[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF INDIANA UNIVERSITY AND THE UNIVERSITY OF OREGON]

REACTIONS OF HALOGENS WITH ARYLSULFONATES.* II. IODINATION *VIA* IODINE AND SILVER 2-NAPHTHALENESULFONATE [1, 2]

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Only a few instances of the treatment of silver arylsulfonates with halogen have been reported. Thus Suter (1) mentions four cases in which silver benzenesulfonates were treated with aqueous bromine to give bromination of the ring, but without replacement of the sulfonate group. Also Birckenbach and Meisenheimer (2) found that iodination of the solvent occurred when silver *p*-toluenesulfonate was treated with iodine in refluxing benzene. This latter reaction, moreover, resulted in the evolution of a gas which produced a precipitate with barium hydroxide. From these results and from analogy with the extensively investigated reactions between halogens and silver salts of carboxylic acids (2–5) one might expect (using an equimolar ratio of halogen and silver salt) either to obtain an intermediate of the type $ArSO_3X$ which ought to be a more potent halogenating agent than the corresponding $ArCO_2X$, due to the much larger electron-attracting tendency of the sulfonate group over the carboxylate group, or to obtain replacement of the sulfonate group by some unknown mechanism, such as loss of sulfur dioxide or sulfur trioxide. This paper is a report of our first investigations on the reaction between silver arylsulfonates and halogens in an effort to determine the course of the reaction.

In general, equimolar quantities of iodine and silver 2-naphthalenesulfonate were heated in an anhydrous solvent (benzene, toluene, carbon tetrachloride, nitrobenzene, or ethyl benzoate) at a temperature in the range of 75–150° for a period of 1 to 186 hours, during which time an exothermic (at least in many cases) reaction occurred accompanied by the formation of a precipitate and the partial or total disappearance of the iodine color of the solution. Examination of the products formed (Table I) showed that silver ion was quantitatively precipitated as silver iodide while organic acids and iodinated neutral compounds also resulted. Titration showed the formation of essentially one hydrion per silver ion used in the solvents benzene, toluene, and carbo tetracloridhe but of excessive hydrion (up to 1.3 equivalents) in ethyl benzoate and of limited hydrion (0.6–0.8 equivalent) in nitrobenzene. The acidic product was identified as 2-naphthalenesulfonic acid (isolated as the S-benzylisothiuronium derivative) in the cases of benzene and toluene only. For the other slovents the same mono-

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[1] Abstracted in part from a thesis submitted by Paul F. Silva to the Graduate School of Indiana University in partial fulfillment of the requirements for the degree, Doctor of Philosophy, November, 1952.

[2] For paper I in this series see Klemm and Rawlins, *J. Org. Chem.*, **17,** 613 (1952).

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TABLE I

DATA FOR THE INTERACTION OF IODINE AND SILVER 2-NAPHTHALENESULFONATE IN SELECTED SOLVENTS

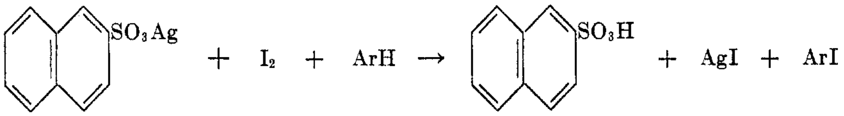
RUN[a] NO.	SOLVENT		REACTION TIME (hrs.)	TEMP., °C.	YIELD OF AgI, %[b]	YIELD OF HYDRION, %[c]	TOTAL RECOVERED IODINE, %	ORGANIC PRODUCTS[d]
	Formula	Ml.						
1–3	ϕH	100	40	Reflux	98	97	0.9	ϕI, $C_{10}H_7SO_3H$
4, 5[e]	ϕCH_3	150	184	Reflux	98	96	2.6	$CH_3C_6H_4I$, $C_{10}H_7SO_3H$, neut. cmpds.[h]
6[f]	ϕCH_3	50	1	Reflux	—	—	0[g]	
7, 8	ϕCH_3	50	1	Reflux	97	—	0[g]	
9	ϕCO_2Et	50	10	115–150	100	—	—[i]	Neut. cmpd.[k]
10[j]	ϕCO_2Et	50	20	96–105	—	—	—[i]	
11	ϕCO_2Et	50	48	100	99	107[l]	4.9	$C_{10}H_6ISO_3H$, ϕCO_2H, neut. cmpd.[n]
12[j]	ϕCO_2Et	75	2	90–110	99	123[l]	4.3	
13[m]	ϕCO_2Et	75	2	90–102	—	—	—[i]	
14	ϕNO_2	150	20	110–122[o]	97	86[p, q]	—[i]	$C_{10}H_6ISO_3H$, neut. cmpd.[n]
15[j]	ϕNO_2	75	10.5	99–113	98	60[q]	6.5	
16	CCl_4	130	66	Reflux	98	91	7.6[r]	$C_{10}H_6ISO_3H$, $C_{10}H_7SO_3I$(?), iodinated solvent[s]
17	CCl_4	50	66	Reflux	103	94	4.8[r]	

[a] Runs listed together were made under identical conditions and the results listed represent composite data. Unless otherwise indicated 15.0 g. (47.7 millimoles) of silver 2-naphthalenesulfonate and 12.1 g. (47.7 millimoles) of Merck's resublimed iodine were used in each run. Numbering of the runs is chronological only as it applies to any one particular solvent. [b] Based on the transformation $C_{10}H_7SO_3Ag \rightarrow AgI$. [c] Based on the transformation $C_{10}H_7SO_3Ag \rightarrow C_{10}H_7SO_3H$. [d] For each solvent identification of neutral compounds was accomplished on mixtures of products from two or more runs. Except for the case of ethyl benzoate the sulfonic acid produced was identified in only one typical run for each solvent. [e] In a third run, started in the same manner, the solvent was inadvertently boiled away to leave a black mass which smelled strongly of sulfur dioxide. Similar results were obtained in an exploratory run without solvent conducted on an intimate mixture of the dry reactants in a sealed tube at 110°. [f] Using only 6.0 g. (23.8 millimoles) of iodine. [g] Iodine color absent at end of reaction. [h] A test for benzyl iodide with hot alcoholic silver nitrate was negative. The presence of iodocompounds other than iodotoluene was assumed on the basis of the high refractive index found for fractions of the liquid neutral product. [i] Iodine color still present at end of reaction. [j] Using 30.0 g. (95.4 millimoles) of silver 2-naphthalenesulfonate and 24.2 g. (95.4 millimoles) of iodine. [k] Non-hydrolyzable iodine-bearing solid isolated in small yield. No effort was made to identify acidic products in these runs. [l] Part of this acidity arose from benzoic acid as a product. The total yield of hydrion was distributed as follows for runs 11 and 12, respectively: combined aqueous washings, 50%, 90%; alkaline washings of ester layer, 57%, 33%. [m] Using 45.0 g. (143 millimoles) of silver 2-naphthalenesulfonate and 36.3 g. (143 millimoles) of iodine. [n] Iodine-bearing solid residue from steam-distillation of solvent; maximum yield, 0.8 g. (crude) per 15 g. of silver salt used. [o] A preliminary run which involved refluxing in nitrobenzene for 45 hours gave only tarry carbonaceous material. [p] Includes titrated recovered iodine for which no correction was made. [q] The low yield may be ascribed to inefficient extraction of the sulfonic acid by water from the organic layer in which the acid has considerable solubility. [r] This value would have included the titration of iodine derived from any $C_{10}H_7SO_3I$ present. [s] As evidenced by photochemical formation of iodine from the colorless recovered solvent.

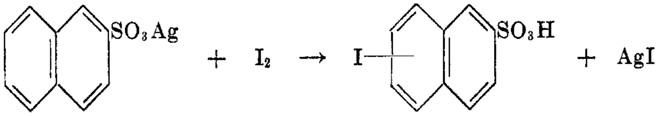
iodonaphthalenesulfonic acid (isolated also as the S-benzylisothiuronium salt) was found instead. In addition ethyl benzoate yielded benzoic acid in appreciable quantity, a fact which doubtlessly accounts for the excess hydrion titrated in this case. The mechanism of formation of the benzoic acid is not immediately apparent. Test runs indicated it was unlikely that such an amount of benzoic acid could have arisen either from hydrolysis of ethyl benzoate during the process of working up the reaction mixture or from the interchange $ArSO_3H + \phi CO_2Et \rightarrow ArSO_3Et + \phi CO_2H$ and subsequent hydrolysis of the sulfonate ester. The low yield of acid from the nitrobenzene may be ascribed to inefficient removal of sulfonic acid by aqueous extraction of the organic layer.

A 42% yield of iodobenzene (identified by conversion to *p*-nitroiodobenzene) resulted from benzene, while a mixture of neutral iodinated products (which did not include benzyl iodide but did include *p*-iodotoluene) was produced from toluene. Careful search for possible nuclearly iodinated products of nitrobenzene or ethyl benzoate was fruitless. Both of these solvents, however, did produce small amounts of the same non-steam-distillable neutral by-product, probably a triiodonaphthalene from desulfonation. Consistent with the formation of this by-product was the evolution of sulfur dioxide, readily detected by odor, from the reactions in these two solvents. Carbon tetrachloride gave traces of other iodinated products, probably derived from the solvent.

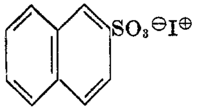
Iodine was recovered from most of the reactions. That this iodine was really the result of secondary decomposition rather than the result of incomplete reaction was indicated in the case of toluene. Thus in run 7 all the iodine had disappeared after only one hour of heating while in run 5, where the only major variation was a long period of refluxing, iodine was recovered in considerable quantity. Moreover, in general, the yields of silver iodide and hydrion were independent of the yield of iodine recovered.



(Equation A)



(Equation B)



I

On the bases of these results one can classify the main stoichiometric reactions between silver 2-naphthalenesulfonate and iodine into two different categories dependent on the particular solvent used. Thus for benzene and toluene iodination of the solvent proceeds according to Equation A, while for the other cases the solvent is chemically inert and instead iodination of the naphthalenesulfonate occurs (Equation B). These results seem indicative of the intermediate formation of an $I^{\oplus}$ entity for which we propose the structure I. Further evidence that such an intermediate was actually present in the reaction was obtained in the case of carbon tetrachloride from which precipitated a gelatinous product, soluble in water to give a solution which showed positive tests for hydrion and iodide. Since this precipitate was too unstable for complete identification, the indirect procedure of attempting to isolate a pyridine-stabilized salt of I, as used with notable success for the analogous iodine (I) carboxylates (6) was pursued. A pale yellow crystalline material, of composition corresponding to dipyridine iodine (I) 2-naphthalenesulfonate, was obtained. This product exhibited (a) the expected instability toward moisture, strong light, heat and solvents, (b) enhanced electrolytic conductance (over that of the solvent) in pyridine and (c) an absorption spectrum in pyridine which varied markedly with aging of the solution (Fig. 1). The spectrum for our complex was somewhat different from that reported by Kleinberg, VanderWerf, *et al.* (7) as characteristic of $I^{\oplus}$ compounds. The relatively intense absorption of the 2-naphthalenesulfonate ion (as evidenced by its silver salt) obscured details in the region below 320 mμ. Variation in the region 340–440 mμ was so rapid in a fresh solution that consistent results were obtainable only after aging the solution for 10 minutes, whereupon a well-defined maximum had already developed at 390–400 mμ. This maximum broadened somewhat and the intensity of absorption increased with time, but no maximum appeared at the previously reported 375 mμ region. The reason for this latter discrepancy between the spectra is not clear though it may be due to a bathochromic shift accompanying a more extensive acid-base interaction (8) between iodine in some form and the naphthalene nucleus than for iodine in the same form and the benzene nucleus (present in the compounds of the previous workers). It is worthy of note that the 2-naphthalenesulfonate ion, in common with nitrate and perchlorate (9), other anions of strong acids, forms a dipyridine iodine (I) salt, whereas only one mole of base has been found in any of the corresponding carboxylate salts (6, 10).

In accordance with the general properties of positive halogens one might expect I to exhibit some free radical reaction of the iodine atom. Only limited evidence for such behavior was found. Thus in both the regular runs with carbon tetrachloride and in the petroleum ether washings of the dipyridine iodine (I) salt, the solvent was found to contain organically bound iodine, for exposure of the colorless bisulfite-washed solvent to sunlight or concentrated sulfuric acid caused the reappearance of a limited amount of iodine in the solvent. Such replacement by iodine of chlorine or hydrogen in these solvents, respectively, would seem almost certainly to involve atomic iodine. That the extent of substitution of iodine for chlorine in carbon tetrachloride was very small, indeed, was shown by failure to detect either appreciable free chlorine or chlorinated products from the reac-

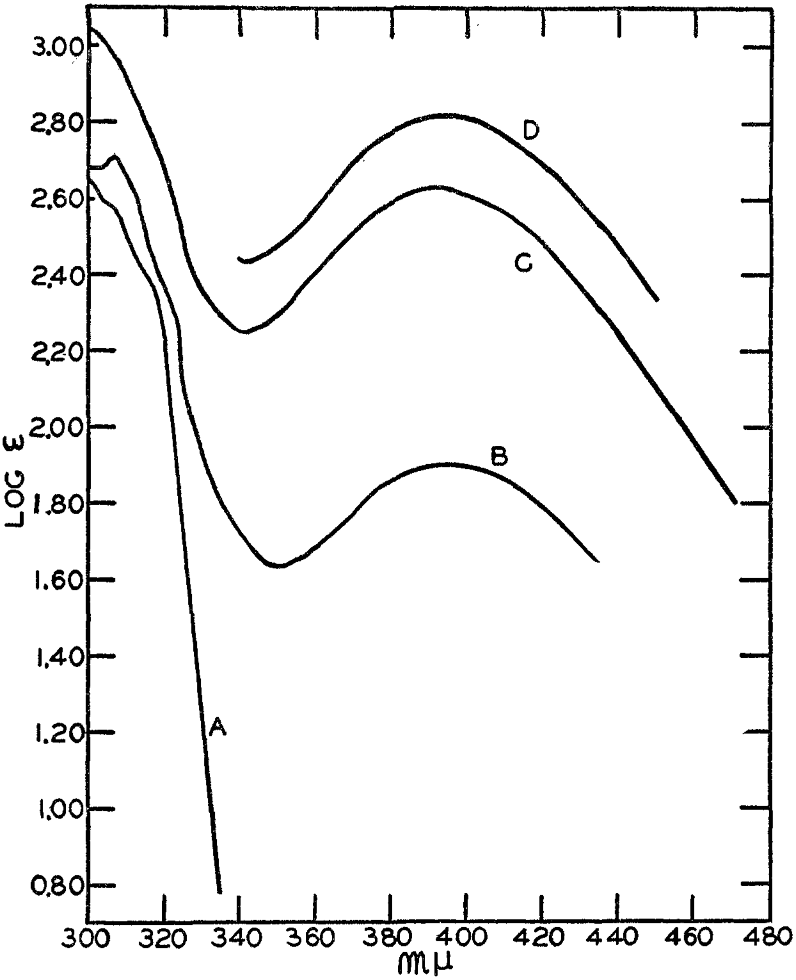


FIG. 1. ABSORPTION SPECTRA IN PYRIDINE. Curve A: For silver 2-naphthalenesulfonate; concs. 1 × 10^{-3} *M* (300–305 mμ), 3.9 × 10^{-3} *M* (305–335 mμ). Curve B: For dipyridine iodine (I) 2-naphthalenesulfonate, solution aged 0–20 min.; concs. 8.61 × 10^{-4} *M*. (300–315 mμ), 1.03 × 10^{-3} *M* (316–330 mμ), 1.29 × 10^{-3} *M* (340–435 mμ). Curve C: Same as B, aged 2 hrs.; conc. 5.04 × 10^{-4} *M*. Curve D: Same as B, aged 7.3 hrs.; conc. 9.34 × 10^{-4} *M*.

tion. The failure to isolate either benzyl iodide from the toluene runs or nuclearly iodinated solvent from the nitrobenzene or ethyl benzoate runs must be considered inconclusive inasmuch as intermediately formed benzyl iodide, especially if present in small amount, might have reacted further and Haszeldine and Sharpe (5) have argued that atomic iodine is not known to attack the aromatic nucleus.

As based on the very limited information which is now available on the reactions of silver arylsulfonates with halogens it appears that desulfonation of the intermediate $ArSO_3X$ is much less facile than is decarboxylation of the analogous intermediate RCO_2X (where R = aryl or alkyl).

TABLE II

X-RAY DATA FOR SILVER 2-NAPHTHALENESULFONATE

INTERPLANAR SPACING, Å	RELATIVE INTENSITY[a]	INTERPLANAR SPACING, Å	RELATIVE INTENSITY[a]
9.11	1.0	3.19	0.1
6.04	0.9	3.08	.3
5.05	.4	2.85	.2
4.27	.5	2.78	.1
3.94	.2	2.59	.1
3.74	.7	2.54	.1
3.33	.5	2.43	.1

[a] Estimated visually.

EXPERIMENTAL[5]

Silver 2-naphthalenesulfonate. A filtered (Celite) solution of 230 g. (*ca.* 1 mole) of technical grade β-naphthalenesulfonic acid monohydrate in 170 ml. of water was stirred and refluxed with 0.5 mole of freshly prepared silver carbonate in a cloth-covered flask for 3 hours until a grayish precipitate remained and the solution tested only faintly acidic to Congo Red paper. The solid product from evaporation and filtration of the solution was recrystallized from water (Norit) as lustrous white plates, dried for 36 hours at 60–75°, and stored in brown bottles; yield, 260 g. (82%); analyzed according to the procedure of Wegscheider and Lux (11).

Anal. Calc'd for $C_{10}H_7AgO_3S$: Ag, 34.24. Found: Ag, 34.29, 34.28, 34.31.

X-ray diffraction data for the salt (taken by means of a North American Philips machine with a camera diameter of 106.74 mm. and light of wavelength 1.539 Å) are given in Table II. The ultraviolet absorption spectrum of the salt in pyridine is shown in Figure 1.

Dipyridine iodine(I) 2-naphthalenesulfonate. About 5 g. of silver 2-naphthalenesulfonate was accurately weighed into a 125-ml. glass-stoppered Erlenmeyer flask, dried at 110° for one hour, and allowed to cool to room temperature with protection from atmospheric moisture. At night under only the regular electric lighting of the room, 25 ml. of anhydrous chloroform followed by two or three crystals of freshly sublimed iodine was added to the flask. After the contents were shaken, 3 ml. of freshly purified pyridine was added. Thereafter a total amount of iodine just 50–100 mg. short of the theoretical quantity was added in small portions with sufficient shaking to cause each portion to dissolve. The mixture was filtered under anhydrous conditions and the filtrate was transferred to a dry-box (containing phosphorus pentoxide) and treated with 100 ml. of purified (free of unsaturation) petroleum ether (b.p. 27–37°). The yellow oil which immediately precipitated solidified upon swirling the flask for a short time. The supernatant liquid was decanted, 50 ml. of fresh petroleum ether was added, and the precipitate was crushed with a stirring rod. Washings (by decantation) with the same solvent were continued until the supernatant liquid remained colorless or only faintly pink. The pale yellow prisms were dried for 5–10 minutes (in air of the dry-box) and placed over Drierite in a cloth-wrapped vacuum desiccator, evacuated to 5 mm. pressure. The next day dry air was let into the wrapped desiccator which was kept in the dry-box for storage, yield 56–72%.

The product turned reddish brown at 115° and melted at 130–134° (sealed tube). It was soluble in chloroform, ether, carbon tetrachloride, and absolute or 95% alcohol to form solu-

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[5] Melting points are uncorrected. Except as otherwise noted all analyses were performeP by one of us (P. F. S.). Absorption spectra were obtained with a Beckman Model DU spectrophotometer. All reagents used were especially purified according to conventional methods.

tions which showed decomposition upon being heated. It was extremely sensitive to traces of moisture and decomposed in cold water. It was rather readily decomposed by sunlight in the presence of a solvent but could be handled dry in diffuse daylight. In pyridine it formed an almost colorless solution (which turned yellow in a short time) which showed enhanced electrical conductivity over that of the solvent itself. Absorption spectra of variously aged pyridine solutions of the product are given in Figure 1.

Anal. Calc'd for $C_{10}H_7IO_3S{\cdot}2C_5H_5N$: C, 48.85; H, 3.48; I, 25.8; N, 5.69; S, 6.51.
Found: C, 48.71;[6] H, 3.70;[6] I, 27.2, 28.8;[7] N, 5.44;[6] S, 6.52, 6.77.[7]

Reactions of silver 2-naphthalenesulfonate with iodine in various solvents. Data on the reactions between silver 2-naphthalenesulfonate and iodine in various solvents are given in Table I. The reagents were heated (sometimes with stirring) in a flask (wrapped with a cloth to exclude light) to which a reflux condenser, usually attached to a mercury trap, was fitted. In run 6 (excess silver salt used) careful observation of the reaction showed that the iodine color was first dissipated, a bright yellow precipitate appeared shortly thereafter, and, with continued refluxing, this precipitate gradually changed to the final greenish-yellow or gray found in all runs. In run 13 a complete log of the temperature of the stirred mixture (heated by means of a glass mantle maintained at constant voltage input) showed that a maximum temperature was attained about 10–15 minutes after the first appearance of the precipitate and a constant temperature was reached in another 10–15 minutes. In various other runs it was likewise apparent that the over-all reaction was exothermic. In general, upon termination of the heating period, the reaction mixture was allowed to cool to room temperature and the precipitate present was collected in a sintered glass funnel, washed with fresh solvent (runs 1–8, 16, 17), or with ether (runs 9–15) and then with hot and cold distilled water. The precipitate was dried at 110° and weighed. Washing and drying were repeated to constant weight.

An x-ray diffraction pattern of the precipitate from one run indicated the product was silver iodide containing only a trace of impurity, probably silver oxide. In another run the purity of the silver iodide was checked by fusion of a sample with sodium carbonate and reprecipitation of iodide with silver nitrate; recovery, 99.9%.

Investigations on the aqueous and organic solutions are detailed in succeeding paragraphs.

A. Benzene runs. The benzene filtrates were combined and washed with 50 ml. of hot water (added to the combined aqueous washings of the precipitate). In one run residual iodine in the benzene layer was determined by titration with standard thiosulfate solution. In other runs the benzene layer was washed (aqueous sodium bisulfite), dried, and fractionated to yield *iodobenzene* (42%), b.p. 85–86° (20 mm.), n_D^{18} 1.6200 [reported (13a) $n_D^{17.8}$ 1.6213], identified by nitration (14a) to *p*-iodonitrobenzene, m.p. 171–172°, undepressed on admixture with an authentic sample thereof prepared from known iodobenzene by the same procedure.

In one run the brown combined aqueous washings were tested for unreacted silver ion or suspended silver compounds by conversion to silver chloride; yield of precipitate 0.03 g. In other runs the combined aqueous washings were diluted to a measured volume and an aliquot portion was titrated for acidity using phenolphthalein and standard sodium hydroxide. Remaining aqueous solutions were evaporated to dryness at room temperature under reduced pressure and the residue was converted to the S-benzylisothiuronium salt (15) which was crystallized from 50% alcohol to a constant melting point, 184–184.5°. It was identified as probably *S-benzylisothiuronium 2-naphthalenesulfonate* by virtue of its mixture melting point, 186.5–188°, with an authentic sample thereof, m.p. 188.5–189°.

B. Toluene runs. In general the toluene filtrates were treated by the same procedures as for the benzene runs. In run 8 the toluene solution was diluted with one-half its volume of chloroform, cooled in ice, and saturated with chlorine. The yellow needles which pre-

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[6] Analyzed by Micro-Tech Laboratories, Skokie, Illinois.

[7] Analyzed by the Parr bomb method of Shriner (12).

cipitated were collected, washed with ice-cold chloroform, and pyrolyzed at 150°. An ethereal solution of the resultant liquid was washed (aqueous sodium bisulfite), dried (magnesium sulfate), and distilled *in vacuo*. The b.p. of the product was determined to be 207° (uncorr.) by the microprocedure of Shriner and Fuson (14b) [reported (13b) b.p. of iodotoluenes 211–213°]. In other runs the toluene solution was dried and fractionated as for the benzene runs, 24–52% yield of product, b.p. 63–74° (16–20 mm.), n_D^{20} 1.5959–1.6250 for various fractions; n_D^{21} found for Eastman Kodak White Label iodotoluenes: *o*, 1.6095 [reported (13a) n_D^{20} 1.6085]; *m*, 1.6050; *p*, 1.603.[8] Carbonation of the Grignard reagent prepared from a sample of the distillate gave *p-toluic acid*, m.p. 176–177°, undepressed on admixture with an authentic sample thereof.

From the aqueous washings there was obtained the *S-benzylisothiuronium salt*, m.p. 189–189.8° after two crystallizations from 50% alcohol; m.m.p. with authentic S-benzylisothiuronium 2-naphthalenesulfonate 188–189°.

C. Ethyl benzoate runs. The ester layer was washed with hot water, and ethereal washings (where present) of the precipitate were washed with cold water. All aqueous washings were combined and aliquot portions were titrated for hydrion and iodine as previously. The main portion of the aqueous washings was treated with a slight excess of 10% aqueous sodium hydroxide, cooled in an ice bath, and filtered with suction to collect the precipitated sodium salt. Additional batches of the salt were obtained upon concentrating the mother liquors. A sample of this salt, when treated with S-benzylisothiourea hydrochloride as previously, deposited *S-benzylisothiuronium iodonaphthalenesulfonate*, as small white plates, m.p. 168.5–170° after four crystallizations from 50% ethanol. The crystals gave a positive Beilstein test for halogen.

Anal. Calc'd for $C_{10}H_7IO_3S \cdot C_8H_{10}N_2S$: I, 25.4. Found: I, 26.4.

Aliquot portions of the washed ethyl benzoate and ethereal solutions were titrated for iodine. In run 11 the remaining ester was shaken with excess 0.2 *N* (*ca.* 0.8%) sodium hydroxide and an aliquot portion of the separated aqueous layer was back titrated with standard hydrochloric acid to give total hydrion plus iodine. Acidification of another portion of the alkaline extract caused deposition of a white precipitate, purified by washing with water and recrystallization from 30% alcohol, m.p. 121–122.5°, undepressed on admixture with an authentic sample of benzoic acid. A test extraction of the mother liquors with carbon tetrachloride confirmed that iodine had been extracted by the alkali. A test on fresh ethyl benzoate showed only a negligible extraction of acid (*via* saponification) under the conditions used in the experiment. Another test reaction was conducted by heating 75 ml. of ethyl benzoate with 8 g. (50 millimoles) of anhydrous benzenesulfonic acid at 110° for 2 hours. The mixture was extracted first with water and then with 2% aqueous sodium hydroxide. Acidification of the alkaline extract caused precipitation of only a minute amount of benzoic acid.

The residue from evaporation of the ethereal solutions was combined with the preceding alkaline-washed ethyl benzoate layer and the whole was washed successively with aqueous sodium bisulfite and water and then steam-distilled. The distillate (negative Beilstein test) was discarded. The oily solid residue was separated from water, triturated with ether, dried, and recrystallized from absolute ethanol to constant m.p., 157–158° (as clusters of fine colorless needles, presumably *triiodonaphthalene*). The product was soluble in benzene, somewhat soluble in ether, and insoluble in aqueous sodium carbonate. It was unchanged on heating with concentrated hydrochloric acid for 36 hours on a steam-bath. It gave a positive Beilstein test, negative tests for sulfur (both after sodium fusion and Parr bomb decomposition), and a negative Ferrox test (14c) for oxygen. The ultraviolet absorption spectrum of the compound is shown in Figure 2.

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[8] Obtained by extrapolation to N = 1 of the experimentally observed straight line plot of n_D *versus* N, the mole fraction of *p*-iodotoluene, for solutions of *p*-iodotoluene in *o*-iodotoluene as solvent.

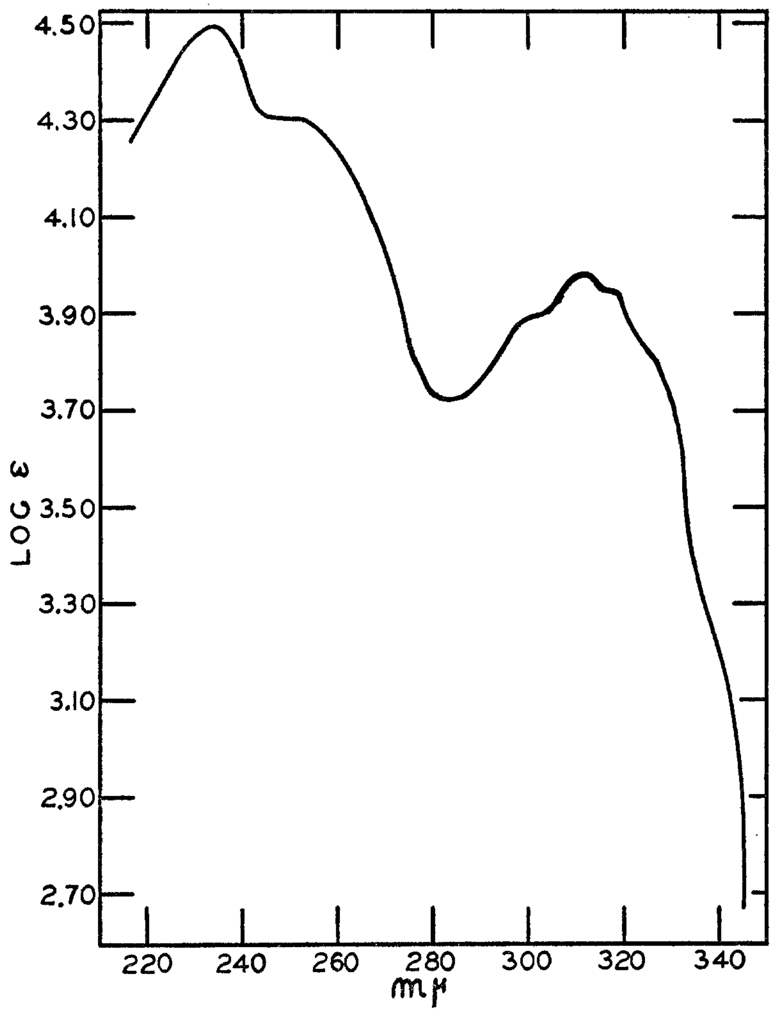

FIG. 2. ULTRAVIOLET ABSORPTION SPECTRUM OF PRESUMED TRIIODONAPHTHALENE. Solvent 95% ethanol; concs. 1.02×10^{-2} g./l. (217–275 mμ), 5.08×10^{-2} g./l. (275–350 mμ). Assumed mol. wt. 506.

Anal. Calc'd for $C_{10}H_5I_3$: C, 23.74; H, 1.00; I, 75.3; Mol. wt., 506.

Found: C, 23.73;[6] H, 1.40;[6] I, 70.9, 74.9, 73.7;[7] Mol. wt. (Rast), 473, 478.[9]

D. Nitrobenzene runs. In run 15 the nitrobenzene solution was shaken with boiling water. Total combined water washings were extracted repeatedly with carbon tetrachloride until the final extract was essentially colorless. Aliquot portions of the combined carbon tetrachloride solutions, the dried (calcium chloride) nitrobenzene solution, and ether wash solutions were titrated for iodine separately. The extracted aqueous solution (still very darkly colored) was boiled with Norit and Celite, filtered, and titrated for total acidity by means of 0.4 *N* sodium hydroxide and a Sargent oscillometer. Excess sodium hydroxide was then added and the sodium salt was collected and converted to the S-benzylisothiuronium

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[9] Determined by Clark Microanalytical Laboratory, Urbana, Illinois.

derivative as previously, m.p. (after two crystallizations from 50% ethanol) 168–171°, undepressed on admixture with the corresponding derivative from the ethyl benzoate runs.

The remaining nitrobenzene solution was washed and steam-distilled as in the ethyl benzoate case and with similar results. The dried residue was boiled with ethanol and the soluble portion was crystallized thrice from ethanol, m.p. 156–157.5°, undepressed on admixture with the preceding presumed triiodonaphthalene.

In run 14 the washed and dried nitrobenzene layer was distilled at reduced pressure. Only a trace of tarry residue remained and the distillate appeared to be pure nitrobenzene.

E. Carbon tetrachloride runs. In run 16 the combined carbon tetrachloride washings of the precipitate contained suspended gelatinous material which was collected as a sticky honey-colored residue by filtration through paper. The residue dissolved readily in a small amount of hot water to give an acidic solution (to litmus) which yielded a white precipitate when tested with silver nitrate solution but gave no reaction with aqueous sodium chloride. More precipitate formed on diluting the carbon tetrachloride filtrate with three volumes of petroleum ether. Efforts to dry the precipitate in a vacuum desiccator led to decomposition.

In the same run the dark brown aqueous washings of the precipitated silver iodide were titrated for hydrion using standard sodium hydroxide with β-methylumbelliferone and ultraviolet light as indicator.

Run 17 was conducted using a trap containing aqueous potassium iodide to collect any chlorine which might be evolved. Only a negligible amount of free iodine formed therein. The organic and aqueous layers were titrated for hydrion and recovered iodine. Evaporation of the organic layer gave a small amount of light yellow oil which crystallized on standing, m.p. 88–95°, not further identified. The aqueous washings yielded an S-benzylisothiuronium derivative, m.p. 168.5–170° after three crystallizations from 50% alcohol, undepressed on admixture with the corresponding derivative from the ethyl benzoate runs.

SUMMARY

1. Treatment of silver 2-naphthalenesulfonate with iodine in five anhydrous solvents gave silver iodide in quantitative yield.

2. The reactive solvents benzene and toluene were iodinated to iodobenzene and a mixture of products including *p*-iodotoluene, respectively. Quantitative yields of 2-naphthalenesulfonic acid were also produced.

3. In the inert solvents carbon tetrachloride, nitrobenzene, and ethyl benzoate the naphthalene nucleus was iodinated instead to a monoiodonaphthalenesulfonic acid. The latter two solvents also gave small amounts of a neutral compound, probable a triiodonaphthalene.

4. An intermediate of the formula $ArSO_3^{\ominus}I^{\oplus}$ is proposed as the iodinating entity in the reaction. Correspondingly a crystalline complex assigned the structure of dipyridine iodine (I) 2-naphthalenesulfonate has been isolated and characterized.

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