phenylosotriazoles only the 1,2 derivative is obtained from D-fructose. It is not excluded, however, that some of the 2,3 derivative could have been formed and escaped detection.

Experimental

An amount of 4.00 g. of D-fructose of high purity was converted to the phenylosazone; yield 2.70 g. (34%). This phenylosazone (2.70 g.) was then converted to the phenylosotriazole according to the procedure of Hann and Hudson[4] and the product was recrystallized once from hot water; yield 0.80 g. (40%), m. p. 195–195.5° (cor.) unchanged on admixture with material prepared from D-glucose, $[\alpha]^{25}D$ −80° (c 0.07, 4 dm. tube, pyridine), accepted values[4]: m. p. 195–196° and $[\alpha]^{20}D$ −81.6° (pyridine). Concentration of the mother liquor yielded only a trace of the same material.

Anal. When oxidized heterogeneously at 25° for twenty-four hours in 0.0127 M solution with 0.05 M sodium metaperiodate (3.9 molar ratio) there was obtained: 1.0 mole of formaldehyde (dimedon method); 2.0 moles of formic acid (by acidity); 3.0 moles of oxidant consumed; 0.9 mole of 2-phenyl-4-formyl-osotriazole of m. p. 68–69° (accepted value[4] 68–69°).

An amount of 50 mg. of the above phenylosotriazole was dissolved with heating in 20 ml. of 95% acetic acid, cooled to 25° and a solution of 20 ml. of 0.05 M lead tetraacetate (5.3 molar ratio) in absolute acetic acid was added; extrapolated (Fig. 1) rapid oxidant consumption, 3.0 moles.

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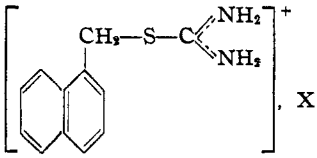
RECEIVED JULY 6, 1948

S-1-Naphthylmethylthiuronium Chloride for the Characterization of Organic Acids

BY WILLIAM A. BONNER

In 1924 Chambers and Scherer[1] introduced the use of S-benzylthiuronium chloride as a reagent for the separation and characterization of several naphthalenesulfonic acids. These results were later broadly extended by Donleavy,[2] Anderson,[3] and Veibel and co-workers[4,5] to the preparation of derivatives of simple carboxylic and sulfonic acids. Later Dewey and co-workers[6,7] employed S-p-chloro- and S-p-bromobenzylthiouronium chlorides in place of the unsubstituted reagent. Several disadvantages, however, attend the use of S-benzylthiuronium chlorides for characterization. Most serious is the fact that the melting points of such salts of certain of the aliphatic acids lie ambiguously close together, necessitating the use of mixed melting points for final characterization. With the exception of those of the sulfonic acid, the salts tend to hydrolyze rather easily, necessitating their preparation and storage under more or less anhydrous conditions. In view of these disadvantages it seemed desirable to attempt the application of S-1-naphthylmethylthiuronium chloride (I) to the preparation of derivatives of organic acids, and to determine if its use obviates any of the above disadvantages



I, X = Cl
II, X = RCOO
III, X = ArCOO
IV, X = ArSO₃

S-1-Naphthylmethylthiuronium chloride was prepared easily and in good yield by refluxing molar quantities of thiourea and 1-chloromethylnaphthalene in ethanol. Derivatives of aliphatic (II), aromatic (III) and arylsulfonic acids (IV) were readily prepared from I by heating the sodium salt of the organic acid with a slight excess of I in ethanol (or water in the case of sulfonic acids), The derivatives precipitated instantly, and in the majority of cases the yields obtained were nearly quantitative. In many cases the product was almost analytically pure as first precipitated or after a single recrystallization.

A comparison of the melting points in Table I of the S-1-naphthylmethylthiuronium derivatives of the lower aliphatic acids with melting points of the simple or substituted S-benzylthiuronium salts of these acids indicates that the former have a slightly greater spread in melting points on ascending the homologous series. Derivatives of the higher fatty acids, however, from lauric acid up show the same close proximities of melting points characteristic of the S-benzyl- or substituted S-benzylthiuronium series. Five representative pairs of derivatives having close melting points, however, showed mixed melting point depressions ranging from four to nine degrees. It is interesting to note that the S-1-naphthylmethylthiuronium salts generally show slightly higher melting points than the corresponding simple or substituted S-benzylthiuronium salts. No evidence of polymorphism was noted for any of the S-1-naphthylmethylthiouronium salts.

As previously observed[2,6,7] for the mononuclear analogs, the S-1-naphthylmethylthiuronium salts of carboxylic acids tend to hydrolyze in water and are best prepared in alcohol, while these salts of the sulfonic acids may be prepared and recrystallized from water solution. No attempt was made to establish which series of compounds underwent hydrolysis most readily.

Attempts were made to prepare derivatives of several lower members of the dicarboxylic acid series with I. By concentrating the reaction mixture it was possible to obtain crystalline derivatives, but these proved too soluble in ethanol to permit good yields or satisfactory recovery on recrystallization.

Experimental Part

S-1-Naphthylmethylthiuronium Chloride.—Thiourea (35.7 g., 0.47 mole) was dissolved with heating and stirring

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[1] Chambers and Scherer, *Ind. Eng. Chem.*, **16**, 1272 (1924).

[2] Donleavy, THIS JOURNAL, **58**, 1004 (1936).

[3] Anderson, *J. Biol. Chem.*, **74**, 548 (1927).

[4] Veibel and Lillelund, *Bull. soc. chim.*, [5] **5**, 1153 (1938).

[5] Veibel and Ottung, *ibid.*, **6**, 1434 (1939).

[6] Dewey and Sperry, THIS JOURNAL, **61**, 3251 (1939).

[7] Dewey and Shasky, *ibid.*, **63**, 3526 (1941).

in ethanol (83 ml.). 1-Chloromethylnaphthalene (83.1 g., 0.47 mole) (prepared by the method of Fuson and McKeever[8]) was added rapidly from a separatory funnel to the vigorously stirred refluxing mixture. The product precipitated instantly. The mixture was stirred under reflux for an hour, cooled to 0°, filtered, pressed, and the crude product rinsed with cold ethanol and air-dried. The crude product weighed 95.9 g. (81%) and had m.p. 226–228°. One recrystallization from ethanol raised the m.p. to 232°. The highest m.p. obtained on further recrystallization was 233°.

Anal. (By a semi-micro Kjeldahl determination) Calcd. for $C_{12}H_{13}N_2SCl$: N, 11.09. Found: N, 11.10.

S-1-Naphthylmethylthiuronium Salts of Organic Acids.—Derivatives of aliphatic and aromatic carboxylic acids were most readily prepared in the following manner. The acid (0.10 g.) was dissolved in ethanol (about 1 ml.) using heat if necessary. A drop of 1% phenolphthalein solution was added and the mixture titrated to a faint pink with a 10% solution of sodium ethoxide prepared by dissolving sodium in the correct amount of ethanol. The suspension of the sodium salt of the acid was warmed and treated at once with a boiling solution consisting of a 10% excess of S-1-naphthylmethylthiuronium chloride dissolved in a minimum quantity of boiling ethanol. The product usually crystallized immediately, and the suspension was boiled gently for a minute or so under vigorous stirring, permitted to cool slowly, chilled, collected, and rinsed with cold ethanol. The crude products were recrystallized twice from ethanol with the aid of a centrifuge, air dried and the melting points and analyses conducted. Nitrogen analyses by a semi-micro Kjeldahl procedure agreed acceptably with calculated values. Yields in the majority of cases were close to quantitative, and the melting points of the first seven crude products listed were not raised materially by the two succeeding recrystallizations. Melting points of the remaining products were not determined before recrystallization. The preparation of sulfonic acid derivatives was similar to that described above, except that aqueous media were employed throughout. Yields of sulfonic acid derivatives were considerably lower when alcoholic media were employed. Corrected melting points of the S-1-naphthylmethylthiuronium salts of the acids studied are listed in Table I.

TABLE I

S-1-NAPHTHYLMETHYLTHIURONIUM SALTS OF ORGANIC ACIDS

No.	Acid	M. p., °C., of salt	% Nitrogen Calcd.	% Nitrogen Found[b]
1	Formic	183.5	10.71	10.95
2	Acetic	160.5	10.13	10.13
3	Propionic	142.5	9.64	9.85
4	Butyric	160.0	9.20	9.30
5	Valeric	167.0	8.80	9.02
6	Isovaleric	153.0	8.80	8.39
7	Caproic	152.5	8.42	8.40
8	Isocaproic	163.5	8.42	8.09
9	Heptylic	156.5	8.13	8.22
10	Caprylic	165.0	7.78	7.24
11	Pelargonic	159.5	7.48	7.66
12	Capric	163.0	7.19	7.14
13	Undecylic	160.5	6.96	6.95
14	Lauric	155.0	6.72	6.70
15	Myristic	152.5	6.30	6.42
16	Palmitic	150 5	5.92	5.70
17	Stearic	150.0	5.59	5.45
18	Crotonic	180.5	9.26	9.31
19	Levulinic	146.5	8.42	8.23
20	Trichloroacetic	143.0	7.36	7.24
21	Phenylacetic	166.5	7.94	8.05
22	Furoic	220.0	8.52	8.42
23	Benzoic	181.5	8.27	8.33
24	*o*-Benzoylbenzoic	193.5	6.32	6.39
25	β-Naphthoic	186.5	7.20	7.03
26	Cinnamic	179.5	7.67	7.71
27	Anisic	189.0	7.59	7.20
28	Salicylic	170.0	7.88	7.81
29	Benzenesulfonic[a]	186.0	7.48	7.54
30	*p*-Toluenesulfonic	178.0	7.20	7.76
31	β-Naphthalenesulfonic[a]	179.5	6.59	6.50
32	*p*-Phenolsulfonic[a]	106.0	7.16	6.84
33	Benzenesulfinic[a]	177 (dec.)	7.83	7.36

[a] Made directly from sodium salt.
[b] By semi-micro Kjeldahl method.

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RECEIVED MARCH 20, 1948

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[8] Fuson and McKeever in "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 78.

A Reaction between Carbon Tetrachloride and Ammonium Chloride

BY D. D. CUBICCIOTTI AND WENDELL M. LATIMER

From thermodynamic considerations it would appear that ammonium chloride should react with carbon tetrachloride. The reaction

$$NH_4Cl(g) + CCl_4(g) \longrightarrow {}^1/_3(CNCl)_3(s) + 4HCl(g)$$

has a favorable free energy change. The ΔH of the reaction is -20 kcal.,[1] and the ΔS must be positive because of the increase in number of moles of gas on reaction. It seemed reasonable, therefore, to investigate the possible reaction experimentally.

The first experiments involved passing a mixture of carbon tetrachloride and nitrogen (to carry the vapor) over a container of ammonium chloride heated to 350–400°. Although varying pressures of carbon tetrachloride vapor (up to one atmosphere) and varying temperatures (up to 400°) were applied, no apparent reaction occurred.

In order to attain more extreme conditions a closed system was tried. The reactants were sealed into an evacuated Pyrex "bomb" tube and heated to 450–475° for an hour or longer. This treatment yielded a yellow solid and hydrogen chloride gas together with traces of hydrogen cyanide and possibly other compounds. From the amount of hydrogen chloride gas formed in one experiment it was estimated that the pressures in the containers reached about twenty atmospheres.

The yellow solid was insoluble in water, alcohol, ether and hydrocarbons, but dissolved after long treatment with hot, concentrated alkali. It did not melt at 300° but does darken slightly at this temperature. For analysis a sample of the yellow solid was prepared as above and washed with water and heated *in vacuo* to 300° (to remove all the ammonium chloride). The sample gained in

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[1] Heat of formation of (CNCl) from Lemoult, *Ann. chim.*, [7] 16, 344 (1899).