TABLE II

Amine	Derivatives: Dipicrate M. p., °C.	Dipicrate N, % Calcd.	Dipicrate N, % Found	Phenylurea M. p., °C.	Phenylurea N, % Calcd.	Phenylurea N, % Found
N,N′-Dibutylethylenediamine	148–149.5[a,6]	17.78	17.43	174–174.5	13.65	13.31
N,N′-Dioctylethylenediamine	158–159.5[b,7]	15.09	14.73	129.5–130	10.72	10.30
N,N′-Didodecylethylenediamine	152–154.5[c,7]	13.11	13.11	235 (subl.)	8.83	8.64
N,N′-Dicyclohexylethylenediamine	210 (dec.)	16.42	16.04	206	12.11	12.45
N,N′-Dibenzylethylenediamine	208–210[d] (dec.)	14.93	14.71	182[8]	11.71	11.73
N,N′-Dibutylpiperazine	155–156	17.07	16.89	....	...	...

[a] King and McMillan reported 188°. [b] Linsker and Evans reported 108°. [c] Linsker and Evans reported 112°. [d] Monopicrate.

isolation. This was not possible in the case of dibenzylethylenediamine, which did not form a solid monohydrate under the conditions employed. The by-products listed in Table I were obtained by fractional distillation of the dialkyl ethylenediamines.

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(6) King and McMillan, THIS JOURNAL, **68**, 1776 (1946).

(7) Linsker and Evans, *ibid.*, **68**, 1432 (1946).

(8) Van Alphen, *Rec. trav. chim.*, **54**, 93 (1935).

DEPARTMENT OF CHEMISTRY
CLARK UNIVERSITY
WORCESTER, MASSACHUSETTS RECEIVED JUNE 17, 1949

Acetyldesoxycellulose Quaternary Salts

BY F. N. HAYES AND CHAO-HAN LIN

A cellulose acetate tosylate was prepared by the method of Malm, Tanghe and Laird.[1] Separate portions of it were heated with pyridine, 3-picoline and isoquinoline to give quaternary salts, resulting from displacement of tosylate ions. Similar reactions of *p*-toluenesulfonate esters with tertiary amines are well known.[2,3] Table I gives analytical data and the calculated values for free hydroxyls, unreacted tosylate ester groups, and quaternary salt groups per glucose unit for each of the three products.

The average over-all percentage conversion of the original hydroxyl groups to quaternary salt groups may be used as an estimate of the per cent. primary free hydroxyl in the original cellulose acetate. Our value of 28% compares favorably with a reported value of 25% on a similar sample,[1] determined by the method of tosylation and iodination.

TABLE I

Sample	Percentage		Amount per g. u.			Tos. replaced	Percentage Conv. of OH to quat. salt
	N[a]	S[a]	Free[b] OH	Tos.[b] ester	Quat.[b] salts		
I	..	6.85	0.96	0.69	..	..	..
II	1.93	5.81	1.02	.14	0.49	71	30
III	1.77	5.96	0.97	.26	.42	61	26
IV	1.72	5.74	0.96	.22	.47	68	29

[a] Analyses by Micro-Tech Laboratories, Skokie, Ill. [b] Calculated from the analyses, assuming that the acetyl content remains unchanged.

A sample of cellulose acetate, EK-102893,[4] was tosylated[1] and the product (I) was reprecipitated from acetone by alcohol. Pyridine, 3-picoline and isoquinoline were dried and redistilled.

A solution of 6.0 g. of cellulose acetate tosylate in 60 ml. of pyridine was heated on a steam-bath for twenty-four hours, at the end of which time, it was diluted with 40 ml. of acetone and treated with just enough water to obtain a homogeneous solution. This was slowly poured into excess acetone with good stirring. The precipitated product was filtered, washed with acetone and twice reprecipitated from hot alcohol by ether. The yield of the purified product (II) was 5.5 g.

In a similar manner, 3.0 g. of the tosyl ester gave 2.8 g. of a 3-picolinium salt (III) and 8.0 g. yielded 7.8 g. of an isoquinolinium salt (IV).

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(1) Malm, Tanghe and Laird, THIS JOURNAL, **70**, 2740 (1948).

(2) Cary, Vitcha and Shriner, *J. Org. Chem.*, **1**, 280 (1936).

(3) King, Dodson and Subluskey, THIS JOURNAL, **70**, 1176 (1948).

(4) Kindly supplied for this project by Eastman Kodak Company, with analysis: 1.35 acetyls per glucose unit.

DEPARTMENT OF CHEMISTRY
ILLINOIS INSTITUTE OF TECHNOLOGY
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Separation of Hafnium and Zirconium by a Fractional Distillational Procedure

BY D. M. GRUEN AND J. J. KATZ

In view of current interest in hafnium–zirconium separations,[1] we have investigated a separation method first reported by van Arkel and De Boer.[2] This method involves fractional distillation at atmospheric pressure of the volatile complex compounds formed by reaction of zirconium and hafnium tetrachlorides with either phosphorus pentachloride or phosphorus oxychloride. Although van Arkel and De Boer showed that distillation resulted in considerable separation of hafnium and zirconium they gave no quantitative data on the relative volatilities of the zirconium and hafnium compounds.

The present work is concerned chiefly with the phosphorus oxychloride complexes, since these have lower boiling points and greater thermal stability than the corresponding phosphorus

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(1) K. Street and G. T. Seaborg, THIS JOURNAL, **70**, 4268 (1948).

(2) A. E. van Arkel and J. H. De Boer, *Z. anorg. Chem.*, **141**, 289–296 (1924).

pentachloride compounds. van Arkel and De Boer assigned the formula 2 $ZrCl_4 \cdot POCl_3$ on the basis of zirconium and chlorine analyses. However, analyses for phosphorus, a more sensitive criterion of composition, indicate a more probable formula $3ZrCl_4 \cdot 2POCl_3$ (phosphorus: Calcd. 6.17%; found, 6 27, 6.12, 6.10%).

The vapor pressures of pure $3ZrCl_4 \cdot 2POCl_3$ and $3HfCl_4 \cdot 2POCl_3$ have been determined in the range 0.1–1.0 atmosphere and are represented graphically in Fig. 1. The boiling points are 360 and 355° for the zirconium and hafnium compounds, respectively; the 5° difference in boiling points (which we feel is accurate to ±1°) leads to a calculated value of $\alpha_0 = 1.14$ for the ratio of the vapor pressures at the boiling points. The heat of vaporization for both complexes is 20.5 ± 0.5 kcal.

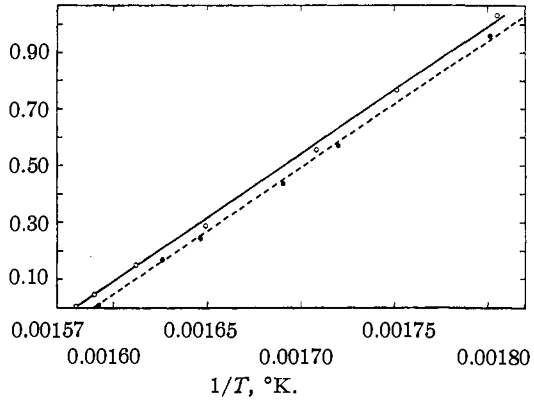

Fig. 1.—Vapor pressure of $HfCl_4$–$POCl_3$ and $ZrCl_4$–$POCl_3$ complexes: —, Zr complex; - - -, Hf complex.

A glass perforated plate column[3] with 50 physical plates was used in the distillation. In a typical experiment $3ZrCl_4 \cdot 2POCl_3$ containing 2.5% hafnium (on the weight of zirconium) yielded a first fraction (5%) containing 16% hafnium. The residue, after distilling 40% away, contained <0.2% hafnium.

Calculation shows the column can also be operated to yield essentially pure hafnium. This aspect, as well as further studies of the chemical and physical properties of these interesting compounds, is presently being investigated.

(3) C. F. Oldershaw, *Ind. Eng. Chem., Anal. Ed.*, **13**, 265 (1941).

CHEMISTRY DIVISION
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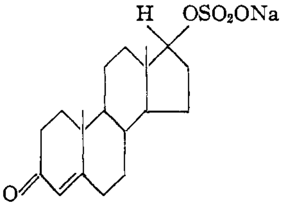
Sodium Testosterone Sulfate

BY G. W. HOLDEN, I. LEVI AND R. BROMLEY

Sodium testosterone sulfate has been prepared with the object of comparing its androgenic activity with that of testosterone and other of its derivatives. The results of the biological tests will be reported later.

With the exception of the use of charcoal in the purification procedure, the method followed was that described by Butenandt and Hofstetter[1] for the preparation of sodium estrone sulfate.

In alcohol, sodium testosterone sulfate exhibits an absorption maximum at 241 mμ, characteristic of testosterone. In water the maximum is shifted to 248–249 mμ.



A solution of chlorosulfonic acid, prepared by dissolving chlorosulfonic acid (1 ml.) in dry chloroform (30 ml.), cooling to 0° and adding pyridine (15 ml.), was added to a solution of testosterone (1.5 g.) in dry pyridine (20 ml.) and dry chloroform (50 ml.). After forty-eight hours at room temperature the solvent was removed *in vacuo* with a water-bath temperature of 40–50°. The solid residue was dissolved in methanol and the acidic solution almost neutralized (litmus) by the addition of methanolic sodium hydroxide. Aqueous sodium bicarbonate was then added to make the solution alkaline and the methanol removed *in vacuo* in the presence of water. The final volume of about 50 ml. was quite clear. This solution was shaken occasionally with Nuchar C (3 g.) at room temperature during one day. The Nuchar was filtered, washed several times with water (negative test for chloride) and eluted by suspending in methanol while still moist. Sodium testosterone sulfate (714.8 mg., 35%) was obtained by concentrating the methanol to small volume, clarifying by filtration using a little Nuchar to remove some yellow color, and precipitating with several volumes of ether. The product, thus obtained, is almost colorless. The m. p. (Fisher–Johns) is quite sharp at 215° with a green color changing to a clear brown at practically the same temperature; $[\alpha]^{25}D$ +74.5° (1% in water), +68° (1% in ethanol); $\epsilon_{(248-249)}$ 20,300 (in water): $\epsilon_{(240.5-241)}$ 17,700 (in ethanol). *Anal.* Calcd. for $C_{19}H_{27}O_5SNa$: C, 58.43; H, 6.97; Na, 5.88. Found: C, 58.54; H, 6.38; Na, 6.03. The semicarbazone precipitated at once on addition of semicarbazide hydrochloride to an aqueous solution of sodium testosterone sulfate. It does not melt up to 300° but starts to darken at 240° becoming slate-gray and finally chocolate-brown. For the determination of testosterone, 53.4 mg. of sodium testosterone sulfate was added to the barium chloride sodium acetate solution described by Talbot[2] for the hydrolysis of sodium dehydroisoandrosterone sulfate. After four hours heating on the steam-bath the solution was extracted with ether. Only 6.5% of the theoretical weight of residue was obtained. Fifty milligrams of sodium testosterone sulfate was then hydrolyzed by refluxing one hour with a mixture of 100 ml. of water and 15 ml. of concd. hydrochloric acid in the presence of 75 ml. of toluene. The toluene was separated, the aqueous solution further extracted with ether and the combined extracts distilled after washing with sodium bicarbonate and water. The yellowish gummy residue weighed 26.8 mg. (68%). It was crystallized by means of aqueous acetone to yield 9.3 mg. (25.3%) of testosterone m. p. 153.5° and mixed m. p. with pure testosterone undepressed.

RESEARCH LABORATORIES
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MONTREAL, CANADA

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[1] Butenandt and Hofstetter, *Z. physiol. Chem.*, **259**, 222 (1939).

[2] Talbot, Ryan and Wolfe, *J. Biol. Chem.*, **148**, 593 (1943).