in acid solution in the form of a positive ion, III, similar to that found in the case of pyridine.

Experimental

The Sulfonation of Pyridine-N-oxide.—A mixture of 20 g. of fuming sulfuric acid (20%), 2 g. of pyridine-N-oxide[13] and 0.2 g. of mercuric sulfate was heated at 220–240° for 22 hours. The reaction mixture was poured into 20 ml. of water and neutralized with a hot saturated solution of barium hydroxide and finally with powdered barium carbonate. The mixture was cooled and filtered through Celite and the filtrate was treated with Norit and evaporated to a volume of 50 ml. The Norit was removed and the filtrate was evaporated to dryness leaving a solid residue. The residue was stirred with 10 ml. of ethanol, cooled overnight and filtered giving 3.5 g. of a white crystalline solid. The salt was dissolved in a minimum of water, the barium was precipitated with an equivalent amount of sulfuric acid and the mixture was filtered. Evaporation of the filtrate left 1.9 g. (51%) of solid which on recrystallization from methanol melted at 237–238°. The ammonium salt melted 261–263°.

Anal. Calcd. for $C_5H_5NO_4S$: C, 34.28; H, 2.88; equiv. wt., 175. Found: C, 34.35, 34.48; H, 2.90, 3.02; equiv. wt., 176.

A mixture of 12 g. of fuming sulfuric acid (20%) and 2 g. of pyridine-N-oxide was heated at 220–240° for 24 hours in the absence of mercuric sulfate. Upon working up the mixture as described above, an oil was obtained from the neutral solution which gave a picrate, m.p. 178–181°, which represented a 90% recovery of the pyridine-N-oxide.

A mixture of 40 g. of fuming sulfuric acid (20%), 10 g. of pyridine-N-oxide and 0.3 g. of mercuric sulfate was heated at 150–170° for 18 hours. After working up the mixture as described, an oil, 7.3 g., was obtained which gave the picrate of pyridine-N-oxide, m.p. 178–180°.

The Reduction of 3-Pyridine-N-oxidesulfonic Acid.—A solution of 3.5 g. of 3-pyridine-N-oxidesulfonic acid, prepared by the sulfonation of pyridine-N-oxide, in 200 ml. of 95% ethanol was treated with hydrogen at 60–70° in the presence of Raney nickel at three atmospheres pressure. The theoretical pressure drop was observed after one hour. The hot mixture was filtered and the filtrate was evaporated to dryness leaving 2.2 g. of pale green solid. The residue was dissolved in water and the solution was made basic with a saturated solution of barium hydroxide. The mixture was filtered and the barium was precipitated from the filtrate with an equivalent quantity of sulfuric acid. The mixture was filtered and the filtrate was evaporated to a volume of 5 ml. and cooled. The crystals which separated were removed, m.p. 338–339°; mixture melting point with a sample of 3-pyridinesulfonic acid, m.p. 330–334°, prepared by the sulfonation of pyridine[10] was 332–336°.

Anal. Calcd. for $C_5H_5NO_3S$: equiv. wt., 159. Found: equiv. wt., 160.

The ammonium salt was prepared from the reduction product, m.p. 217–233° dec. An authentic sample of ammonium 3-pyridinesulfonate melted at 217–233° dec. either alone or when mixed with the above sample.

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(13) H. S. Mosher, L. Turner and A. Carlsmith, *Org. Syntheses*, **33**, 79 (1953).

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2,2,2-Trifluoroethylnitroguanidine[1]

BY VIRGIL MILANI, SOL SKOLNIK AND ROBERT EVANS

RECEIVED DECEMBER 18, 1954

2,2,2-Trifluoroethylnitroguanidine has been obtained by the amination of N-nitro-S-methylpseudothiourea[2] with 2,2,2-trifluoroethylamine. This compound was used as an intermediate in the preparation of the picrate and nitrate salts of 2,2,2-trifluoroethylguanidine.

Experimental[3]

2,2,2-Trifluoroethylnitroguanidine.—To 10.1 g. (0.0747 mole) of N-nitro-S-methylpseudothiourea was added 15.0 g. (0.151 mole) of 2,2,2-trifluoroethylamine diluted with 1.0 g. of water. The mixture was heated at the reflux temperature for six hours, 2.2 g. (0.022 mole) of the amine added and then refluxed for an additional seven hours. The water and excess amine were removed under a vacuum and the residual crystalline material recrystallized from 90 ml. of hot water adjusted to a *p*H of 6 with sulfuric acid. The product was recovered in 94% yield based on the N-nitro-S-methylpseudothiourea and melted at 147–148°.

Anal. Calcd. for $C_3H_5O_2N_4F_3$: N, 30.1; F, 30.62; NO_2-N, 7.52. Found: N, 29.75; F, 30.51; NO_2-N, 7.45.

2,2,2-Trifluoroethylguanidine Picrate.—A mixture of 2.5 g. (0.0134 mole) of 2,2,2-trifluoroethylnitroguanidine, 0.125 g. of palladium black and 62 ml. of 15% acetic acid was placed in a modified Skita[4] hydrogenation apparatus and subjected to hydrogenolysis[5] overnight at slightly above atmospheric pressure and room temperature. The palladium black was removed and the filtrate treated with 3.07 g. (0.0134 mole) of picric acid in 25 ml. of hot absolute ethanol. The solution was allowed to crystallize overnight at room temperature. The yellow needle-like crystals began decomposing at 183° and were completely liquid at 193°.

Anal. Calcd. for $C_9H_9O_7N_6F_3$: N, 22.70; F, 15.40. Found: N, 22.7; F, 15.32.

2,2,2-Trifluoroethylguanidine Nitrate.—The picrate of 2,2,2-trifluoroethylguanidine (2.0 g., 0.0054 mole) was treated with 10 ml. of 20% nitric acid, the precipitated picric acid removed, and the filtrate extracted with ether until colorless. The remaining aqueous solution was evaporated to dryness, the residue dissolved in ethanol, and ether added until the crystalline precipitate of 2,2,2-trifluoroethylguanidine nitrate appeared. The nitrate salt melted at 134–136°.

Anal. Calcd. for $C_3H_7O_3N_4F_3$: N, 27.45; F, 27.94. Found: N, 27.40; F, 27.85.

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(1) Publication approved by the Bureau of Ordnance, Navy Department. The conclusions and opinions are those of the authors and are not to be construed as representing an official statement of the Navy Department.

(2) L. Fishbein and J. A. Gallaghan, THIS JOURNAL, **76**, 1877 (1954).

(3) All melting points were measured on a Kofler micro hot-stage.

(4) A. Skita and W. A. Meyer, *Ber.*, **45**, 3589 (1912).

(5) Procedure of Dr. J. A. Gallaghan of this Laboratory.

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Substituent Effects on the Reactions of Benzoate Ions with 2,4-Dinitrochlorobenzene and Methyl Iodide

BY LAWRENCE R. PARKS, GEORGE S. HAMMOND AND M. FREDERICK HAWTHORNE

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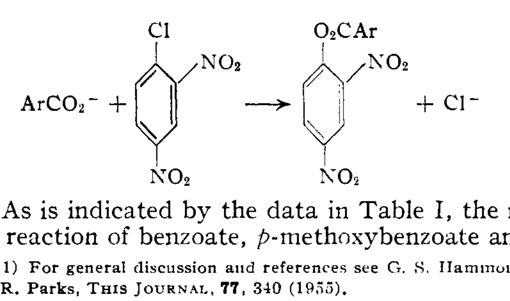
In a continuation of our studies designed to cast light upon the transition state configurations[1] involved in aromatic nucleophilic displacements we have investigated the effects of substituents on the nucleophilic reactivity of benzoate ions in reaction 1.



(1)

As is indicated by the data in Table I, the rates of reaction of benzoate, *p*-methoxybenzoate and *p*-

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(1) For general discussion and references see G. S. Hammond and L. R. Parks, THIS JOURNAL, **77**, 340 (1955).