

**4-N,N-Dimethylamino-7-nitrohydrindene.**—A mixture containing 4-amino-7-nitrohydrindene (4 g.), sodium hydroxide (4 g.), methyl iodide (17 g.) and methanol (20 ml.) was heated at 140–150° for six hours. The solution was extracted with benzene after having been made alkaline and the benzene was removed by steam distillation. The residue was refluxed with acetic anhydride (30 ml.) for three hours and decomposed with water. Extraction with benzene followed by extraction of the benzene layer with hydrochloric acid (6 N) and then neutralization gave 4-N,N-dimethylamino-7-nitrohydrindene. Recrystallization from alcohol gave 2.9 g. of pure product; m. p. 81–82°.

*Anal.* Calcd. for  $C_{11}H_{14}N_2O_2$ : C, 64.06; H, 6.85. Found: C, 64.01; H, 7.00.

**5-Amino-8-nitro-1,2,3,4-tetrahydronaphthalene.**—5-Acetamido-1,2,3,4-tetrahydronaphthalene (18 g.) dissolved in sulfuric acid (100 ml.) and nitrated at 0° with nitric acid (6.3 ml.) dissolved in sulfuric acid (30 ml.). The residue obtained after decomposition with ice (800 g.) was taken up in hot alcohol (200 ml.). To this was added hydrochloric acid (80 ml., 6 N) and the whole was heated under reflux for thirty minutes. One-half of the alcohol was removed by distillation, water (300 ml.) was added and the solution was neutralized with ammonium hydroxide. The solid which formed was

dried, dissolved in nitrobenzene (250 ml.) and treated with dry hydrogen chloride for fifteen minutes at 0°. A solid (hydrochloride) weighing 14.1 g. was formed. Neutralization by alkali followed by recrystallization from alcohol gave 5-amino-8-nitro-1,2,3,4-tetrahydronaphthalene; wt. 10.2 g.; m. p. 114.5–116°.

**5-N,N-Dimethylamino-8-nitro-1,2,3,4-tetrahydronaphthalene.**—Following the procedure for methylation as described above for the corresponding hydrindene derivative, there was obtained from the amino compound (4 g.) a 45% yield of the anticipated methylated product; m. p. 61–62°.

*Anal.* Calcd. for  $C_{12}H_{16}N_2O_2$ : C, 65.45; H, 7.32; N, 12.7. Found: C, 65.76; H, 7.35; N, 12.7.

### Summary

1. A number of nitroamines in the hydrindene and tetralin series have been prepared.

2. The ultraviolet spectra of these compounds have been used to support the view that methylene groups in five-membered rings offer less steric hindrance than those in six-membered rings.

(7) Schroeter, *Ann.*, **426**, 60 (1922).

MINNEAPOLIS, MINNESOTA RECEIVED APRIL 30, 1948

## NOTES

### The Homogeneity of the Phenylsazone Prepared from D-Fructose

BY W. W. BINKLEY<sup>1</sup> AND M. L. WOLFROM

Wolfrom, Thompson and Evans<sup>2</sup> have reported an instance of phenylsazone formation, in 1-desoxy-D-psicose, in which the carbonyl carbon and the secondary hydroxyl of carbon three were concerned. It was considered of interest to investigate the phenylsazone formation from the ketose D-fructose to determine if the phenylsazone produced might be a mixture of the 1,2 and 2,3 derivatives.<sup>3</sup> To this end the phenylsazone produced from D-fructose was converted to the phenylsotriazole. The phenylsotriazole obtained was found to be identical with that obtained from D-glucose and which Hann and Hudson<sup>4</sup> had found to be homogeneous and to produce on periodate oxidation 2-phenyl-4-formyl-osotriazole with the concomitant formation of 1 mole of formaldehyde and 2 moles of formic acid. These oxidation results were confirmed by us on our product and we report further that the oxidation with lead tetraacetate, a homogeneous reaction (the periodate oxidations are heterogeneous),

(1) Sugar Research Foundation Associate of The Ohio State University Research Foundation (Project 190).

(2) M. L. Wolfrom, A. Thompson and E. F. Evans, *THIS JOURNAL*, **67**, 1793 (1945).

(3) See E. G. V. Percival, *Advances in Carbohydrate Chem.*, **3**, 44 (1948).

(4) R. M. Hann and C. S. Hudson, *THIS JOURNAL*, **66**, 735 (1944).

yielded the same over-all result. Any 2,3-osazone present would have yielded a phenylsotriazole that would have consumed 2 moles of oxidant with the concomitant formation of 1 mole of formaldehyde, 1 mole of formic acid and 2-phenyl-4-formyl-5-hydroxymethyl-osotriazole.

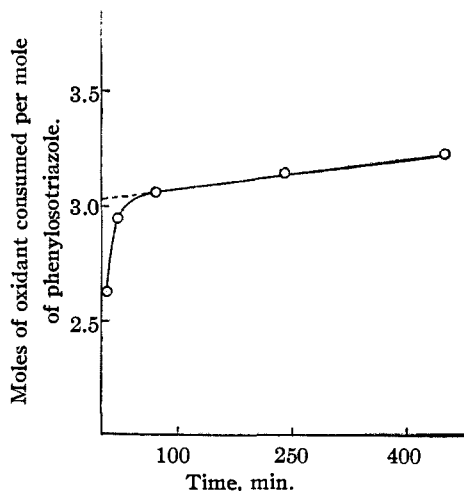


Fig. 1.—Lead tetraacetate oxidation of phenylsotriazole from D-fructose in 97.5% acetic acid at 25°. Points shown corrected for reagent blanks.

Thus it has been determined that in the normal procedures for preparing phenylsazones and

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<sup>4</sup> 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,  $[\alpha]^{20}_D -80^\circ$  ( $c$  0.07, 4 dm. tube, pyridine), accepted values<sup>4</sup>: m. p. 195–196° and  $[\alpha]^{20}_D -81.6^\circ$  (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<sup>4</sup> 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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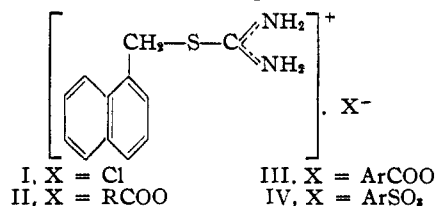
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### S-1-Naphthylmethylthiuronium Chloride for the Characterization of Organic Acids

BY WILLIAM A. BONNER

In 1924 Chambers and Scherer<sup>1</sup> 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,<sup>2</sup> Anderson,<sup>3</sup> and Veibel and co-workers<sup>4,5</sup> to the preparation of derivatives of simple carboxylic and sulfonic acids. Later Dewey and co-workers<sup>6,7</sup> employed S-*p*-chloro- and S-*p*-bromobenzylthiuronium 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



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-naphthylmethylthiuronium salts.

As previously observed<sup>2,6,7</sup> 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

- (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.*, **68**, 3526 (1941).