apparently did not occur. since the use of heat (100°) to complete the reaction gave the same purity as the room temperature reaction. and the final product had a vapor tension of 546.6 mm. (cor.) at 0°—nearly 1 mm. lower than the literature value,[9] and suggesting slightly higher purity.

$(CH_3)_2NBD_2$.—The compound $(CH_3)_2NBD_2$ was prepared by heating 112.2 cc. of B_2D_6 and 203.7 cc. of $(CH_3)_2ND$ (gases at S.C.) in a sealed 300-cc. bulb for 6 hours at 137°. After separation of the $(CH_3)_2NBD_2$ (90% yield) from the by-product $(CH_3)_2NB_2D_5$, the m.p. of the former was observed as 74.3–74.5°—within the half-degree experimental error of the m.p. of pure $(CH_3)_2NBH_2$.[8] The vapor tension at 0° may have been 2% higher than that of $(CH_3)_2NBH_2$.

$(CH_3)_2NB_2D_5$.—More B_2D_6 now was added to the $(CH_3)_2NBD_2$ at 106° (12 hours), quantitatively forming $(CH_3)_2NB_2D_5$. This showed a vapor tension of 105.2 mm. at 0°, or 4.0 mm. higher than $(CH_3)_2NB_2H_5$. Its m.p. was −57.0° —a drop of 2.4° below $(CH_3)_2NB_2H_5$.[8]

BD_3CO.—The compound BD_3CO was prepared in 85% yield by treating B_2D_6 (one atm.) in a bomb tube with CO (ten atm.) during one week at room temperature. Since it is less volatile than BH_3CO, while B_2D_6 is more volatile than B_2H_6, the purification, by fractional condensation at −150°, proved to be easier than in the case of BH_3CO. The m.p. of BD_3CO was observed as −134.4° (2.6° above that of BH_3CO).[10] The vapor tensions of BD_3CO at three widely different temperatures, determining the equation $\log_{10} p_{\text{mm.}} = 7.810 - 1040/T$ are given in Table I. This equation implies the same heat of vaporization as for BH_3CO; only the entropy factor is slightly smaller. Even the downward-concavity of the curve of log p *vs.* $1/T$ is nearly the same for both substances.

TABLE I

VAPOR TENSIONS OF DEUTEROBORINE CARBONYL

t (°C.)	−111.85	−95.5	−95.4	−78.5
p_{mm} (obsd.)	23.0	90.6	91.4	294
p_{mm} (calcd.)	23.0	92.0	93.0	294
v.t. of BH_3CO [10]	25.4	99.2	100.2	322

Acknowledgment.—The generous support of this work by the Office of Naval Research is gratefully acknowledged.

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(10) A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **59**, 782 (1937).

DEPARTMENT OF CHEMISTRY
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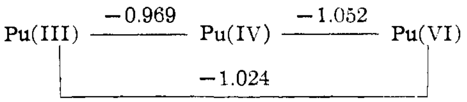
Oxidation Potential of the Pu(III)–Pu(IV) Couple in Perchloric and Hydrochloric Acid

BY ROBERT E. CONNICK AND W. H. MCVEY

It was pointed out by Rabideau and Lemons[1] that the value given by us[2] for the Pu(III)-Pu(IV) formal potential in 1 *M* hydrochloric acid is in error. The mistake, which arose from a typographical error in an earlier paper,[3] makes necessary a change of the hydrochloric acid potential scheme and the discussion of chloride complexing.

The formal potential scheme for 1 *M* hydrochloric acid at 25° becomes



$$\underbrace{\mathrm{Pu(III)}\ \overset{-0.969}{\text{———}}\ \mathrm{Pu(IV)}\ \overset{-1.052}{\text{———}}\ \mathrm{Pu(VI)}}_{-1.024}$$

Our value for the Pu(III)–Pu(IV) couple differs 2 millivolts from that of Rabideau and Lemons because of a different weighting of the original experimental data of Hindman and because we used an activity coefficient of hydrochloric acid based on moles per liter of solution rather than moles per 1000 g. of water.

The per cent. Pu(IV) complexed by chloride ion at 25° in 1 *M* hydrochloric acid becomes 40%.

The anomaly of a more negative potential for the Pu(III)–Pu(VI) couple in hydrochloric acid than in perchloric acid is now intensified. We believe the discrepancy arises primarily from an error in the Pu(III)–Pu(IV)–Pu(VI) equilibrium constant caused by reduction of Pu(IV) to Pu(III) by the products of the α-particles of the plutonium. This effect is more important in one molar perchloric acid than in hydrochloric acid and accounts for the major part of the discrepancy. A fuller account will be published.

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(1) S. W. Rabideau and J. F. Lemons, THIS JOURNAL, **73**, 2895 (1951).

(2) R. E. Connick and W. H. McVey, *ibid.*, **73**, 1798 (1951).

(3) R. E. Connick, Manhattan Project Report CC-3869 (May 5, 1948).

Methylation of Partially Methylated Sugar Anilides[1]

BY I. EHRENTHAL, M. C. RAFIQUE AND F. SMITH

In an attempt to ascertain the ring structure of sugar anilides,[2] Irvine and Gilmour were able to show that when D-glucose anilide was treated with silver oxide and methyl iodide some 2,3,4,6-tetramethyl-D-glucose anilide could be isolated in spite of the fact that oxidation occurred and repeated treatment was necessary.[3] Methylation can also be carried out with methyl sulfate.[4]

For some time we have been making use of an extension of this reaction to partially methylated sugar anilides.[5,6] Whether the latter are crystalline or not most of them undergo complete methylation with silver oxide and methyl iodide to give good yields of the corresponding crystalline fully methylated sugar anilides which have proved to be valuable in the characterization of sugars. The reaction proceeds best with those partially methylated anilides which are soluble in methyl iodide but it can also be applied to those which require methanol or acetone to dissolve them.

Inasmuch as the crystalline anilides of the fully methylated sugars have pyranose structures it would appear, if it can be assumed that no change in ring form occurs during methylation, that most if not all the anilides of partially methylated sugars also have a pyranose structure.

In most instances in the past. the characterization of the parent sugar of an unknown partially methylated derivative has involved its complete methylation to give the fully methylated methyl glycoside which was hydrolyzed to give the fully methylated

(1) Paper No. 2694, Scientific Journal Series, Minnesota Agricultural Experiment Station.

(2) B. Sorokin, *Ber.*, **19**, 513 (1886); *J. prakt. Chem.*, [2] **37**, 291 (1888).

(3) J. C. Irvine and R. Gilmour, *J. Chem. Soc.*, **93**, 1429 (1908).

(4) G. P. Ellis and J. Honeyman, *Nature*, **167**, 239 (1951).

(5) F. Smith, THIS JOURNAL, **70**, 3249 (1948).

(6) M. C. Rafique and F. Smith, *ibid.*, **72**, 4634 (1950).

TABLE I

METHYLATION OF SUGAR ANILIDES

Partially methylated sugar	Anilide, m.p., °C.	Solvent used in methylation	Fully methylated product Name	M.p., °C.	$[\alpha]^{15}\text{D}$ (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 $[\alpha]^{25}\text{D}$ +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°, $[\alpha]^{25}\text{D}$ −141° (*c* 1.0) in pyridine (after crystallization from ethanol). Other typical results are given in Table I.

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(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).

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

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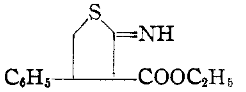
Styrene Sulfide

BY CYRUS O. GUSS[1] AND D. L. CHAMBERLAIN, JR.

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 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.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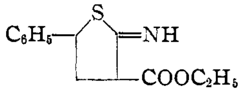
II

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: $n^{20}\text{D}$ 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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(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).

(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.