TABLE I

MELTING POINTS AND MOLECULAR WEIGHTS OF THE O-ALKYL DERIVATIVES OF SACCHARIN

Alkyl	M. p., °C.	Molecular weight Calcd.	Found
Methyl[a]	182	197	191
Ethyl[a]	219	211	205
n-Propyl	124.5	225	228
n-Butyl	96	239	242
n-Amyl	62	233	245
n-Hexyl	60	267	259
n-Heptyl	55	281	290
n-Octyl	46	295	289
n-Nonyl	49	309	306
n-Decyl	47.5	323	316
n-Undecyl	58.5	337	338
Lauryl	54	351	340
n-Tridecyl	66	365	354
Myristyl	62	379	395
n-Pentadecyl	72	393	382
Cetyl	69.5	407	390
n-Heptadecyl	76	421	410
n-Octadecyl	74.5	435	416
n-Nonadecyl	80.5	449	446
i-Propyl	137	225	216
i-Butyl	100	239	233
s-Butyl	65.5	239	236
i-Amyl	64	253	242
s-Amyl	38	253	247
2-Ethylhexanol	53.5	295	303
3-Methylheptanol	24	295	280
4-Methylheptanol	34	295	285
5-Methylheptanol	53	295	282
Octanol-4	10	295	269
Benzyl	130	273	281
μ-Ketostearyl	77	449	462

[a] These two melting points by Fisher–Johns apparatus.

display the usual alternation. Up to the hexyl the melting points of the even-numbered derivatives are above the average of those of the adjacent but from the heptyl on this is reversed. The regularity of such a melting point pattern is the best evidence of the purity of the individual compounds. This does not apply to the first few members.

From a few experiments the same reagent appears to be suitable for the identification of phenols. The pseudo-chloride was heated with an excess of the phenol to 125–140° for fifteen to twenty minutes. Hydrogen chloride was evolved. The products were washed with sodium hydroxide solution and with water and recrystallized from alcohol. The results are in Table II.

TABLE II

MELTING POINTS AND ANALYSES OF DERIVATIVES OF PHENOLS

Phenol	M. p., °C.	S Analyses, % Calcd.	Found
Phenol	182	12.32	12.03
o-Cresol	163	11.72	11.47
m-Cresol	146	11.72	11.85
p-Cresol	171.5	11.72	11.32
Thymol	147	...	...
o-Nitrophenol	236	...	...
p-Nitrophenol	192	...	...

Summary

1. Pseudo-saccharin chloride has been found to be a convenient reagent for the identification of primary and secondary alcohols.

2. It can be used for phenols also.

3. A considerable number of derivatives have been prepared for reference.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Several Alkyl-β-thioethylamines and the Corresponding Ureas, Sulfoxides and Sulfones[1]

BY K. W. BRIGHTON AND E. EMMET REID

Schneider[2] prepared two alkyl-β-thioethylamines from β-bromethylphthalimide and mercaptans but several steps were required of which the final one, hydrolysis, was difficult. We have found it much simpler to cause β-bromethylamine to react with sodium mercaptides. Similarly we have obtained the already known[3] β-methoxy- and β-ethoxy-ethylamines, boiling at 95° and 108°, from the sodium alcoholates but the yields were poor.

Procedure

β-Bromethylamine hydrobromide, m. p. 174.5°, was prepared by dropping ethanolamine into cold, concd. aqueous hydrobromic acid, refluxing and finally distilling off the excess acid. After our work was completed a similar method was published by Cortese.[4]

(1) From a part of the Dissertation of K. W. Brighton, June, 1936. Original manuscript received March 23, 1942.

(2) Schneider, *Ann.*, **386**, 337 (1912).

(3) Traube and Pieser, *Ber.*, **53**, 1501 (1920).

(4) Cortese, THIS JOURNAL, **58**, 191 (1936).

TABLE I

ALKYL-β-THIOETHYLAMINES, THEIR HYDROCHLORIDES AND UREAS

	$RSCH_2CH_2NH_2$			$RSCH_2CH_2NH_2 \cdot HCl$			$RSCH_2CH_2NHCONH_2$		
	B. p., °C.	% N Calcd.	Found	M. p., °C.	% Cl Calcd.	Found	M. p., °C.	% N Calcd.	Found
n-Butyl	211	10.53	10.52	118	20.92	20.87	91	15.91	15.83
n-Amyl	231	9.52	9.40	..	...	...	101	14.74	14.70
i-Amyl	231	9.52	9.37	167	19.33	19.26	111	14.74	14.61
n-Hexyl	252	8.69	8.68	131	17.96	18.02	99	13.73	13.80
n-Heptyl	270	8.00	7.99	121	16.77	16.58	95	12.84	12.76

To prepare butyl-β-thiolethylamine, 46 g. of sodium was dissolved in 500 cc. of alcohol, 90 g. of butyl mercaptan was added followed by an alcoholic solution of 205 g. of the above salt. After refluxing the solution was decanted from the precipitated sodium bromide, acidified and evaporated to dryness. The base was set free by concentrated sodium hydroxide solution and taken up in ether. This solution was concentrated and distilled, the 200–220° cut being taken and redistilled. The other bases were prepared similarly. The hydrochlorides were precipitated from dried petroleum ether solutions of the bases by passing in hydrogen chloride. They were recrystallized from absolute alcohol and acetone.

The ureas were made by the cyanate method and recrystallized from benzene.

The amines, in dilute hydrochloric acid solution, were oxidized to the sulfoxides by standing two days with the calculated amount of 30% hydrogen peroxide. An excess of this reagent carried them to the sulfones.

The amines are strong bases, insoluble in water but soluble in the usual organic solvents. They form stable hygroscopic hydrochlorides. The ureas are only slightly soluble in water. The properties and analyses are in Tables I and II.

The original purpose in preparing the alkyl-β-thioethylamines was to condense them with chloracetophenone in order to contrast the physiological properties of the expected sulfur compounds with the corresponding ones containing oxygen. For some unknown reason it was found impossible to effect the desired condensations. Different solvents and different temperatures were tried; either there was no reaction or tarry masses were produced from which nothing could be isolated.

TABLE II

HYDROCHLORIDES OF THE SULFOXIDES AND SULFONES FROM THE ALKYL-β-THIOLETHYLAMINES

	$RSOCH_2CH_2NH_2 \cdot HCl$			$RSO_2CH_2CH_2NH_2 \cdot HCl$		
	M. p., °C.	% Cl Calcd.	Found	M. p., °C.	% Cl Calcd.	Found
n-Butyl	112	19.12	19.08	211	17.60	17.50
n-Amyl	121	17.78	17.75	221	16.45	16.38
n-Hexyl	127	16.61	16.60	238	15.46	15.41
n-Heptyl	123	15.59	15.51	230	14.56	14.49

Summary

Several alkyl-β-thioethylamines have been prepared by a new method and from them the corresponding ureas.

The amine hydrochlorides have been oxidized to the sulfoxides and sulfones.

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[CONTRIBUTION FROM THE DEPARTMENT OF MEDICINE AND CHEMISTRY DEPARTMENT, STANFORD UNIVERSITY]

Solubility and Electrophoretic Studies of Serum Globulins. I. Gamma Globulin

BY ELOISE JAMESON AND C. ALVEREZ-TOSTADO[1]

Introduction

The object of the present communication is to advance experimental evidence leading to a definite explanation as to why proteins usually do not appear to obey the phase rule, and yet under other conditions can be found to behave in accordance with it. As early as 1937[1a] we were able to describe a globulin fraction exhibiting definite true solubility in the phase rule sense. We should hesitate to call even this a single pure protein component. Indeed we feel sure that it is not. Our present hypothesis serves to explain not only the solubility relations of globulins but also their otherwise rather complicated electrophoretic behavior. The work reported in this paper constitutes only a sorting or mapping out of this field. It does not attempt a precise specialized purification such as that of Kuntz and Northrop with crystalline enzymes. The main results of our present work stand, regardless of these considerations.

(1) Now at Santa Clara University, Santa Clara, Calif.

(1a) E. Jameson and D. B. Roberts, *J. Gen. Physiol.*, **21**, 249 (1937).