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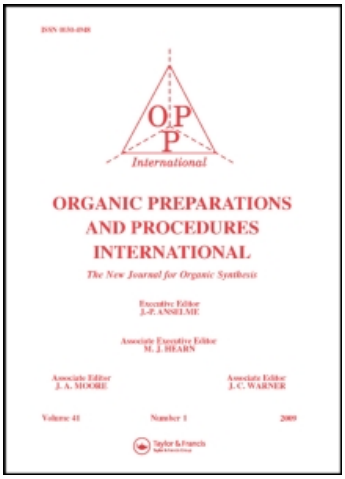

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AN EFFICIENT SYNTHESIS OF 5-SULFOSALICYLALDEHYDE SODIUM SALT

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2-Nonanone-2-^{13}C was similarly obtained in 42% yield, bp. 75-78°/20 mm.

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AN EFFICIENT SYNTHESIS OF 5-SULFOSALICYLALDEHYDE SODIUM SALT

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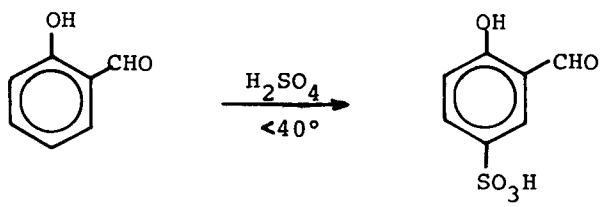
Because of several recent reports in which 5-sulfosalicylaldehyde is prepared either by protection of the aldehyde group prior to sulfonation[1-4] or by catalytic oxidation of 3-(hydroxymethyl)-4-hydroxybenzenesulfonic acid,[5] a more direct preparation seems worth reporting. Although it is well documented that aromatic aldehydes are easily oxidized to the corresponding carboxylic acids in sulfuric acid,[6,7] it has been recognized for a long time that the carbonyl group of benzaldehyde is stable in concentrated sulfuric acid at low temperatures.[8] Using this basic knowledge, we developed a direct synthesis of 5-sulfosalicylaldehyde by sulfonation of salicylaldehyde in sulfuric acid at 40°.



By proper control of the temperature during the reaction and by careful dilution of the sulfuric acid during the work-up, no oxidation occurs. On the other hand if the protecting group method is used, aniline must be ultimately removed by steam distillation which results in a more involved preparation and purification.[9]

The sodium 5-sulfosalicylaldehyde was characterized by its IR, ^{1}H NMR and ^{13}C NMR spectra. All of the carbon resonances of the ^{13}C spectrum agreed very well with calculated values based upon substituent effects for substituted benzenes.[11] The carbonyl carbon at 198.5 ppm agreed well with the reported value for the carbonyl carbon of salicylaldehyde at 196.7 ppm.[13]

EXPERIMENTAL

The proton magnetic resonance spectrum was obtained on a Varian HA-100 spectrometer in D_2O with Tiers' salt as the internal standard.[10] The ^{13}C NMR spectrum was recorded on a JEOL FX90Q instrument at 22.5 M Hz.

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Sodium salicylaldehyde-5-sulfonate.- Sulfuric acid (95%, 250 ml) was slowly added to a 500 ml round bottom flask containing salicylaldehyde (Aldrich 98%, 29 g). The temperature was kept at 40° or lower to prevent oxidation of the aldehyde. The reaction mixture was stirred for 18-24 hrs at 35° and then cooled in an ice bath prior to being poured very slowly over 500 g of distilled-water ice. The solution was diluted with water (500 ml), sodium carbonate (250 g) was added to neutralize the acid, and the volume was reduced by about one-half on a rotary evaporator at 40°. The gray precipitate of sodium salicylaldehyde-5-sulfonate one-sixth hydrate was recrystallized from hot water and dried at 100° in vacuo. The isolated yield of feathery white needles was 14.5 g (27%). The solid was found to be hygroscopic and was protected from moisture. A smaller scale experiment with 5 g of salicylaldehyde gave a yield of 45%, mp. > 304°; ν_{max}^{KBr} 3530, 3440, 2900, 1660, 1180, 1035; ^{1}H NMR (D_2O);[10] δ 9.98 (s, aldehydic), 8.12 (d, J =

2.3 Hz), 7.94 (q, J = 8.7, 2.3 Hz), 7.08 (d, 1.0 H, J = 8.7 Hz); ^{13}C NMR (D_2O):[12] δ 198.5, 163.2, 136.3, 135.4, 131.8, 121.3, 118.9.

Anal. Calcd for $C_7H_5O_5SNa \cdot \frac{1}{6} H_2O$: C, 37.01; H, 2.37.

Found: C, 37.00; H, 2.20.

The phenylhydrazone was prepared by addition of phenylhydrazine hydrochloride (1.0 g; 6.9 mmol) to an aqueous solution of 5-sulfosalicylaldehyde sodium salt (0.5 g; 2.2 mmol). The solution was warmed to 60-70° and stirred for ∿2 hrs. The golden-yellow precipitate was filtered and washed with ethanol and ether and was recrystallized from hot water in which it was only slightly soluble. The solid was dried in vacuo at 100°. The product was found to be the phenylhydrazinium salt of the phenylhydrazone derivative as described by Blau,[6] mp. 224-226.5°, lit.[6] 224-225°.

Anal. Calcd for $C_{19}H_{20}N_4O_4S$: C, 56.99; H, 5.03; N, 13.99.

Found: C, 56.70; H, 5.09; N, 14.00.

Acknowledgement.- This work was supported by the U.S. Department of Energy, contract No. W-7405-Eng-82, Division of Chemical Sciences, budget code AK-01-03-02-1. The assistance of W. J. McGranahan with ^{13}C nmr is gratefully acknowledged. I would also like to thank Dr. J. H. Espenson for helpful discussions.

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A CONVENIENT METHOD FOR THE PREPARATION OF 1-ACYL-2-PHENYLHYDRAZINES

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Substantial control over the extent of acylation of N,N-dimethylhydrazine with acid chlorides has been achieved by appropriate choice of solvent [E. A. Sedor, R. E. Fries and H. J. Richards, Org. Prep. Proced., 2, 275 (1970)]. The highly exothermic reaction of phenylhydrazine with acid chlorides in dry ether leads to formation of the insoluble 1-acyl-2-phenylhydrazine [R. F. Moore and S. G. P. Plant, J. Chem. Soc. (C), 3475 (1951)]. Although the mesomeric effect of the phenyl group in phenylhydrazine serves to reduce diacylation as a secondary reaction, milder reactions have been