ACTA CHEMICA SCANDINAVICA 9 (1955) 1425—1430

S-Benzylthiuronium Salts

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171 S-Benzylthiuronium salts were prepared and were, if possible, titrated with perchloric acid. Melting points and a brief discussion on the influence of functional groups on the titration are given.

In the course of an investigation on the use of S-benzylthiuronium salts as derivatives of organic acids we have prepared a number of such salts which have not been described before.

Melting points and analyses of the derivatives are listed in the following tables, Table 1 giving the carboxylic acid derivatives and Table 2 derivatives of sulfonic acids. Melting points are uncorrected, they were measured in a paraffin-bath, the rate of heating being 2°/min.

Besides we have prepared a large number of already described salts [2,3,6,7 etc.], and as a rule we were able to reproduce the melting points given by these authors. In a few cases, when the melting points found by us deviated 10° or more from those reported by others, we have included the corresponding acid in Tables 1 or 2. However, as mentioned by Berger [2], the melting points of S-benzylthiuronium salts depend to a great extend on the rate of heating, and are, as such, not of much use for identification purposes.

Salts of xanthic acids (ROCSSH) have been prepared in two cases (Table 1); several others were synthesized, but could not be purified to give correct analysis. A salt of picric acid has been prepared (Table 1), whereas salts of dinitrophenols, 5-aminotetrazol and barbituric acids were not obtained in a sufficient degree of purity. We were unable to obtain salts from alifatic amino acids. Alifatic hydroxy acids have given salts in all cases tried: citric acid, however, gave a mixture of the normal and the secundary salts, which we were unable to separate.

EXPERIMENTAL

The derivatives of the monobasic acids were prepared according to Veibel *et al.*[6,7]: 10 m.equiv. of the acid is dissolved in 10 ml 1 N NaOH, the solution made slightly acidic (methyl red) or, if the acid is insoluble, as weakly alkaline as possible; if the sodium salt of the acid is insoluble it may be necessary to add more water. To the hot solution of the acid is added a hot solution of benzylthiuronium chloride (2 g, 10 m.equiv.), in 10 ml of

Table 1.

Acid	m. p.	equiv. weight	
		calc.	found
Acetic acid, allyl-	155—158	266	269
Acetic acid, bromo-	144—145	305	303
Acetic acid, dibenzyl-	138—139	407	402
Acetic acid, ethylxantogen-	149—150	347	345
Acetic acid, 1-naphthyl-	162—163	352	354
Acetic acid, phenyl-	165—166	302	300
Acetic acid, *n*-propylxantogen-	141—142	361	361
Acetic acid, thiol-	140—141	242	240
Acetic acid, triphenyl-	176—177	455	455
Acetoacetic acid, 2-benzeneazo-	175—176	372	370
Acetylenedicarboxylic acid, disalt,	160	223	226
Acrylic acid, 3-benzoyl-	127—129	342	346
Acrylic acid, 2-cyano-3-phenyl-	173	339	335
Acrylic acid, 3(2-furyl)-	170—171	304	308
Acrylic acid, 2-methyl-	156	252	249
Anthranilic acid, N-phenyl-	152—153	380	375
Azobenzene, 2,3,2′,3′-tetracarbonic acid, tetrasalt,	194	256	257
p-Benzenediacetic acid, 2,5-dihydroxy-, disalt,	199—200	279	280
Benzilic acid,	140	395	392
Benzoic acid, 2-acetoxy-5-nitro-	163—165	391	386
Benzoic acid, 3-amino-	160—161	303	302 (B)
Benzoic acid, 2-amino-5-chloro-	153—154	12.4 %	12.6 % (A)
Benzoic acid, 2-benzoyl-	177—178	393	388
Benzoic acid, 4-bromo-	195—196	367	365
Benzoic acid, 2-chloro-	165—166	323	319
Benzoic acid, 3-chloro-	164—165	323	319 (H)
Benzoic acid, 4-chloro-	190	323	321
Benzoic acid, 2-(4-chlorobenzoyl)-	165—166	427	422
Benzoic acid, 2,4-dichloro-	163—165	357	357
Benzoic acid, 3,4-dichloro-	168—169	357	353
Benzoic acid, 2,4-diethoxy-	145—146	377	374
Benzoic acid, 2,4-dihydroxy-	165—166	320	316
Benzoic acid, 2,4-dihydroxy-5-bromo-	170—171	399	395
Benzoic acid, 3,4-dinitro-	151—152	378	374
Benzoic acid, 3,5-dinitro-	178	378	373
Benzoic acid, 2-formyl-	121—122	316	320
Benzoic acid, 3-hydroxy-	161—162	304	304
Benzoic acid, 2-hydroxy-5-acetyl-	134—136	346	343
Benzoic acid, 2-(4-hydroxybenzoyl)-	195—196	408	403
Benzoic acid, 2-hydroxy-5-bromo-	183—184	383	385
Benzoic acid, 2-hydroxy-3,5-dichloro-	158—159	373	378
Benzoic acid, 2-hydroxy-3,5-diiodo-	103—107	556	562
Benzoic acid, 2-hydroxy-3,5-di*iso*propyl-	167—168	389	386
Benzoic acid, 2-hydroxy-5-iodo-	197—198	430	428
Benzoic acid, 2-hydroxy-5-nitro-	171—172	349	345
Benzoic acid, 2-iodo-	162—163	414	412
Benzoic acid, 3-iodo-	178—179	414	418
Benzoic acid, 2-methoxy-	163—164	318	323
Benzoic acid, 3-methoxy-	176	318	318
Benzoic acid, 3-nitro-4-methyl-	167—168	347	350

Table 1. continued.

Acid	m. p.	equiv. weight	
		calc.	found
Benzoic acid, 2-propionyl-	135	344	346
Benzoic acid, 2-(4-toluyl)-	171—172	407	400
Benzoic acid, 3,4,5-trimethoxy-	162—164	378	383
n-Butyric acid, 2-bromo-	146—147	333	335
n-Butyric acid, 2-bromo-3-methyl-	151—152	347	345
n-Butyric acid, 2-chloro-	166—167	289	285
n-Butyric acid, 4-*cyclo*hexyl-	154—155	337	335
n-Butyric acid, 2-ethyl-	133—134	282	280
d-Camphoric acid, disalt	137—138	266	264
Cinnamic acid, α-acetamino-	182—183	372	367
Cinnamic acid, α-methyl-	130—131	328	333
Cinnamic acid, 4-methyl-	175—176	328	325
Cinnamic acid, 3-nitro-	158—159	359	354
Cinnamic acid, 4-nitro-	208—209	359	354
Cinnamic acid, α-phenoxy-	177—178	407	402
Coumarin, 3-carboxylic acid,	167	356	359
Coumaric acid, O-methyl-	147—148	344	346
Coumarinic acid, O-methyl-	146—147	344	340
*Cyclo*hexane carboxylic acid,	165—166	294	292 (C)
Decanoic acid,	148—149	339	338
2,2′-Diphenic acid, monosalt,	174—176	409	412
Glutaric acid, disalt,	152—153	232	230
Glycine, N-acetyl-	166—167	283	280
Glycine, N-carbobenzyloxy-	139—140	375	374
10-Hendecenoic acid,	145—146	351	353
Hexanoic acid, 6-benzoylamino-	151—152	402	397
Hexanoic acid, 2-butyl-2-cyano-	150—151	364	362
Hexanoic acid, 2-ethyl-	129—130	311	315
Hippuric acid,	158—159	345	340
Hydrocinnamic acid, α-benzyl-α-cyano-	112—113	432	436
Levulinic acid,	133—134	282	279
Maleic acid, 2-chloro-, monosalt,	186—187	317	318
Malonic acid, allyl-, disalt,	147—153	238	235
Malonic acid, allylethyl-, disalt,	141—144	252	252
Malonic acid, benzyl-, disalt,	161—162	263	264
Malonic acid, *n*-butyl-, disalt,	132—135	246	246
Malonic acid, butylethyl-, monosalt	137—138	355	351
Malonic acid, diethyl-, monosalt,	148—149	326	325
Malonic acid, dimethyl-, monosalt,	159—160	298	294
Malonic acid, *iso*amyl-, disalt,	136—137	253	256
Malonic acid, *iso*butyl-, disalt,	136—137	246	250
Malonic acid, *iso*propyl-, disalt,	133—134	239	240
Malonic acid, *iso*propyl-, monosalt,	147—148	312	309
Malonic acid, methyl-, monosalt,	145—146	284	281
Malonic acid, methylphenyl-, monosalt,	137—138	360	364
Malonic acid, 3-nitrobenzylidene-, disalt,	146—147	285	288
Malonic acid, phenyl-, disalt,	144—145	256	258
Mandelic acid, 4-methyl-	164—165	332	328
1-Naphthoic acid,	147—148	338	341
1-Naphthoic acid, 2-hydroxy-	203—204	354	354 (D)
Nicotinic acid,	156—157	145	144
2,3-Nonenylic acid,	169—170	322	322

Table 1. continued.

Acid	m. p.	equiv. weight.	
		calc.	found
Penta-2,4-dienic acid, 2-(4-nitrophenyl)-	136—137	385	389
Phenoxyacetic acid	180—181	318	317 (E)
Phenoxyacetic acid, 2-chloro-	167—168	353	351 (F)
Phenoxyacetic acid, 4-chloro-	198—199	353	351 (G)
Phenoxyacetic acid, 2,4-dibromo-	173—175	476	474
Phenoxyacetic acid, 2,4-dichloro-	177—178	387	384
Phenoxyacetic acid, 2,4-dichloro-5-nitro-	166—167	432	429
Phenoxyacetic acid, 2-methyl-	162—163	332	329
Phenoxyacetic acid, 3-methyl-	166—168	332	329
Phenoxyacetic acid, 2-methyl-4-chloro-	164—165	367	368
Phenoxyacetic acid, 3-methyl-4-chloro-	168—169	367	363
Phenoxyacetic acid, 2-nitro-	155—156	363	359
Phenoxyacetic acid, 2,4,6-trichloro-	198—199	422	420
Phenylacetic acid, 3-methoxy-	160—161	332	333
Phenylacetic acid, 4-nitro-	166—168	347	348
Phthalic acid, 4-iodo-, monosalt,	191	457	461
Phthalic acid, mono-*n*-butylester-	137—138	388	385
Phthalic acid, mono*cyclo*hexylester-	159—160	415	412
Phthalic acid, monomethylester-	133—134	346	345
Phthalic acid, 3-nitro-, disalt,	177—178	272	273
Phthalic acid, 4-nitro-, disalt,	176—177	272	272
Phthalic acid, 4-nitro-, monosalt-	183—185	377	381
α-Picolinic acid,	185—186	14.5 %	14.4% (A)
Picric acid,	186—187	395	392
Pimelic acid, disalt,	162—163	246	245
Piperonylic acid,	172—173	332	330
Pivalic acid,	153—154	268	271
Propiolic acid, 3-phenyl-	184—186	312	308
Propionic acid, 3-benzoyl-	147—148	344	348
Propionic acid, 2-chloro-	168—169	275	278
Propionic acid, 3-chloro-	148—149	275	275
Propionic acid, 3-(4-chlorobenzoyl)-	159—160	379	374
Propionic acid, 3-*cyclo*hexyl-	175—177	323	319
Propionic acid, 2,3-dichloro-	138—139	309	305
Propionic acid, 2-ethylxantogen-	134—135	361	364
Propionic acid, 2-methylxantogen-	142—143	347	347
Propionic acid, 2-phenoxy-	154—156	332	335
Propionic acid, 3-phenyl-	151—152	316	312
Propionic acid, 2-phenyl-3-benzoyl-	158—159	421	427
Propionic acid, 3,3,3-triphenyl-	157	469	469
Pyruvic acid,	157—158	254	251
Sorbic acid,	183—184	278	279
Suberic acid, disalt,	150—151	253	252
Succinic acid, 2-chloro-, disalt,	138—139	243	243
Succinic acid, 2-methyl-, disalt,	127—129	232	234
Succinic acid, α(α-methylbenzylidene)-monoethylester-	159—160	409	412
Succinic acid, monobenzylester-	134—135	375	376
Succinic acid, monomethylester-	135—136	298	295
Succinic acid, 2-phenyl-, disalt,	164—165	263	261
cis-Δ^4-Tetrahydrophthalic acid, monosalt,	158—159	336	335
Tiglic acid,	163—164	266	263

Table 1. Continued.

Acid	m. p.	equiv. weight	
		calc.	found
2-Toluic acid, α-carboxy-, disalt,	155—156	256	253
Valeric acid, 2-chloro-	162—163	303	300
Vanillic acid,	166	334	333
Xanthic acid, methyl-	81— 83	274	277
Xanthic acid, *n*-propyl-	106—107	303	308

A) analyzed according to Dumas.
B) Donleavy [3] gives m. p. 149.
C) Tinker [5] gives m. p. 155—156.
D) Veibel [6] gives m. p. 216—217.
E) Levey and Lewis [4] m. p. 170.
F) Levey and Lewis [4] m. p. 159—159.5.
G) Levey and Lewis [4] m. p. 183.5—184.
H) Donleavy [3] gives m. p. 155.

water. The mixture is immediately cooled in ice, whereby the salt separates, often as an oil which crystallises on standing or scratching. The salts were recrystallised from 96 % ethanol, if necessary mixed with water or ether.

In case of dibasic acids it was tried to prepare both the normal and the acidic salts; the normal salts by dissolving 20 m.equiv. of the acid in 20 m.equiv. of NaOH and adding 20 m.equiv. of benzylthiuronium chloride, the acidic salts by dissolving 20 m.equiv. of the acid in 10 m.equiv. of NaOH and adding 10 m.equiv. of benzylthiuronium chloride. In most cases both procedures gave the same salt, either the normal or the acid one; only in case of *iso*propylmalonic acid, 4-nitrophthalic acid and benzoic acid, 3-sulfonic acid, could both salts be isolated. As mentioned by Berger [2], adipic acid gives both a di- and a monosalt by nearly the same procedures.

Table 2.

Acid	m. p.	equiv. weight or % nitrogen	
		calc.	found
Azobenzene, 4-dimethylamino-4′-sulfonic acid-	213—214	14.9	14.8
Azobenzene, 3,4-disulfonic acid, monosalt,	202—203	13.4	13.6
Azobenzene, 4-hydroxy-4′-sulfonic acid-,	228—229	12.6	12.6
Benzenesulfinic acid, 4-acetamino-	193—194	11.5	11.5
Benzenesulfonic acid, 4-acetamino-	248—249	11.0	11.1
Benzoic acid, 2-hydroxy-5-sulfonic acid-, disalt,	160—161	551	547 (A)
Benzoic acid, 3-sulfonic acid, disalt,	130—133	535	539 (B)
Ethylsulphuric acid,	112—113	9.6	9.3 (C)
2-Naphtol-1-sulfonic acid,	131—132	7.2	7.3
Phenol, 2-amino-4-sulfonic acid-	80— 81	11.8	11.6
Quinoline, 8-sulfonic acid-	>250	376	372
Toluene, 2-chloro-5-amino-4-sulfonic acid-,	210—215	10.8	10.6
Toluene, 4-nitro-2-sulfonic acid-,	173—174	11.0	11.0

A) Veibel [6] isolated a monosalt with m. p. 203—204.
B) Veibel [6] isolated a monosalt with m. p. 163—164.
C) Bair and Suter [1] could not prepare this derivative.

The carboxylic acid derivatives were titrated with perchloric acid in glacial acetic acid according to Berger [2], using crystal violet as an indicator. The sulfonic acid derivatives, which can not be titrated [2], were analysed (Dumas).

Derivatives of acids with strongly basic groups will titrate sharply, using two equivalents of perchloric acid; examples of this type of compounds are *m*-aminobenzoic acid, nicotinic acid and quinoline-8-sulfonic acid (the latter using one equiv. of $HClO_4$, only).

Where derivatives of acids containing less basic nitrogen are concerned, complications may arise as the basicity of the nitrogen may be high enough to allow reaction with perchloric acid, but not high enough to take up a whole equiv., resulting in an unsharp endpoint. Examples of this type of compounds, which had to be analysed (Dumas), are *o*- and *p*-aminobenzoic acid, aminochlorobenzoic acid, picolinic acid and several others.

Very weakly basic groups such as N-substituted amides, azo-groups and cyano-groups do not interfere at all in the titration.

(Microanalyses by Mr. W. Egger.)

Thanks are due to professor dr. phil. Stig Veibel who, besides valuable advices, with the financial support of "*Statens almindelige videnskabsfond*", has enabled one of us (C. P.) to take part in this work. Besides we want to thank Miss A. L. Puranen for assistance in this work.

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Received July 1, 1955.