[Contribution from Chemistry Laboratory of Southwestern University]

Pseudo-saccharin Chloride, a Reagent for the Identification of Alcohols[1]

By Jacob R. Meadoe and E. Emmet Reid

We have found that pseudo-saccharin chloride, originally prepared by Jesurum,[2] is a useful reagent for the identification of primary and secondary alcohols. The derivatives form easily and are readily purified by crystallization from alcohol or other organic solvent. Many of them have convenient melting points.

In the preparation of pseudo-saccharin chloride Jesurum[2] used two molecules of phosphorus pentachloride for one of saccharin, but we prefer slightly over one; the two substances being mixed in a flask and heated gently until the reaction subsides. The flask is then heated at 175° for one and one-half hours, suction being applied at the end to eliminate phosphorus oxychloride. The product is then pressed on a porous plate, a yield of 80% being obtained. Recrystallized from benzene, an almost white product resulted, m. p. 141–144°.

Anal. Calcd.: S, 15.84; Cl, 17.61. Found: S, 15.36; Cl, 17.38.

The derivatives are prepared by heating the pseudo-saccharin chloride with the anhydrous alcohol in a test-tube until hydrogen chloride is no longer evolved. With the lower alcohols 100° for ten minutes suffices; with the higher alcohols a higher temperature up to 125° is preferable. Secondary alcohols require longer heating at 125°. It is desirable with the lower alcohols to use a considerable excess of the alcohol and get rid of it by evaporation. With the higher alcohols an excess of the chloride is used and the product washed with dilute aqueous alkali.

The melting points and molecular weights of a number of these derivatives are given in the following table and are represented graphically in Fig. 1. The alcohols used in preparing the derivatives from decyl to octadecyl were those prepared by Meyer and Reid.[3] The derivatives were recrystallized until the melting point was constant within about 0.5°. The melting points were corrected for emergent stem and may be considered to be precise within 0.5°.

The purity of these derivatives was demonstrated by a number of analyses as follows.

Anal. Calcd. for the *n*-propyl: S, 14.22; N, 6.22. Found: S, 14.20; N, 6.01. Calcd. for the *n*-butyl: S, 13.40. Found: S, 13.34. Calcd. for the *n*-amyl: N, 5.51. Found: N, 5.60. Calcd. for the myristyl: S, 8.44. Found: S, 8.41. Calcd. for the *n*-octadecyl: N, 3.22. Found: N, 3.25.

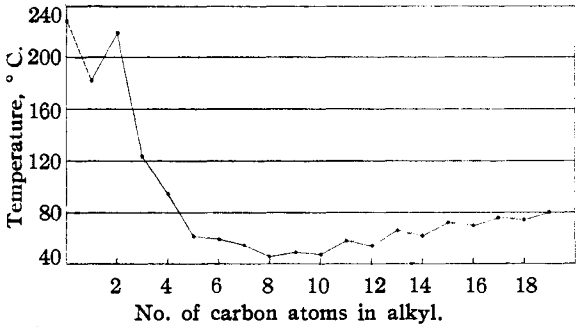

Fig. 1.—Melting points of O-alkylsaccharin derivatives.

The derivatives appeared to be quite pure to start with and were readily brought to substantially constant melting points as is illustrated by the following typical examples:

	Melting points, °C.		
Alkyl	1st.	2nd.	3rd.
i-Propyl	136	136.8	...
n-Hexyl	59	59.7	...
s-Amyl	oil	37	38
n-Heptyl	54.5	55	...
n-Octyl	46	46	...
n-Octadecyl	73	74	74.5

Mixed melting points taken with several pairs of adjacent derivatives showed considerable depressions and wide spreads: the *n*-amyl and *i*-amyl, 37–42°; the 2-ethylhexanol and 5-methylheptanol, 33–36°; the *n*-undecyl and lauryl, 48–52°; the lauryl and *n*-tridecyl, 52–58°; and the *n*-heptadecyl and *n*-octadecyl, 54–67°. The molecular weights were determined by the cryoscopic method[4] with camphor or borneol as solvent.

The remarkably high melting point of the ethyl derivative is interesting. This may be related to its symmetry, since the $-COC_2H_5$, md. wt. 61, nearly balances the $-SO_2-$, md. wt. 64. It can be seen from Fig. 1 that the melting points

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(1) Original manuscript received May 27, 1941.

(2) Jesurum, *Ber.*, 26, 2287 (1893).

(3) Meyer and Reid, This Journal, 55, 1574 (1933).

(4) Niederl and Niederl, "Quantitative Organic Micro-analysis," John Wiley and Sons, Inc., New York, N. Y., 1938, pp. 171–173.

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]

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[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).