Addition of Sulfur Trioxide–Pyridine to Aldehydes

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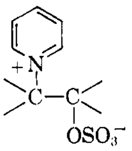
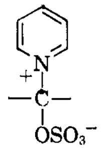
Sulfur trioxide–pyridine adds to the carbonyl group of aliphatic aldehydes to form 1-alkyl-1-(1-proto-1-pyridyl)-1-methanesulfate derivatives. Structural assignments were made by examination of the physical and chemical properties and the infrared spectra of the addition products. The direct addition of sulfur trioxide–pyridine to carbonyl groups appears to be a general reaction for substituted and unsubstituted aliphatic aldehydes.

Selected coordinate covalent complexes of sulfur trioxide such as sulfur trioxide–dioxane and bis(sulfur trioxide)–pyridine have been employed for the sulfonation of saturated aldehydes and ketones under mild conditions.[1–3] The reactions were carried out with a suspension of the complex in an ethylene chloride solution of the carbonyl compound at temperatures ranging from 0 to 40°. Sulfonation occurs on the carbon atom adjacent to the carbonyl group with the formation of the mono- or disulfonic acid derivative depending upon the ratio of reactants and the degree of substitution in the starting carbonyl compound. Sulfur trioxide–pyridine, however, was reported by Terent'ev and Yanovskaya to be unsatisfactory as a sulfonating agent for carbonyl compounds because practically no reaction was observed under the usual sulfonating conditions.[3] At temperatures in the 100 to 140° range, tar formation and polymerization of the carbonyl compound were observed. During the course of an investigation of the addition of sulfur trioxide–pyridine to epoxides,[4] consideration of the possible mechanisms of formation of the 2-(1-proto-1-pyridyl)-1-ethanesulfate adducts (A) led us to speculate that sulfur trioxide–pyridine should react with carbonyl compounds to form the corresponding 1-(1-proto-1-pyridyl)-1-methanesulfate adducts (B).[5,6] The reaction of carbonyl compounds with sulfur trioxide–pyridine was therefore re-examined, and the results of our study are reported in this paper.



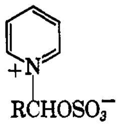
A



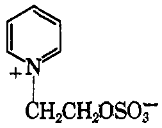
B

Several attempts were made to react acetone and benzaldehyde with equimolar quantities of sulfur trioxide–pyridine in ethylene chloride solvent under room temperature and reflux conditions. In these experiments, the unreacted complex was recovered in high yields, and unreacted carbonyl compound was found in the solvent. It is possible that small amounts of reaction product were produced under these conditions, but no clear evidence of reaction was observed.

The reaction of sulfur trioxide–pyridine with an aldehyde was first carried out successfully with formaldehyde in ethylene chloride solvent at 70 to 80°. The addition of the complex to the carbonyl group of the aldehyde took place smoothly without tar formation or polymerization to form the betaine salt,[7] 1-(1-proto-1-pyridyl)-1-methanesulfate (I), in high yield. The adduct was characterized by elemental analyses and qualitative tests. All of the experimental data supported the betaine salt structure. Because of its internal salt structure, a compound of structure I would be expected to have a high melting point, to be soluble in polar solvents and insoluble in nonpolar solvents, to be neutral in aqueous solution, and to produce sulfate anion only after hydrolysis of the C–O–SO_3^- group. The reaction product exhibited these properties. Also, a compound of structure I would be expected to liberate pyridine on treatment with warm alkali because structurally similar 2-(1-proto-1-pyridyl)-1-ethanesulfonates, which contain pyridine nuclei bonded to carbon through nitrogen, liberate pyridine under the same conditions.[8] If the reaction product were a simple pyridine salt, free pyridine should be liberated when aqueous solutions are made basic at room temperature. Free pyridine was not detected under these latter conditions, but was detected when the alkaline solution was warmed for a few minutes. The structure of the reaction product of sulfur trioxide–pyridine and formaldehyde was established by direct comparison with an authentic sample of I prepared from methylene sulfate dimer and pyridine.[9] Paraformaldehyde was also found to react with sulfur trioxide–pyridine to yield I.



I, R = hydrogen
II, R = methyl
IV, R = *n*-propyl
V, R = isopropyl
VI, R = *t*-butyl
VII, R = trichloromethyl



III

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[1] W. E. Truce and C. C. Alfieri, *J. Am. Chem. Soc.*, **72**, 2740 (1950).

[2] A. P. Terent'ev and L. A. Yanovskaya, *Dokl. Akad. Nauk SSSR*, **75**, 235 (1950).

[3] A. P. Terent'ev and L. A. Yanovskaya, *J. Gen. Chem. USSR*, **23**, 643 (1953).

[4] The betaine salt III was prepared by addition of sulfur trioxide–pyridine to ethylene oxide. The results of the investigation of the addition of sulfur trioxide–pyridine to epoxides will be published in a future paper.

[5] This nomenclature has been employed previously by Professor Bordwell and co-workers.[6] Footnote 7 of ref. 6 is reproduced: "This nomenclature has been suggested by Dr. F. Y. Wiselogle to fill the need for a suitable prefix to designate a substitutuent which bears a positive charge. 'Proto' signifies the addition of a proton; $C_5H_5NH^+$ is then protopyridine and $C_5H_5N^+$– is the 1-proto-1-pyridyl group. According to this nomenclature a dipolar ion, such as sulfanilic acid, can be given the systematic name, *p*-protoaminobenzenesulfonate, rather than *p*-aminobenzenesulfonic acid, which misrepresents the structure."

[6] F. G. Bordwell, M. L. Peterson, and C. S. Rondestvedt, Jr., *J. Am. Chem. Soc.*, **76**, 3945 (1954).

[7] Betaine salts are defined in this paper as internal salts containing the anion of a covalently bonded acid sulfate group and a quaternary fully alkylated nitrogen atom.

[8] F. G. Bordwell and M. L. Peterson, *J. Am. Chem. Soc.*, **76**, 3952 (1954).

[9] W. Baker and F. B. Field, *J. Chem. Soc.*, 86 (1932).

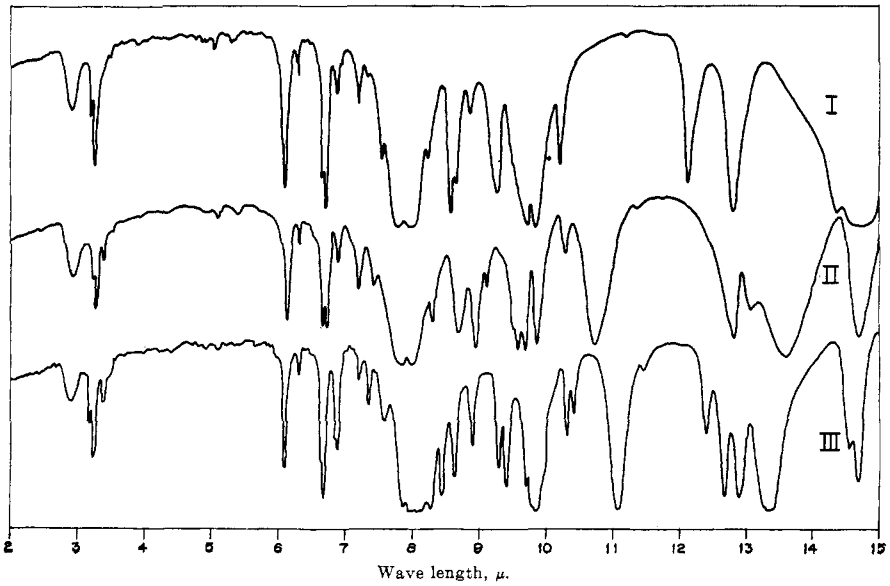

Fig. 1.—Infrared spectra of potassium bromide pellets of 1-(1-proto-1-pyridyl)-1-methanesulfate (I), 1-methyl-1-(1-proto-1-pyridyl)-1-methanesulfate (II), and 2-(1-proto-1-pyridyl)-1-ethanesulfate (III).

Successful preparation of I encouraged extension of the reaction to other aldehydes and aldehyde polymers. Acetaldehyde, *n*-butyraldehyde, isobutyraldehyde, pivaldehyde, and chloral each gave good yields of the corresponding 1-alkyl-1-(1-proto-1-pyridyl)-1-methanesulfate (II and IV through VII) on treatment with sulfur trioxide–pyridine at room temperature in ethylene chloride solvent. The reaction products exhibited the physical and chemical properties expected for the betaine salt structures. Under reflux conditions, paraldehyde gave a clean reaction product (II), but para-*n*-butyraldehyde formed an intractable mass. However, when this latter reactant was treated with sulfur trioxide–pyridine at room temperature, IV was formed in good yields. Since IV and V were found to be different, evidently no isomerization of the aldehyde occurred during the reaction. Further evidence in support of structure II was obtained when II was found to be different from the isomeric betaine salt (III), 2-(1-proto-1-pyridyl)-1-ethanesulfate.[4]

Infrared analyses supported the betaine salt structures. As expected, carbonyl group absorption was absent in the spectrum of each compound. Each betaine prepared in this investigation exhibited an intense absorption band in the 7.7–8.1-μ region which we attribute to the monocovalent sulfate group. The second sulfonyl vibration band was not assigned because of the complexity of the spectra. It would be expected that the characteristic absorption bands caused by sulfonyl vibrations at 8.27 to 8.70 μ and 9.43 to 9.71 μ in covalent sulfonate salts would be shifted to shorter wave lengths in the corresponding monocovalent sulfate salts.[10]

Other interesting characteristics of the infrared spectra of the betaine salts are illustrated in Fig. 1 which is a reproduction of the infrared curves for I, II, and III. All of the betaines prepared in this work exhibited two absorption bands that are apparently characteristic of the C=C and C=N vibrations of the N-alkylated pyridine ring. A sharp peak of strong intensity near 6.1 μ and a sharp peak of medium to weak intensity near 6.3 μ were observed for all betaine salts as illustrated by the infrared curves of I, II, and III. Similar bands are present in the double bond region of the infrared spectrum of pyridine, but these bands occur at slightly longer wave lengths. Their intensities are also reversed under the conditions used to record the spectra, and band separation is about one-third as large as that of the betaines. The CH deformation band at 13.4 μ[10] in the spectrum of pyridine also appears to be shifted to shorter wave lengths in spectra of the betaine salts. Each betaine exhibited a sharp peak of strong intensity at 12.75 to 12.95 μ. This band may correspond to the 13.4-μ CH deformation band in the spectrum of pyridine, although some of the betaine salts also exhibited a band between 13.3 and 13.6 μ as shown in the curves of II and III in Fig. 1. The 13.7–14.1-μ CH deformation band, which is considered to be characteristic of pyridine and its derivatives,[10] is shifted to 14.5 to 14.7 μ in the spectra of the betaine salts. It seems clear that the usual pyridine ring vibrations and hydrogen deformations are perturbed in the betaine salts. The quaternary nitrogen atom and possibly interaction between the negative sulfate group and the pyridine ring may cause these perturbations.

Although we were unable to convert acetone and benzaldehyde to the betaine salts, the direct addition of sulfur trioxide–pyridine to carbonyl groups appears to be a general reaction for substituted and unsubstituted aliphatic aldehydes and their corresponding linear and cyclic polymers. The polymers are probably depolymerized to the free aldehydes before reaction with sulfur trioxide–pyridine, but our investigation has not eliminated the possibility that the polymers react directly with the complex to form the betaine salts. Since there are a considerable number of sulfur trioxide–tertiary amine complexes that can be substituted for sulfur trioxide–pyridine in conventional sulfonation and sulfation reactions,[11] it is probable that many of these complexes will also add to the

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[10] *Cf.* L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

[11] E. E. Gilbert, *Chem. Rev.*, **62**, 549 (1962).

TABLE I

ADDITION PRODUCTS OF SULFUR TRIOXIDE–PYRIDINE AND ALDEHYDES

Adduct	Crude yield, wt. %	Recrystallization solvent	Melting point, °C.[a]	Empirical formula	Molecular weight, calcd.	Analyses[b]					
							% C	% H	% N	% S	% Cl
1-(1-Proto-1-pyridyl)-1-methanesulfate (I)[c]	98.4	Water	221–225	$C_6H_7O_4NS$	189.19	Calcd.	38.09	3.73	7.40	16.95	...
						Found	38.31	4.00	7.25	17.23	...
1-Methyl-1-(1-proto-1-pyridyl)-1-methanesulfate (II)[c]	79.8	Aq. Formula 30 alcohol	148–150	$C_7H_9O_4NS$	203.22	Calcd.	41.37	4.46	6.89	15.78	...
						Found	41.49	4.33	6.90	15.90	...
1-*n*-Propyl-1-(1-proto-1-pyridyl)-1-methanesulfate (IV)[c]	58.9	Water	134–136	$C_9H_{13}O_4NS$	231.27	Calcd.	46.74	5.66	6.06	13.86	...
						Found	46.65	5.95	6.16	14.02	...
1-Isopropyl-1-(1-proto-1-pyridyl)-1-methanesulfate (V)	58.0	Water	139–140	$C_9H_{13}O_4NS$	231.27	Calcd.	46.74	5.66	6.06	13.86	...
						Found	47.02	5.78	6.28	14.01	...
1-*t*-Butyl-1-(1-proto-1-pyridyl)-1-methanesulfate (VI)	75.9	Methanol	152–154	$C_{10}H_{15}O_4NS$	245.29	Calcd.	48.96	6.16	5.71	13.07	...
						Found	49.11	6.15	5.57	13.11	...
1-Trichloromethyl-1-(1-proto-1-pyridyl)-1-methanesulfate (VII)	50.7	Water	165–166	$C_7H_6O_4NSCl_3$	306.56	Calcd.	27.42	1.97	4.57	10.46	34.70
						Found	27.45	2.05	4.59	10.55	34.79

[a] Melting points were measured in open capillary tubes and are reported without stem corrections. All products listed in Table I melt with decomposition. [b] Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill., and the Analytical Research and Services Division of The Pure Oil Co., Crystal Lake, Ill. [c] Experimental data shown for these derivatives were obtained from syntheses in which aldehyde polymers were used.

carbonyl groups of aldehydes to afford the corresponding betaine salts. A more detailed study would be required to answer these questions. The betaine salts prepared in this investigation are listed in Table I along with pertinent experimental data.

As indicated in the introductory paragraph of this paper, sulfur trioxide–pyridine has been reported to be unsatisfactory as a sulfonating agent for aldehydes and ketones because of tar formation and polymerization.[3] The conversion of *n*-butyraldehyde to the betaine salt under room temperature conditions and the formation of an intractable mass under reflux conditions suggested that the betaine salt might be thermally decomposed to yield polymers or perhaps sulfonic acid derivatives. This was found to be the case when 1-*n*-propyl-1-(1-proto-1-pyridyl)-1-methanesulfate (IV) was decomposed in a sealed tube at 125 to 135° in ethyléne chloride solvent. The barium salt of *n*-butyraldehyde-1-sulfonic acid monohydrate was isolated in 45.0% yield and identified by direct comparison with an authentic sample prepared from *n*-butyraldehyde and sulfur trioxide–dioxane. No attempts were made to improve the yield or to isolate other reaction products. Our data show that sulfur trioxide–pyridine can be employed as a sulfonating agent, at least for *n*-butyraldehyde, if the betaine is formed before subjecting the reaction mixture to elevated temperatures. The theoretical implications of this conversion have not been developed; the betaine salt may be an intermediate in the sulfonation of aldehydes with sulfur trioxide–pyridine, or some unknown reaction may occur at a greater rate than sulfonation or betaine formation when an aldehyde is treated with sulfur trioxide–pyridine at elevated temperatures.

Experimental

Unless noted otherwise, all products were prepared from reagent grade chemicals of Distillation Products Industries, Eastman Organic Chemicals. The melting point data and elemental analyses of the betaines are shown in Table I. The instrument used for measurement of the infrared spectra was a Perkin-Elmer Model No. 21 recording spectrophotometer. The spectra of potassium bromide pellets or Nujol mulls of each compound were measured in the usual manner. The spectrum of pyridine was measured in a potassium bromide cell. Aqueous solutions of each salt prepared in this investigation were tested for sulfate anion by treatment with a few drops of dilute aqueous barium chloride solution. Hydrolysis of the salts was effected by boiling an aqueous solution with either an equal volume of concentrated hydrochloric acid or 20 wt. % sodium hydroxide solution for 10 min.

Sulfur Trioxide–Pyridine.—Liquid sulfur trioxide,[12] 80.1 g. (1.00 mole), was added to a solution of 79.1 g. (1.00 mole) of pyridine in 250 ml. of ethylene chloride. The reaction mixture was maintained between 0 and 10° by cooling with an ice bath and vigorous stirring. After the addition of sulfur trioxide was completed, the white, amorphous complex was separated by filtration, washed with fresh ethylene chloride, and dried in an evacuated desiccator; yield, 143.7 g. (90.3%). The complex was stored in a desiccator and used as needed.

Attempts to Add Sulfur Trioxide–Pyridine to Acetone.—Several experiments were carried out with equimolar quantities of sulfur trioxide–pyridine and acetone in ethylene chloride solvent at room temperature (43 and 67 hr.) with agitation, and under reflux conditions at 80 to 85° (3 hr.) with agitation. Concentration and filtration of the reaction mixture gave unreacted complex in 80 to 90% yields. The complex was identified by infrared analysis. The filtrate contained 85 to 100% of the charged acetone by quantitative infrared analysis.

Attempts to Add Sulfur Trioxide–Pyridine to Benzaldehyde.—Several experiments were carried out with equimolar quantities of sulfur trioxide–pyridine and benzaldehyde in ethylene chloride solvent at room temperature (22, 47, and 66 hr.), and under reflux conditions (2 and 3 hr.). Vigorous stirring was provided for each experiment. Unreacted complex was recovered in 75 to 85% yields by concentration and filtration of the reaction mixture. The complex was identified by infrared analysis. Quantitative infrared analysis indicated that 75 to 90% of the charged benzaldehyde remained in the filtrate.

In one experiment, which was carried out for 3 hr. under reflux conditions, an amorphous, insoluble product was first separated from the ethylene chloride solution before the solution was concentrated. Concentration of the filtrate afforded additional material as fluffy, white crystals. This product appeared to be something other than the complex due to its crystalline structure, but infrared comparison of Nujol mulls of both the amorphous and crystalline products and authentic sulfur trioxide–pyridine showed that the products and the complex were identical. Ethylene chlo-

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[12] Sulfan purchased from General Chemical Division, Allied Chemical Corp., New York, N. Y.

ride may therefore be useful as a recrystallization solvent for sulfur trioxide–pyridine.[13] In this particular experiment, the total recovery of complex was 80.5%.

1-(1-Proto-1-pyridyl)-1-methanesulfate.—A slurry of 3.0 g. (0.1 mole formaldehyde equivalent) of paraformaldehyde and 15.9 g. (0.1 mole) of sulfur trioxide–pyridine in 100 ml. of ethylene chloride was refluxed for 3 hr. No visible change occurred in the reaction mixture during the reflux period. After cooling the slurry to room temperature, the insoluble product was filtered, washed with ether, and dried; crude yield, 18.6 g. (98.4%); m.p. 175–200° dec. with gas evolution. Recrystallization from water gave the pure betaine salt as white needles, m.p. 221–225° dec. with gas evolution. The salt was soluble in water, methanol, and ethanol, and insoluble in benzene and petroleum ether. Aqueous solutions of the product were neutral, gave negative tests for sulfate anion unless hydrolyzed with hydrochloric acid, and liberated pyridine on treatment with sodium hydroxide. The product was identified as the betaine salt by mixture melting point determination with an authentic sample of 1-(1-proto-1-pyridyl)-1-methanesulfate prepared by the method of Baker and Field,[9] and by direct comparison of the infrared spectra.

The betaine salt was also prepared from free formaldehyde by the following procedure. Gaseous formaldehyde, 1.2 g. (0.04 mole), from the thermal decomposition of paraformaldehyde, was dissolved in 25 ml. of ethylene chloride at −20° to give a clear solution containing little or no paraformaldehyde.[14] The solution was treated with 5.8 g. (0.036 mole) of sulfur trioxide–pyridine, and the tube containing the reaction mixture was sealed, warmed to 80° in an oil bath, kept at this temperature for 3 hr., and then cooled to room temperature. The sealed tube was opened, and the insoluble product was filtered, washed with ether, and dried; crude yield, 5.5 g. (79.9%). One recrystallization from water gave pure 1-(1-proto-1-pyridyl)-1-methanesulfate.

1-Methyl-1-(1-proto-1-pyridyl)-1-methanesulfate.—The salt was prepared from a slurry of 4.4 g. (0.1 mole acetaldehyde equivalent) of paraldehyde and 15.9 g. (0.1 mole) of sulfur trioxide–pyridine in 100 ml. of ethylene chloride by the procedure used with paraformaldehyde except that the reaction mixture was refluxed for 1 hr. Recrystallization of the crude product, which was isolated in 79.8% yield, from aqueous Formula 30 alcohol[15] gave the betaine salt as white crystals, m.p. 148–150° dec. with gas evolution. The pure salt was soluble in water and methanol, and insoluble in acetone and benzene. Aqueous solutions of the salt exhibited the same properties as aqueous solutions of the formaldehyde adduct.

A second experiment carried out at room temperature for 8 hr. with 0.1 mole of acetaldehyde and 0.1 mole of sulfur trioxide–pyridine in 100 ml. of ethylene chloride gave 18.0 g. (88.7%) of crude product. Recrystallization from aqueous Formula 30 alcohol afforded the pure betaine salt.

1-*n*-Propyl-1-(1-proto-1-pyridyl)-1-methanesulfate.—The salt was prepared from 7.2 g. (0.1 mole *n*-butyraldehyde equivalent) of para-*n*-butyraldehyde and 15.9 g. (0.1 mole) of sulfur trioxide–pyridine in 100 ml. of ethylene chloride by the procedure used with paraformaldehyde except that the reaction mixture was kept at room temperature for 24 hr. with occasional agitation. The supernatant liquid changed from light yellow to brown during this time. The crude product was isolated in 58.9% yield by filtration from the reaction mixture. Recrystallization from water gave the pure betaine salt as white platelets, m.p. 134–136° dec. with gas evolution. Aqueous solutions of the salt exhibited the same properties as aqueous solutions of the formaldehyde adduct. The salt was soluble in water and ethanol, and insoluble in acetone and ether.

A second experiment carried out at room temperature for 22 hr. with 0.1 mole of *n*-butyraldehyde and 0.1 mole of sulfur trioxide–pyridine in 150 ml. of ethylene chloride afforded the betaine salt in 61.9% crude yield. During the 22-hr. period, the color of the reaction mixture progressively changed from white to amber to dark brown. No evolution of heat was detected. Recrystallization of the crude product from water gave the betaine salt.

1-Isopropyl-1-(1-proto-1-pyridyl)-1-methanesulfate.—The crude isobutyraldehyde adduct was prepared in 58.0% yield by the procedure used with *n*-butyraldehyde. The change in color of the reaction mixture was not so pronounced as with the *n*-butyraldehyde preparation; the reaction mixture was yellow prior to work-up. Three recrystallizations from water afforded the pure salt as small, fluffy, white crystals, m.p. 139–140° dec. with gas evolution. The pure salt was soluble in water, methanol and ethanol, and insoluble in ether, benzene, and petroleum ether.

1-*t*-Butyl-1-(1-proto-1-pyridyl)-1-methanesulfate.—The crude pivaldehyde[16] adduct was prepared in 75.9% yield by the procedure used with *n*-butyraldehyde. Two recrystallizations from methanol gave the pure betaine salt as white plates, m.p. 152–154° dec. with gas evolution.

1-Trichloromethyl-1-(1-proto-1-pyridyl)-1-methanesulfate.—The crude chloral adduct was prepared in 50.7% yield by the procedure used with *n*-butyraldehyde. Two recrystallizations from water gave the pure betaine salt as white needles, m.p. 165–166° dec. with gas evolution.

Thermal Decomposition of 1-*n*-Propyl-1-(1-proto-1-pyridyl)-1-methanesulfate.—A slurry of 15.2 g. (0.066 mole) of 1-*n*-propyl-1-(1-proto-1-pyridyl)-1-methanesulfate in 80 ml. of ethylene chloride was warmed in a sealed tube at 125–135° for 55 min. with occasional agitation. The resulting brown solution was cooled to room temperature and extracted twice with water. The aqueous extract was treated with excess powdered barium carbonate, filtered to remove unreacted carbonate, and evaporated to yield a yellow oil which crystallized on addition of anhydrous ethanol. Recrystallization from aqueous Formula 30 alcohol afforded 6.8 g. (45.0%) of the monohydrate of the barium salt of *n*-butyraldehyde-2-sulfonic acid as amorphous, white crystals.

Anal. Calcd. for $C_8H_{14}O_8S_2Ba \cdot H_2O$ (457.70): C, 20.99; H, 3.52. Found: C, 21.24; H, 3.41.

The salt was hygroscopic. Aqueous solutions of the salt gave negative tests for sulfate anion even after prolonged warming with hydrochloric acid. The infrared spectrum of a Nujol mull of the salt showed carbonyl group and sulfonate group absorption. The salt was identified by direct comparison of the infrared spectrum with the spectrum of an authentic sample.

Barium Salt of *n*-Butyraldehyde-2-Sulfonic Acid.—The salt was prepared by a modification of the method of Terent'ev and Yanovskaya.[3] A slurry of sulfur trioxide–dioxane, which was prepared from 40.0 g. (0.5 mole) of sulfur trioxide and 72.5 g. (0.82 mole) of dioxane in 150 ml. of ethylene chloride, was treated with a solution of 36.1 g. (0.5 mole) of *n*-butyraldehyde in 150 ml. of ethylene chloride over a 1.5-hr. period. The reaction mixture was maintained at 0° by stirring and cooling during the addition. After the addition of aldehyde was completed, the brown reaction mixture was stored at −18° for 64 hr. and then filtered to remove a small amount of insoluble precipitate. The filtrate was then neutralized with an aqueous suspension of powdered barium carbonate. Filtration of this mixture to remove unreacted barium carbonate and evaporation of the filtrate gave a yellow oil. The oil was crystallized by addition of anhydrous ethanol to yield 39.1 g. (34.2%) of the sulfonate salt. Recrystallization from aqueous ethanol afforded the pure salt as the monohydrate.

Anal. Calcd. for $C_8H_{14}O_8S_2Ba \cdot H_2O$ (457.70): C, 20.99; H, 3.52. Found: C, 21.41; H, 3.37.

Terent'ev and Yanovskaya reported that most of the barium sulfonate derivatives of aldehydes including the *n*-butyraldehyde derivative crystallize with one molecule of water of hydration, and that this water is difficult to remove.[3] Various attempts were made in our work to prepare the anhydrous salt by drying the monohydrate at elevated temperatures and reduced pressure. We were unable to remove the water of hydration by this technique.

Acknowledgment.—The author is indebted to Mr. J. A. Fyfe who carried out the experiments with sulfur trioxide–pyridine, and to Mr. L. J. Miller who performed the thermal decomposition of the *n*-butyraldehyde adduct.

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[13] No attempts were made to examine the utility of this technique for the purification of sulfur trioxide–pyridine. However, it may be quite useful since no method for purification of the complex has been suggested previously.[11]

[14] We have determined that the solubility of solid paraformaldehyde is of the order of 0.1 g./100 ml. of ethylene chloride at room temperature.

(15) Formula 30 alcohol is 90.8 wt. % ethanol and 9.2 wt. % methanol.

(16) Pivaldehyde purchased from Gallard-Schlesinger Chemical Manufacturing Corp., New York, N. Y.