Notes

Tsutomu Momose and Hiroko Tanaka: Organic Qualitative Analysis. IV.* Identification of Carboxylic Acids by S-(*p*-Nitrobenzyl)- and S-(2,4-Dinitrobenzyl)-thiuronium Chloride.

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Donleavy[1] reported the usefulness of S-benzylthiuronium chloride as a reagent for identification of carboxylic acids and this reagent is widely used not only for carboxylic acids but also to identify sulfonic[2] and sulfinic acids[3]. Although the S-benzylthiuro-

Carboxylic Acid	S-(*p*-Nitrobenzyl)-thiuronium Salt				
	m.p. (°C)	Crystal Form	Formula	N, Calcd.	N, Found
Formic	153	Prisms	$C_9H_{11}O_4N_3S$	16.34	16.34
Acetic	141	Plates	$C_{10}H_{13}O_4N_3S$	15.45	15.14
Propionic	146	Prisms	$C_{11}H_{15}O_4N_3S$	14.74	14.48
Butyric	138	Plates	$C_{12}H_{17}O_4N_3S$	14.05	13.77
Isovaleric	149	Plates	$C_{13}H_{19}O_4N_3S$	13.74	13.38
Capric	147	Plates	$C_{18}H_{29}N_4N_3S$	10.96	11.16
Myristic	148	Plates	$C_{22}H_{37}O_4N_3S$	9.55	9.12
Palmitic	142	Needles	$C_{24}H_{41}O_4N_3S$	8.98	8.73
Stearic	138	Needles	$C_{26}H_{45}O_4N_3S$	8.48	8.04
Monochloroacetic	163	Plates	$C_{10}H_{12}O_4N_3SCl$	13.75	13.65
Dichloroacetic	184	Plates	$C_{10}H_{11}O_4N_3SCl_2$	12.23	11.99
Trichloroacetic	143	Needles	$C_{10}H_{10}O_4N_3SCl_3$	11.22	11.18
Oxalic	192	Needles	$C_{10}H_{11}O_5N_3S$	12.47	12.13
Maleic	171	Needles	$C_{12}H_{13}O_6N_3S$	12.84	12.44
Fumaric	172	Needles	$C_{12}H_{13}O_6N_3S$	12.84	12.89
Succinic	157	Prisms	$C_{12}H_{15}O_6N_3S$	12.81	12.53
Tartaric	227	Prisms	$C_{12}H_{15}O_8N_3S$	11.64	11.58
Glutaric	110	Plates	$C_{13}H_{17}O_6N_3S$	12.25	12.21
Adipic	148	Needles	$C_{14}H_{19}O_6N_3S$	11.77	11.89
Crotonic	153	Plates	$C_{12}H_{15}O_4N_3S$	14.15	13.75
Dodecanedicarboxylic	167	Plates	$C_{22}H_{35}O_6N_3S$	9.79	10.07
Citric	194	Plates	$C_{14}H_{17}O_9N_3S$	10.43	10.21
D-Glutamic	208	Plates	$C_{13}H_{18}O_6N_4S$	15.64	15.43
β-Alanine	156	Plates	$C_{11}H_{16}O_4N_4S$	18.65	18.18
L-Leucine	293	Plates	$C_{14}H_{22}O_4N_4S$	16.37	15.91
D-Glucuronic	160	Needles	$C_{12}H_{15}O_7N_3S$	12.15	11.70
Benzoic	161	Needles	$C_{15}H_{15}O_4N_3S$	12.61	12.46
p-Nitrobenzoic	167	Plates	$C_{15}H_{14}O_6N_4S$	14.81	14.62
3,4-Dimethylbenzoic	150	Prisms	$C_{17}H_{19}O_4N_3S$	11.65	11.73
Salicylic	187	Needles	$C_{15}H_{15}O_5N_3S$	12.03	11.99
Phthalic	187	Needles	$C_{16}H_{15}O_6N_3S$	11.15	11.45
Cinnamic	177	Plates	$C_{17}H_{17}O_4N_3S$	11.70	11.64
Phenylacetic	161	Needles	$C_{16}H_{17}O_4N_3S$	12.14	12.36
p-Toluenesulfonic	192	Plates	$C_{15}H_{17}O_5N_3S_2$	11.00	10.91
Picric	198	Needles	$C_{14}H_{12}O_9N_6S$	19.09	18.73
Quinophen	209	Needles	$C_{24}H_{20}O_4N_4S$	12.16	11.75

* Part III: Momose, Tanaka: J. Pharm. Soc. Japan, 73, 105 (1953).
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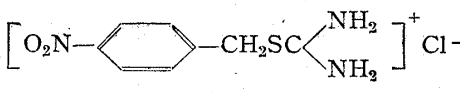
1) Donleavy: J. Am. Chem. Soc., 58, 1004 (1936).
2) Veibel: *Ibid.*, 67, 1867 (1945.)
3) Powell: J. Chem. Soc., 1952, 3728.

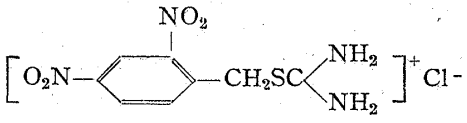
nium salts of carboxylic acids have distinct melting points, their range is very close to each other: e.g. propionic, 148°, and butyric, 146°; myristic, 139°, and palmitic, 141°.

In the present paper, two homologs of the reagent were examined with a view to varying the melting points and increasing the molecular weights.

S-(*p*-Nitrobenzyl)-thiuronium chloride (I), m.p. 223°, and S-(2,4-dinitrobenzyl)-thiuronium chloride (II), m.p. 202°, can be readily prepared by refluxing thiourea with *p*-nitro- or 2,4-dinitro-benzyl chloride in alcohol; they are stable in air, and can be used for identification and separation of carboxylic acids and sulfonic acids. The thiuronium salts of these acids, prepared by mixing of the reagent and their sodium salts, have distinct melting points and depress when admixed with the salts of other carboxylic acids. Carboxylic acids are easily regenerated from these thiuronium salts by acidifying with hydrochloric acid.



(I)



(II)

The salts prepared are shown in the accompanying table.

Carboxylic Acid	S-(2,4-Dinitrobenzyl)-thiuronium Salt				
	m.p. (°C)	Crystal Form	Formula	N, Calcd.	N, Found
Formic	133	Plates	$C_9H_{10}O_6N_4S$	18.60	18.41
Acetic	102	Needles	$C_{10}H_{12}O_6N_4S$	17.66	17.35
Propionic	124	Plates	$C_{11}H_{14}O_6N_4S$	16.90	16.75
Butyric	134	Plates	$C_{12}H_{16}O_6N_4S$	16.24	16.11
Isovaleric	139	Plates	$C_{13}H_{18}O_6N_4S$	15.62	15.89
Capric	124	Plates	$C_{18}H_{28}O_6N_4S$	13.05	13.35
Myristic	128	Plates	$C_{22}H_{36}O_6N_4S$	11.56	11.28
Palmitic	121	Needles	$C_{24}H_{40}O_6N_4S$	10.86	10.69
Stearic	134	Needles	$C_{26}H_{44}O_6N_4S$	10.25	9.84
Monochloroacetic	152	Plates	$C_{10}H_{11}O_6N_4SCl$	15.98	15.91
Dichloroacetic	161	Plates	$C_{10}H_{10}O_6N_4SCl_2$	14.55	14.56
Trichloroacetic	132	Plates	$C_{10}H_9O_3N_4SCl_3$	13.36	13.12
Oxalic	185	Needles	$C_{10}H_{10}O_8N_4S$	14.66	14.36
Maleic	167	Needles	$C_{12}H_{12}O_8N_4S$	15.04	15.27
Fumaric	178	Needles	$C_{12}H_{12}O_8N_4S$	15.04	15.08
Succinic	142	Needles	$C_{12}H_{14}O_8N_4S$	14.95	14.49
Tartaric	254 (decomp.)	Needles	$C_{12}H_{14}O_{10}N_4S$	13.79	13.48
Glutaric	151	Plates	$C_{13}H_{13}O_8N_4S$	14.43	14.21
Adipic	197	Needles	$C_{14}H_{18}O_8N_4S$	14.30	14.52
Crotonic	154	Needles	$C_{12}H_{14}O_6N_4S$	16.42	16.13
Dodecanedicarboxylic	147	Plates	$C_{22}H_{34}O_8N_4S$	10.90	11.25
Citric	176	Plates	$C_{14}H_{16}O_{11}N_4S$	12.50	12.86
-Glutamic	204	Plates	$C_{13}H_{17}O_8N_5S$	17.35	16.97
β-Alanine	195	Plates	$C_{11}H_{15}O_6N_5S$	20.29	20.01
L-Leucine	243	Plates	$C_{14}H_{21}O_6N_5S$	18.09	17.63
-Glucuronic	165	Plates	$C_{12}H_{14}O_9N_4S$	14.35	14.12
Benzoic	164	Plates	$C_{15}H_{14}O_6N_4S$	14.82	14.84
p-Nitrobenzoic	172	Needles	$C_{15}H_{13}O_8N_5S$	16.55	16.78
3,4-Dimethylbenzoic	151	Prisms	$C_{17}H_{18}O_6N_4S$	13.80	14.14
Salicylic	182	Needles	$C_{15}H_{14}O_7N_4S$	14.22	14.40
Phthalic	172	Needles	$C_{15}H_{14}O_8N_4S$	13.27	12.95
Cinnamic	161	Plates	$C_{17}H_{16}O_6N_4S$	13.86	13.65
Phenylacetic	146	Needles	$C_{16}H_{16}O_6N_4S$	14.26	14.51
p-Toluenesulfonic	190	Needles	$C_{15}H_{16}O_7N_4S_2$	13.08	13.03
Pricric	198	Needles	$C_{14}H_{11}O_{11}N_7S$	20.21	19.98
Quinophen	181	Needles	$C_{24}H_{19}O_6N_5S$	13.80	13.42

The authors extend their thanks to Mr. T. Hattori and to Miss T. Kawano for carrying out the elemental analyses.

Experimental*

S-(*p*-Nitrobenzyl)-thiuronium Chloride (I)—To a solution of 17.1 g. of *p*-nitrobenzyl chloride and 50 cc. of alcohol, 7.6 g. of thiourea was added and refluxed for 1 hour. The separated prismatic crystals were collected after cooling, washed with alcohol, and recrystallized from 10% hydrochloric acid, m.p. 223°. *Anal.* Calcd. for $C_8H_{10}O_2N_3ClS$: N, 16.97. Found: N, 16.83.

S-(2,4-Dinitrobenzyl)-thiuronium Chloride (II)—26.6 g. of 2,4-dinitrobenzyl chloride, 7.6 g. of thiourea, and 80 cc. of alcohol were refluxed for 1 hour and the pale yellow plate crystals were recrystallized from 5% hydrochloric acid, m.p. 202°. *Anal.* Calcd. for $C_8H_9O_4N_4ClS$: N, 19.16. Found: N, 19.26.

General Preparation of the Thiuronium Salts of Carboxylic Acids—0.002 mole of carboxylic acid was dissolved in a few cc. of alcohol, neutralized with 1*N* sodium hydroxide, acidified with a small amount of the acid used, then 0.002 mole of reagent (I) or (II) was added. Dissolved by heating a short time on a water bath, it was chilled and the separated salt was recrystallized from diluted alcohol.

Summary

S-(*p*-Nitrobenzyl)- and S-(2,4-dinitrobenzyl)-thiuronium chloride may be used for identification and separation of carboxylic acids, amino acids, and sulfonic acids. The thiuronium salts of these acids are readily prepared and have distinct melting points. The carboxylic acids can easily be regenerated from the thiuronium salts.

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* All melting points are uncorrected.

Tsutomu Momose, Yosuke Ohkura, and Hiroko Tanaka: Organic Qualitative Analysis. V.* Paper Chromatography of Aromatic Hydrocarbons and Ethers.

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The paper chromatography of aromatic hydrocarbons and ethers was carried out leading to their derivatives in the following two methods.

First, aromatic hydrocarbon or ether is condensed with succinic anhydride by the Friedel-Crafts method converting to β-aroylpropionic acid, and developed with butanol-ammonia. β-Aroylpropionic acid, which has an active methylene, can be colored by successively spraying aqueous solution of sodium nitroprusside and of sodium hydroxide.

Naphthalene shows two spots on the paper chromatogram, which indicates that the condensation occurs at α- and β-positions[1]; anisole, also, shows two spots as one methyl

* Part IV: This Bulletin, 2, 152 (1954).

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1) Haworth: J. Chem. Soc., 1932, 1950.