Identification of Organic Compounds. VI.[1] The Preparation of p-Nitrobenzylpyridinium Salts of Aromatic Sulfonic Acids

BY ERNEST H. HUNTRESS AND GORDON L. FOOTE[2]

This paper reports the first fruits of studies on the utility of various pyridinium sulfonates as a means of identification of sulfonic acids. The work here described is limited to a study of certain p-nitrobenzylpyridinium sulfonates. These previously unreported compounds are readily crystallizable solids with sharp and characteristic melting points. They are formed by the interaction of the respective silver sulfonates with p-nitrobenzyl chloride in pyridine, viz.

$$RSO_2OAg + ClCH_2 - \hspace{-2mm}\langle\rangle\hspace{-2mm} - NO_2 + C_5H_5N \longrightarrow$$

$$RSO_2O - \overset{\frown}{N} - CH_2 - \hspace{-2mm}\langle\rangle\hspace{-2mm} - NO_2 + AgCl$$
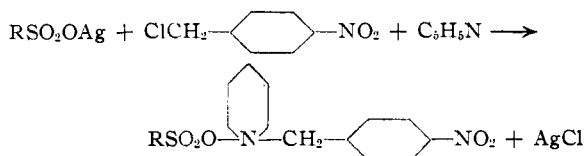
This reaction has been found to be general not only for ordinary aromatic mono- and di-sulfonic acids, but also for those containing other functional groups such as —OH, or —NH₂. There is reason to believe that the reaction is general for any sulfonic acid for which a silver salt may be prepared and work upon its extension is actively in progress.

Characterization of carboxylic acids (or their

salts) by preparation of their p-nitrobenzyl esters is a well-recognized procedure in organic qualitative analysis. Superficially there would appear to be no reason why an analogous reaction should not occur between p-nitrobenzyl chloride and the salts of sulfonic acids leading to p-nitrobenzyl sulfonates. That this analogous reaction does not in fact occur, however, has long been recognized.[3] These authors report that neither in aqueous nor in alcoholic solution did either the sodium or silver salts of sulfonic acids form any appreciable quantity of sulfonic esters. Even heating the reactants to fusion in sealed tubes was without effect. The present work has confirmed and extended these observations since not even in 66% butyl-"carbitol" or in pure diethylene glycol was any reaction observable after three-hour refluxing of p-nitrobenzyl bromide or phenacyl bromide with sodium p-toluenesulfonate.

When the silver salt of a sulfonic acid and p-nitrobenzyl chloride are refluxed in dry pyridine, however, reaction readily occurs. The expected p-nitrobenzyl sulfonate is formed and may readily be isolated in the form of its addition product with the solvent, i. e., as the corresponding p-nitrobenzylpyridinium sulfonate. The formation of these esters is doubtless facilitated not only by their immediate stabilization as quaternary salts, but also by the fact that the by-product

(1) For previous papers in this series, see Huntress and Carten, THIS JOURNAL, **62**, 511, 603 (1940); Seikel, ibid., **62**, 750 (1940); Seikel and Huntress, ibid., **63**, 593 (1941); Huntress and Autenrieth, ibid., **63**, 3446 (1941).

(2) This paper is constructed from part of a dissertation submitted in October, 1940, by Gordon L. Foote to the Faculty of the Massachusetts Institute of Technology in partial fulfilment of the requirements for the Degree of Doctor of Philosophy. It was presented at the Memphis Meeting of the American Chemical Society, April, 1942.

(3) (a) Lyons and Reid, THIS JOURNAL, **39**, 1742 (1917); (b) Rather and Reid, ibid., **41**, 82 (1919).

TABLE I

p-NITROBENZYLPYRIDINIUM SALTS OF CERTAIN AROMATIC
SULFONIC ACIDS

Sulfonic acid	Procedure	AgCl,[a] %	Formula[b]	M. p., °C., uncor.
Benzene-	A	84	$C_{18}H_{16}O_5N_2S$	168°
Toluene-o-	A	82	$C_{19}H_{18}O_5N_2S$	170°
o-Xylene-4-	A	85	$C_{20}H_{20}O_5N_2S$	158.5
p-Xylene-	A	86	$C_{20}H_{20}O_5N_2S$	139.5
Naphthalene-2-	B	..	$C_{22}H_{18}O_5N_2S$	148.5
Anthraquinone-2-	A	67	$C_{26}H_{18}O_7N_2S$	187
Phenol-4-	A	69	$C_{18}H_{16}O_6N_2S$	162
Aniline-4-	C	..	$C_{18}H_{17}O_5N_3S$	211
Acetanilide-4-	B	81	$C_{20}H_{19}O_6N_3S$	79.5
2-Aminotoluene-5-	A, C	83	$C_{19}H_{19}O_5N_3S$	200
Benzene-1,3-di-	C	79	$C_{30}H_{36}O_{10}N_4S_2$	204

[a] This figure is based on the p-nitrobenzyl chloride and represents the fraction of total chloride precipitated as AgCl from the hot pyridine solution.   [b] All products were subjected to combustion analyses for nitrogen and those from benzene-, toluene-o-, and acetanilide-4-sulfonic acid to Carius analyses for sulfur as well. The results of all these determinations were in satisfactory accord with the theory, but in the interest of saving space in THIS JOURNAL are not reproduced here.   [c] Mixed m. p. of the derivatives from benzenesulfonic acid and toluene-o-sulfonic acid was depressed to 150–158° uncor.

readily separated and purified. Those of the simple sulfonic acids or even of the acetylamino-sulfonic acids are white, but the p-nitrobenzyl esters of all the amino sulfonic acids reported here are colored yellow or orange-red.

The characteristics of these p-nitrobenzylpyridinium salts of eleven simple sulfonic acids are summarized in Table I. The methods of procedure developed for these were then applied to the case of naphthionic, Laurent and Peri acids, and Tobias and Broenner acids, together with their N-monoacetyl derivatives (except for Tobias acid) and the characteristics of these products are summarized in Table II.

Although the reaction is not involved in the use of this method for the identification of sulfonic acids (or their salts), the behavior of the p-nitrobenzylpyridinium sulfonates with aqueous alkali early attracted our attention because of the fact that all of the complexes immediately yielded the same insoluble product irrespective of the particular sulfonic acid residue which was present. This product proved to be 4,4′-azoxybenzaldehyde ac-

TABLE II

p-NITROBENZYLPYRIDINIUM SALTS OF SULFONIC ACIDS OF AMINO OR ACETYLAMINONAPHTHALENES

Sulfonic acid	Procedure	AgCl,[a] %	Formula[b]	M. p., °C., uncor.
2-Aminonaphthalene-1- (Tobias acid)	A	..	$C_{22}H_{19}O_5N_3S$	142[c]
1-Aminonaphthalene-4- (Naphthionic acid)	A	86	$C_{22}H_{19}O_5N_3S$	176
1-Aminonaphthalene-5- (Laurent acid)	A	78	$C_{22}H_{19}O_5N_3S$	169[d]
2-Aminonaphthalene-6- (Broenner acid)	C	..	$C_{22}N_{19}O_5N_3S$	218[e,f] dec.
1-Aminonaphthalene-8- (Peri acid)	A	..	$C_{22}H_{19}O_5N_3S$	138[c]
1-Acetylaminonaphthalene-4-	B	85	$C_{24}H_{21}O_6N_3S$	193
1-Acetylaminonaphthalene-5-	B	55	$C_{24}H_{21}O_6N_3S$	159.5
2-Acetylaminonaphthalene-6-	A, B	..	$C_{24}H_{21}O_6N_3S$	172[g]
1-Acetylaminonaphthalene-8-	B	84	$C_{24}H_{21}O_6N_3S\cdot H_2O$	85[h]

[a] Same as for Table I.   [b] All of these products were subjected to combustion analysis for nitrogen and all but those from naphthionic acid and acetylated Broenner acid for carbon and hydrogen as well. To save the space of THIS JOURNAL they are not reproduced here.   [c] Mixed m. p. of pyridinium salt from Tobias acid and Peri acid was depressed to below 128°.   [d] This product was recrystallized twice from pyridine and then from absolute alcohol. It must be carefully dried at 110° or a low m. p. is obtained due to solvent of crystallization.   [e] Recrystallization from water gives yellow hydrated form losing water at 110° to yield orange anhydrous variety.   [f] Due to its insolubility in water, this particular complex can be obtained (82% yield) from the action of sodium 2-aminonaphthalene-6-sulfonate on p-nitrobenzylpyridinium chloride in water solution.   [g] From anhydrous solvents this product separates as an amorphous gummy powder becoming crystalline on the addition of a few drops of water. After drying at 110° the glassy solid was powdered. The hydrated form melts about 115°, varying somewhat according to rate of heating.   [h] This product was recrystallized from 95% ethanol. The compound could not be obtained in anhydrous form, nor could the monohydrate be obtained from anhydrous solvents. A sharp melting point is difficult to obtain, some samples beginning to melt at 82°.

silver chloride is less soluble in hot pyridine than it is in cold.[4] The p-nitrobenzylpyridinium sulfonates are usually soluble in the hot pyridine although in a few cases they separate together with the silver chloride. In any case they are

companied by p-nitrobenzaldehyde. Pyridine and the sodium salt of the sulfonic acid remained in the aqueous alkaline solution.

The formation of these unexpected products doubtless involves the intermediate formation by the mineral alkali of the corresponding p-nitrobenzylpyridinium hydroxide. This is supported

(4) For data see Kahlenberg and Wittich, J. Phys. Chem., 13, 421 (1909).

by the fact that for each molecule of quaternary salt one molecule of alkali is consumed, by the formation of the same 4,4′-azoxybenzaldehyde and *p*-nitrobenzaldehyde from so many different salts, and finally by the formation of these same products when a solution of *p*-nitrobenzylpyridinium hydroxide was similarly treated. Tentatively it may be represented as
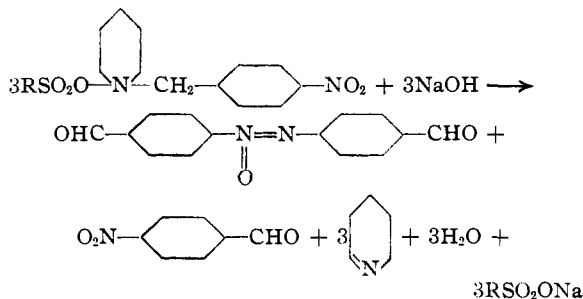
The formation of 4,4′-azoxybenzaldehyde has never, hitherto, been reported as a product of this kind of reaction. It has formerly been obtained mainly by methods based on the reduction[5] of *p*-nitrobenzaldehyde or oxidation of hydroxylaminobenzaldehyde. The probable intermediate *p*-nitrobenzylpyridinium hydroxide[6] has not itself been characterized. Only three remarks regarding the reactions of its salts with alkali could be found in the literature. Treatment of *p*-nitrobenzylpyridinium bromide with alkaline hypobromite is recorded[7] as giving 82% yield of *p*-nitrobenzoic acid; *p*-nitrobenzylpyridinium perchlorate when boiled with sodium hydroxide is stated[8] to yield *p*-nitrotoluene; while the reported[9] reaction of *p*-nitrobenzylpyridinium *bromide* with aqueous alkali and amines makes no mention of any such product.

No attempt to determine the fate of the pyridine during this reaction has been made in this work. The decomposition of many pyridinium salts to yield the enol of glutacondialdehyde or its subsequent condensation products is well known, but no evidence of its formation was observed in this work.

Experimental Work

The melting points reported in this paper are uncorrected unless otherwise stated. They were determined in a copper block of the Berl and Kullmann type, observation of

(5) (a) Beilstein, Vol. XVI, pp. 641–642; (b) Cumming, Duncan, Anderson and Ashcroft, *J. Roy. Tech. Coll.* (Glasgow), **2**, 596–600 (1932); *C. A.*, **26**, 3493 (1932).

(6) Beilstein, Vol. XX, p. 218.

(7) Fisher, THIS JOURNAL, **56**, 2056–2057 (1934).

(8) Pollard and Robinson, *J. Chem. Soc.*, 2779 (1927).

(9) Kröhnke, *Ber.*, **71**, 2588 (1938).

the sample being facilitated by a small 25 power microscope permanently attached to the apparatus.

The pyridine used in this work was of best quality, subsequently dried over potassium hydroxide and fractionated in a fifteen-plate column. The fraction used had a boiling range of 114.9–115.3°.

The various sulfonic acids were Eastman Kodak Co. (Pure Grade) for those of Table I and Eastman (Technical Grade) for those in Table II. Their identity was further established by conversion to other known derivatives and by analysis of the silver salts.

Preparation of the Silver Salts of the Sulfonic Acids.—For sulfonic acids whose silver salts are insoluble in water, their preparation was effected merely by mixing aqueous solutions of equivalent amounts of silver nitrate and of the sulfonic acid (or its alkali salt). For cases where the silver sulfonates proved too soluble in water to precipitate by the above method, the sodium sulfonate was suspended in absolute alcohol and dry hydrogen chloride passed in to substantial saturation. The precipitated sodium chloride was filtered and the alcohol evaporated. The resultant free sulfonic acid was then neutralized with freshly precipitated silver oxide, the excess silver oxide filtered off, and the resultant aqueous solution of silver sulfonate evaporated under reduced pressure.

The silver salts used in this work were analyzed by ignition to metallic silver and all showed a purity of 95% or better.

General Procedures for the Preparation of the *p*-Nitrobenzylpyridinium Sulfonates.—According to the solubility of the resultant complex in hot pyridine three modifications of a single procedure were employed. Procedure A was used for complexes of intermediate solubility, *i. e.*, soluble in hot pyridine and insoluble in cold pyridine. Procedure B was adopted for complexes soluble not only in hot, but even in cold pyridine. Procedure C was used for complexes sparingly soluble even in hot pyridine.

Procedure A.—*p*-Nitrobenzyl chloride (0.01 mole) together with the silver sulfonate (0.01 mole + 3–5% excess) was dissolved in dry pyridine (10–20 ml.) and heated at 100° for one hour. The hot solution was then filtered with suction and allowed to cool for gradual crystallization of the complex. The more soluble members of this group were recrystallized from a mixture of absolute alcohol and ether, the less soluble from alcohol or pyridine.

Procedure B.—The reaction was carried out as in Procedure A and filtered hot. Since on cooling the filtrate failed to deposit crystals, three or four volumes of dry ether was added rapidly with stirring. This action precipitated the desired complex together with a small proportion of silver chloride. Since the latter is insoluble in alcohol, the complex is readily purified by recrystallization from a mixture of absolute alcohol and dry ether.

Procedure C.—The reaction was carried out as in Procedure A, but a bulky precipitate of complex is evident in the hot pyridine. The solution was then cooled (to increase the solubility of silver chloride while decreasing that of the complex) and filtered. The precipitate was then recrystallized from 95% alcohol or dilute alcohol.

Action of Dilute Alkali on *p*-Nitrobenzylpyridinium Complexes.—Any *p*-nitrobenzylpyridinium sulfonate (0.001 mole) together with sodium hydroxide (0.001 mole)

in water (50–100 moles) was heated just to boiling. Within a few seconds the clear solution changed to orange or red in color and a flocculent orange-yellow precipitate of 4,4'-azoxybenzaldehyde separated. This was filtered, dried and several times recrystallized from a mixture of chloroform and carbon tetrachloride. The product melted at 190.5° uncor. (recorded[5] 194.0–195.5° cor.) and did not depress the melting point of an authentic sample prepared according to Alway.[10] From the aqueous filtrate after removal of the above precipitate steam distillation yielded p-nitrobenzaldehyde, m. p. 103.5–104.5° uncor. (recorded[11] 106°) which did not depress the melting point of an authentic sample and which gave a phenylhydrazone of m. p. 157.5–158.5° cor.(recorded[12] 159° cor.).

Amount of Alkali Used.—p-Nitrobenzylpyridinium p-toluenesulfonate (3.031 g. = 0.00785 mole) dissolved in water (100 ml.) was treated with an excess of 1.005 N sodium hydroxide (10.85 ml.) and the solution boiled until precipitation was complete. The filtrate from the precipitated solid then required for neutralization of the alkali 2.6 ml. of 0.995 N sulfuric acid. The amount of sodium hydroxide which disappeared during the reaction was therefore 0.00831 mole. The ratio of alkali which disappeared to the original pyridinium salt was therefore 1.06. The slight error is doubtless due to the use of solutions of high normality and probable occlusion of alkali on the precipitate.

Decomposition of p-Nitrobenzylpyridinium Hydroxide. —p-Nitrobenzyl chloride (10 g.) was dissolved in pyridine (40 ml.), heated to boiling, and the bulky precipitate of p-nitrobenzylpyridinium chloride filtered hot. After cooling the solution the additional precipitate was filtered, combined with the first and dried: yield 14 g., representing 97% theoretical.

This p-nitrobenzylpyridinium chloride was dissolved in cold water (1500 ml.), filtered from a trace of unchanged p-nitrobenzyl chloride and treated with excess moist pure freshly prepared silver oxide. After stirring for half an hour, the silver chloride and excess silver oxide were filtered off, the strongly basic filtrate diluted to 3000 ml. and heated to boiling. A flocculent orange-yellow precipitate formed and a strong odor of pyridine was noted. After boiling the suspension for thirty minutes, the precipitate was filtered with suction and recrystallized from chloroform carbon tetrachloride mixture. The yield of 4,4'-azoxybenzaldehyde was 2.5 g. (53% theoretical) and it melted 190.2–190.5° uncor.

(10) Alway, Am. Chem. J., **28**, 40–44 (1902).

(11) Beilstein, Vol. VII, p. 256.

(12) Beilstein, Vol. XV, p. 137.

This compound was very soluble in chloroform, soluble in acetone, acetic acid, or benzene, but only slightly soluble in absolute alcohol or carbon tetrachloride.

Although a dialdehyde, it gave no test with Schiff fuchsine aldehyde reagent, did not reduce Tollens solution and failed to respond as a ketone to the generic test with phenylhydrazine reagent. Furthermore, due to its characteristic violent deflagration, no concordant combustion analyses could be obtained.

However, the material was characterized as 4,4'-azoxybenzaldehyde by the following observations. Its molecular weight, as measured by the boiling point elevation of chloroform solutions, was found 267 and 273, by the Rast method in camphor 257, 267, 273 (calcd. 254). When heated in a dry test-tube to just above its melting point, it spontaneously decomposed with flame formation. This behavior is recorded[13] as characteristic. On grinding with phosphorus pentachloride it reacted violently, with evolution of heat, yielding a red liquid which presently solidified and from which on recrystallization from ligroin were obtained orange crystals of bis-(ω,ω-tetrachloro-)-4,4'-azoxytoluene, m. p. 114.5–115.5° uncor. (recorded[10] m. p. 115–116°). On solution in fuming nitric acid, heating to boiling and pouring into water, the compounds gave a flocculent yellow precipitate which on recrystallization from 60% acetic acid gave pale yellow hair-like needles of a mononitro derivative, m. p. 173–174° uncor. (recorded[10] m. p. 171–172°).

On steam distillation of the aqueous solution from the precipitated 4,4'-azoxybenzaldehyde above, p-nitrobenzaldehyde distilled over. After recrystallization from 50% acetic acid this melted at 103.5–104.5 uncor. (recorded[11] 106°) and did not depress the melting point of an authentic sample.

Summary

1. The preparation and utility of p-nitrobenzylpyridinium sulfonates in the identification of sulfonic acids (or their salts) has been demonstrated.

2. These quaternary ammonium salts on treatment with hot aqueous alkali have been shown to yield 4,4'-azoxybenzaldehyde and p-nitrobenzaldehyde.

(13) Alway, Ber., **26**, 2306 (1903).