TABLE I (*Continued*)

Calcd.	Found	Calcd.	Found	Calcd.	Found	Infrared,[b] μ
N, 20.74	N, 20.68	O, 23.69	O, 23.97	S, 11.84	S, 11.91	3.06 (m), 3.18 (m)[d]
C, 44.29	C, 44.47	H, 4.73	H, 4.52	N, 18.78	N, 18.61	...
C, 42.25	C, 42.50	H, 4.26	H, 4.16	N, 19.71	N, 19.91	...
C, 33.34	C, 33.48	H, 2.18	H, 2.33	N, 17.28	N, 17.15	...
C, 44.59	C, 44.77	H, 4.08	H, 3.97	N, 18.91	N, 18.63	...
C, 40.24	C, 40.38	H, 3.68	H, 3.73	N, 17.07	N, 16.82	...
C, 50.59	C, 50.61	H, 3.64	H, 3.89	N, 16.86	N, 16.80	...
C, 44.59	C, 44.85	H, 4.08	H, 4.23	N, 18.91	N, 18.64	...
C, 52.31	C, 52.32	H, 3.51	H, 3.35	N, 16.28	N, 16.32	...
C, 47.98	C, 48.16	H, 4.92	H, 5.19	N, 18.65	N, 18.63	2.86 (m), 2.94 (m)[f]
C, 47.14	C, 47.16	H, 4.32	H, 4.49	N, 19.99	N, 19.80	2.86 (m), 2.94 (m)[f]
C, 48.98	C, 48.73	H, 4.49	H, 4.59	N, 15.58	N, 15.82	2.87 (m), 2.95 (m)[g]

addition to the general procedure described above, this may be prepared in the following way. To a solution of 5.27 g. (0.03 mole) of 5-nitro-2-furoyl chloride in 100 ml. of cold acetone was added, in the following order, 2.73 g. (0.03 mole) of thiosemicarbazide and 7 g. of sodium bicarbonate. After stirring for 3 hr., the suspension was heated under reflux for 1 hr., cooled, and filtered. The filtrate was set aside and the filter cake washed with water to provide 5.41 g. (66%) of I, identical in all ways with material prepared by the general procedure.

Evaporation of the filtrate gave a residue which, after repeated crystallization from ethanol, provided 0.3 g. (4.3 %) of 1-(5-nitro-2-furoyl)thiosemicarbazide, identical with authentic[1] material.

Different Colored Modifications of *S*-(*p*-Nitrobenzoyl)acetone Thiosemicarbazone (XI).—This compound could be obtained in either of two colored modifications. When crystallized from benzene, large orange needles were obtained, which melted at 165° dec., turning yellow at about 140°. This material could not be obtained in an analytically pure state. However, if the orange compound was crystallized from ethanol, small yellow needles were obtained of the same melting point. This product gave the analysis shown in Table I. While the yellow form could be induced to crystallize from benzene, only yellow material could be obtained from ethanol. The infrared spectra of the two different colored forms were identical, both in chloroform solution and in Nujol mull.

***S*-(5-Nitro-2-furoyl)-4-benzylidene-1-isopropylidenethiosemicarbazide.**—One-half gram (0.00185 mole) of *S*-(5-nitro-2-furoyl)acetone thiosemicarbazone (I) was covered with a few milliliters of freshly distilled benzaldehyde and the flask flushed with nitrogen. The benzaldehyde was heated at the boiling point until solution occurred. Cooling and scratching provided material which, after crystallization from ethylene glycol dimethyl ether, weighed 0.33 g. (50%) and melted at 213–214°. Repeated crystallization as before gave yellow platelets, m.p. 217°.

Anal. Calcd. for $C_{16}H_{14}N_4O_4S$: C, 53.63; H, 3.94. Found: C, 53.71; H, 3.92.

Solvolysis of Benzylidene Derivative.—To a suspension of 0.23 g. (0.00064 mole) of pure *S*-(5-nitro-2-furoyl)-4-benzylidene-1-isopropylidenethiosemicarbazide in 10 ml. of ethanol was added 1 small drop of concd. hydrochloric acid. When the suspension was heated to the boiling point, solution occurred. Cooling precipitated 0.16 g. (82%) of *S*-(5-nitro-2-furoyl)acetone thiosemicarbazone (I), identical with authentic I in melting point and infrared spectrum.

Nitric Acid and Perchloric Acid Salts of Aminopyridines[1]

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Received November 17, 1961

Very little has been published concerning the preparation and properties of aminopyridine salts with inorganic oxidizer acids. Marckwald[2] reported the preparation of the mononitric acid addition salt of 2-aminopyridine, but no mention was made of reaction conditions or melting point of the product. Monosalts of 2-amino-4-methylpyridine[3] and 2-amino-6-methylpyridine[4] have been prepared by the addition of concentrated nitric acid to an alcoholic solution of the free base. To our knowledge no perchloric acid salts of aminopyridines have been reported.

This paper presents part of a study on amine salts in which the salts of several aminopyridines were prepared through interactions with nitric acid or perchloric acid. The results obtained are shown in Table I. The procedures used were aimed at the isolation, if possible, of the diacid addition compounds, but none were formed. Even electron donating methyl groups in the 6-position or in the 4,6-position did not increase the basicity enough to permit the formation of the diacid salt.

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[1] Published with the permission of the Bureau of Naval Weapons, Navy Department. The opinions and conclusions are those of the authors.

[2] W. Marckwald, *Ber.*, **27**, 1321 (1894).

[3] O. A. Seide, *Ber.*, **57**, 791 (1924).

[4] O. A. Seide, *J. Russ. Phys. Chem. Soc.*, **50**, 534 (1920).

TABLE I

Base	Adduct	Calcd., N	Calcd., Anion	Anal., N	Anal., Anion	M.P.[a]
2-Aminopyridine	$C_5H_6N_2 \cdot HNO_3$	26.74	39.46	26.73	39.76	133–139
4-Aminopyridine	$C_5H_6N_2 \cdot HNO_3$	26.74	39.46	26.46	38.82	172–173
3-Aminopyridine	$C_5H_6N_2 \cdot HNO_3$	26.74	39.46	26.83	39.54	128–132
2-Amino-5-methylpyridine	$C_6H_8N_2 \cdot HNO_3$	24.55	36.29	25.25	36.06	139–140
2-Amino-6-methylpyridine	$C_6H_8N_2 \cdot HNO_3$	24.55	36.29	24.11	35.70	168–170[b]
2-Amino-4,6-dimethylpyridine	$C_7H_{10}N_2 \cdot HNO_3$	22.69	33.48	22.45	33.80	177–178
2-Aminopyridine	$C_5H_6N_2 \cdot HClO_4$	14.40		14.02		185–187
4-Aminopyridine	$C_5H_6N_2 \cdot HClO_4$	14.40		13.79		272–274
3-Aminopyridine	$C_5H_6N_2 \cdot HClO_4$	14.40		14.05		190–224
2-Amino-5-methylpyridine	$C_6H_8N_2 \cdot HClO_4$	13.43		13.51		99–103
2-Amino-6-methylpyridine	$C_6H_8N_2 \cdot HClO_4$	13.43		13.57		100–102
2-Amino-4,6-dimethylpyridine	$C_7H_{10}N_2 \cdot HClO_4$	12.58		12.70		186–187

[a] All melting points are uncorrected. [b] A m.p. of 168° was reported by Seide (ref. 4).

Experimental

Perchloric Acid Salts.—The perchloric acid addition salts were made by adding slowly 20 ml. of 70–72% perchloric acid to a solution of 4–5 g. of base in 20 ml. of alcohol. All reagents and the reaction vessel were kept cold in an ice bath. After allowing the mixture to stand in the ice bath for 1 hr., the salts were isolated by filtration and partially dried. They were recrystallized from glacial acetic acid or ethanol.[5]

Nitric Acid Salts.—The nitric acid salts were prepared by slowly adding 25 ml. of ice cold concd. nitric acid to 5 g. of cold anhydrous base. Excess nitric acid was removed by placing the sample in a wide flat dish and passing a gentle current of air over the sample overnight. If the salt were still moist, it was placed in a vacuum desiccator and the latter evacuated with a water pump intermittently. The salt was then recrystallized from commercial anhydrous ethyl alcohol. Occasionally, in order to avoid extensive decomposition, the nitric acid–base mixture was frozen and evaporated down to a thick slurry. An alternative method, especially when the pure monosalts were desired, was to add nitric acid to an ether solution of the free base.

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[5] Part of this method was suggested to us in a private communication from T. B. Joyner of the U. S. Naval Ordnance Test Station, China Lake, Calif.

D-Mannoheptulose 1-(N^1-Benzyl-N^1-phenyl)-2-(N^1-phenyl)osazone

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Received November 21, 1961

D-Mannoheptulose 1-(N^1-benzyl-N^1-phenyl)-2-(N^1-phenyl)osazone was synthesized in connection with a study on the identification of microgram amounts of D-mannoheptulose.[1] A detailed description of the preparation and structure of this new, characteristic, crystalline osazone is given here because very few hydrazine derivatives of this heptulose are known. The osazone is an acetic acid solvate when synthesized at room temperature, but washing and drying the crude product removes the acetic acid. Recrystallization from glacial acetic acid yields a solvate, but recrystallization from ethyl acetate or absolute ethanol yields the unsolvated osazone.

The osazone was recovered unaltered after attempted formazan formation in alkaline ethanol. The failure to react under these conditions establishes the point of attachment of the primary and secondary hydrazine groups to C-2 and C-1 of the sugar, respectively.[2] The assigned structure is in accord with the conclusions of Henseke and co-workers, who studied some pentose and hexose mixed osazones.[3,4]

Experimental

D-Mannoheptulose 1-(N^1-Benzyl-N^1-phenyl)-2-(N^1-phenyl)osazone (I).—A solution of 210 mg. (1 mmole) of D-mannoheptulose in 0.4 ml. of water was added with stirring to a mixture of 939 mg. (4 mmoles) of recrystallized 1-benzyl-1-phenylhydrazine hydrochloride, 289 mg. (2 mmoles) of ground recrystallized phenylhydrazine hydrochloride, 492 mg. (6 mmoles) of anhydrous sodium acetate, and 5 ml. of glacial acetic acid in a glass-stoppered weighing bottle.[5] After several hours, 2 ml. of glacial acetic acid was added with stirring. The product was removed by filtration after 20 hr.; washed with glacial acetic acid, ether, water, and ether; and air-dried. The yield was 289 mg. (60%). The dried, crude product contained no volatile acid. Recrystallization of 280 mg. of the crude sample from boiling absolute ethanol (7 mg. of sample per ml. of ethanol) gave 242 mg. (87% yield, two crops) of bright yellow, fine needles or filaments. The m.p. was 191–193° dec. (corrected) after two recrystallizations.

Anal. Calcd. for $C_{26}H_{30}N_4O_5$: C, 65.25; H, 6.39; N, 11.71. Found: C, 65.3; H, 6.35; N, 11.8.

D-Mannoheptulose 1-(N^1-Benzyl-N^1-phenyl)-2-(N^1-phenyl)osazone Acetic Acid Solvate.—Recrystallized I was dissolved in hot glacial acetic acid (8 mg. of I per ml. of acid), and the solution was allowed to cool slowly. The fine yellow needles that formed were removed by filtration and washed with cold glacial acetic acid without allowing them to become dry. A thin layer of wet crystals on platinum foil was exposed to air and their weight was recorded at timed intervals. When the weight loss per unit of time decreased

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[1] L. M. White and G. E. Secor, *Anal. Chem.*, **33**, 1287 (1961).

[2] L. Mester, *J. Am. Chem. Soc.*, **77**, 4301 (1955).

[3] G. Henseke and H.-J. Binte, *Chimia*, **12**, 103 (1958).

[4] G. Henseke and W. Liebenow, *Ber.*, **87**, 1068 (1954).

[5] The same mixed osazone was obtained when total hydrazine ranged from 3 moles to 9 moles per mole of sugar and with 1 or 2 moles of 1-benzyl-1-phenylhydrazine hydrochloride per mole of phenylhydrazine hydrochloride.