISTRY
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Styrene Sulfide

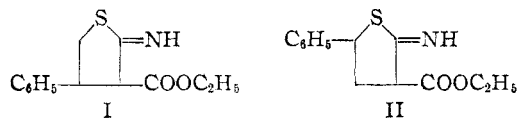
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Styrene sulfide was prepared, as herein described, by a modification of the procedure of Culvenor and co-workers,² who reported that "attempts to make styrene sulfide gave merely high-molecular material." The reaction between potassium thiocyanate 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.

(1) Department of Chemistry, Colorado Agricultural and Mechanical College, Fort Collins, Colorado.

(2) C. C. J. Culvenor, W. Davies and K. H. Pausaker, *J. Chem. Soc.*, 1050 (1946).

The reaction of styrene sulfide with the sodium derivative of ethyl cyanoacetate³ gave a product believed to be 2-imino-3-carbethoxy-4(or 5)-phenylthiophane (I or II). However, the structure



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 morpholine⁴ gave only sulfur-free products.

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

Experimental⁵

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*₂₀²⁰ 1.1044; *n*_D²⁰ 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

(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.