Although the number of compounds sulfonated by this method is not large, there is little doubt that the reaction is quite general for aliphatic hydrocarbons, and has been extended to alkyl halides and many other types of molecules. Since sulfuryl chloride can now be used either as a sulfonating or a chlorinating agent with aliphatic compounds, it should prove a useful reagent in organic chemistry. The primary purpose of the present investigation, however, was to demonstrate that sulfonation should and does take place when sulfuryl chloride reacts with aliphatic hydrocarbons through a free-radical mechanism.

Experimental Part

The cyclohexane (0.5 mole) and sulfuryl chloride (0.25 mole) were introduced into a 125-cc. round-bottomed flask connected by a ground-glass joint to a Hopkins-type condenser, and brought to a gentle reflux. A small amount of catalyst (0.02–0.12 g.) was added, and the reaction mixture was heated over a low flame until no more gas was evolved. The progress of the reaction was followed by means of a bubble counter attached by a rubber tube to the top of the condenser. No attempt was made to trap any of the reactants swept over with the gases, and in cases where oxygen or sulfur dioxide was bubbled through the mixture during the reaction, the losses were appreciable. After the reaction was complete, the mixture was filtered through a glass-wool plug, and the excess cyclohexane was removed by distillation through an indented column 45 cm. long.

The solution was then transferred to a 50-cc. Claisen flask, and the rest of the distillation was carried out at reduced pressure. Cyclohexyl chloride was identified by its boiling point, and cyclohexylsulfonyl chloride by its boiling point and anilide.

The experiments in which the sulfuryl chloride was added slowly, or in which gases were passed through the solution, were carried out in a 125-cc. round-bottomed flask into which was sealed a capillary delivery tube reaching to the bottom of the flask and sealed to a wide neck which held a dropping funnel and gas delivery tube. The flask was connected to the condenser by a ground-glass joint.

The source of illumination was a 2000-watt lamp placed about twelve inches (31 cm.) from the reaction flask. The cyclohexane used was Eastman Kodak Co. practical grade, dried over sodium. The sulfuryl chloride was obtained from the Hooker Electrochemical Company and was not purified further.

The identification of n-heptylsulfonyl chloride, and phenethylsulfonyl chloride was made by conversion to the amides.

Summary

1. Simultaneous chlorination and sulfonation of aliphatic hydrocarbons with the aid of sulfuryl chloride, a catalyst, and light is recorded.

2. It is shown that aromatic nitrogen ring compounds when used as catalysts in this reaction, favor the formation of the aliphatic sulfonyl chlorides.

3. The mechanism of the reaction is discussed.

The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. XXIII. The Reaction of Styrene with Bisulfite
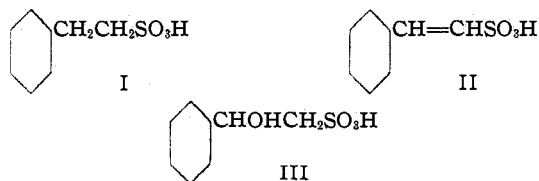
BY M. S. KHARASCH, REMSEN TEN EYCK SCHENCK AND F. R. MAYO

A recent paper from this Laboratory discussed the addition of bisulfite to various olefins.[1] The unique behavior of styrene suggested further study of this reaction.

The Interaction of Styrene and Bisulfite

The formation, by the oxygen-catalyzed reaction between ammonium bisulfite and styrene, of benzoic acid, 2-phenylethanesulfonic acid (I), and 2-phenylethylenesulfonic acid (II) has been confirmed qualitatively. The material isolated in greatest amount, however (about 65% of the total yield in most instances), was found to be not II, as observed by the workers cited, but a new compound, 2-hydroxy-2-phenylethanesulfonic

acid (III). This substance, on treatment with phosphorus pentachloride and then with ammonia, loses the elements of water to form the same amide as II, and can be identified in a mixture of the two only by fractional crystallization of the sodium or potassium salt from dilute alcohol. It is not surprising that the previous workers in the field did not suspect its presence since they for the most part converted the crude salts directly into amides without previous puri-

(1) Kharasch, May and Mayo, J. Org. Chem., 3, 175 (1938); a summary of the earlier literature is given in this article.

fication. The few attempts that were made to work up the products by crystallization from water as the barium salts met with no success, since striking solubility differences between the various components do not exist under such circumstances.

The extent to which styrene will react with bisulfite, and hence the efficiency of the process, has been found to depend somewhat on the pH of the original aqueous salt solution, provided no further additions of material capable of altering the hydrogen ion concentration are made during the course of the reaction. The addition occurs, furthermore, under more extreme conditions of acidity and alkalinity than was formerly believed; such variations, however, are ineffective in causing appreciable changes in the ratio of products formed.

A small but reproducible variation in the proportion of the final products has been observed between two main classes of bisulfites: salts of the ammonium group, including all the alkylamines tested, give rise to somewhat greater amounts of the substitution product (II) at the expense of the addition product (I) than do those of the alkali metals. A number of examples of each type are given in Table I. The anomalous behavior of dimethylanilinium sulfite is probably attributable to the effect of the strongly electronegative phenyl radical, but confirmation of this hypothesis was hindered by the inability of diphenylamines, because of their greatly lowered base strength, to form sulfites at all. Much the same sort of difficulty was encountered in an attempt to relate the variations between ammonium and alkali metal salts to base strength— the alkaline earths, for instance, form water-insoluble sulfites. Dimethylaniline possesses the additional peculiarity of furnishing extraordinarily high yields, apparently as a result of its properties as a mutual solvent together with its ability, when present in excess, to keep the solution at all times very close to neutrality. The behavior of pyridine, which has similar characteristics, was found to be practically identical.

The rate of reaction was found to be effectively independent of the salt employed, but to be closely related to the oxygen concentration. Only the roughest of quantitative observations were made, but even these sufficed to indicate that the speed at which oxygen is consumed increases with its partial pressure. Conversely, the over-all yield

TABLE I

THE ADDITION OF BISULFITE TO STYRENE[a]

Cation of bisulfite used	Oxygen tension, mm.	pH Initial	pH Final	Total % yield on sulfite reacted	% of total yield present as		
					I[b]	II[c]	III[d]
Sodium	760	6.23	2.47	25	28	12	60
Sodium	152	6.23	8.92	43	20	12	68
Sodium	30	6.23	9.81	58	29	11	60
Ammonium	760	6.52	6.90	30	8	28	64
Ammonium	152	6.52	7.40	40	16	14	70
Ammonium	30	6.52	8.72	68	20	7	73
Methylammonium	152	6.55	6.50	32	17	28	55
Dimethylammonium	760	5.97	2.00	29	21	17	62
Trimethylammonium	760	6.40	3.13	30	12	18	70
Ethylenediammonium	152	7.02	7.95	33	8	10	82
Dimethylanilinium	760	[e]	[e]	54	16	5	79
Pyridinium	760	[f]	[f]	66	23	20	57
Ammonium	0[g]	7.81	1.43	15	50	0	50
Ammonium	0[h]	4.87	7.72	20	20	0	80
Sodium	0[i]	4.74	7.11	25	35	0	65

[a] The results herein tabulated are representative examples of a group of 60 consistent experiments. [b] Calculated by difference. [c] By permanganate assay. [d] Weighed as such. [e] pH not measured, maintained approximately constant near neutrality by excess dimethylaniline in second phase. [f] pH not measured, maintained approximately constant near neutrality by excess pyridine employed as solvent. [g] Oxygen excluded, catalyzed by 0.68 mole of ammonium persulfate per mole of sulfite reacted, added over a period of three and one-half hours. [h] Oxygen excluded, catalyzed by 0.3 mole of ammonium nitrite per mole of bisulfite reacted, added over a period of twelve and one-half hours. [i] Oxygen excluded, catalyzed by 0.3 mole of sodium nitrite per mole of bisulfite reacted, added over a period of six and one-half hours.

of organic sulfonates shows an inverse relationship to the oxygen tension. Increasing oxygen pressure, furthermore, results in favoring the substitution reaction, where it occurs to any appreciable extent, as with the ammonium group of salts already referred to, at the expense of the addition reaction. The small amounts of substitution encountered in the use of alkali metal bisulfites are independent of oxygen concentration, as is the ratio of hydroxysulfonate (III) in all oxygen-promoted experiments. The yield of the latter, in fact, remained substantially constant regardless of any alteration of experimental conditions.

The possible effect of bisulfite concentration was investigated in one experiment conducted according to the method of Kolker and Lapworth,[2] as amended by Ashworth and Burk-

(2) Kolker and Lapworth, J. Chem. Soc., 127, 307 (1925).

hardt[3] to include styrene. The use of $M/6$ bisulfite solution in place of the usual $M/1$, in a procedure precluding rate comparisons, gave the same products in about the customary yield.

Replacement of oxygen by nitrite or perdisulfate ion as reaction promoter results in complete suppression of the substitution reaction, the proportion of both the addition product and the hydroxysulfonate being at the same time slightly increased. Over-all yields are here to some extent influenced by the rate at which the oxidant is introduced, but even when the latter is added at the minimum convenient speed they are no better than those resulting from use of oxygen at one atmosphere pressure.

Nitrate ion has been found to be of very slight value as an oxidant in bisulfite additions in comparison with the three foregoing materials. The observable effect, in fact, readily may be ascribed not to the nitrate itself but to the few per cent. of nitrite generally present as impurity in nitrates.

Since we have been totally unable to convert any of the three major products into any other by any means comparable to conditions existing during the reaction or the subsequent isolation of the resulting sulfonates, we have concluded that each is a primary reaction product. For instance, a pure sample of each of the three compounds in turn was treated first with hot acid, then with hot alkali, and finally with sodium bisulfite and oxygen. With one exception the starting materials were in every case recovered unchanged, and in that single instance not one of the previously known substances but a new compound was obtained. Specifically, the action of bisulfite and oxygen upon the substitution product results in the addition of another molecule of bisulfite to the double bond with the production in good yields of 2-phenylethane-1,1-disulfonic acid (IV). From the fact that this compound is never formed during treatment of styrene with bisulfite, even in those experiments in which subsequent analysis shows the unsaturated acid to have been present, it is evident that its formation is prevented by the presence of excess styrene.

IV

V
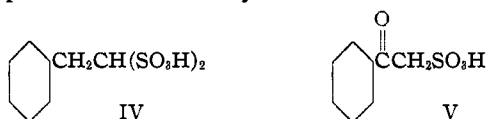
It was anticipated after discovery of the hydroxysulfonate (III) that benzoylmethanesulfonic

(3) Ashworth and Burkhardt. *J. Chem. Soc.*, 1791 (1928).

acid (V) might also logically be included among the products of the reaction, as a result of further oxidation of the former substance. No trace of it, however, has thus far been isolated. It furthermore has been observed in this connection that the hydroxy compound, in view of its structure as a water-soluble secondary alcohol, is surprisingly resistant to oxidation. It is stable to both acid and alkaline permanganate in the cold, and even at 90–100° the oxidation is relatively slow.
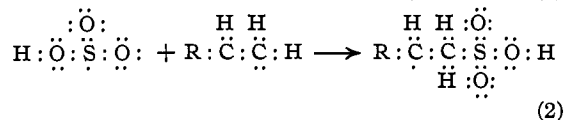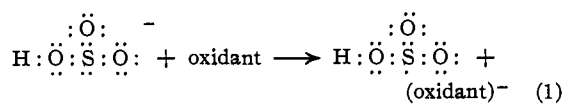
This observation was made the basis of an attempt to determine yields of unsaturated sulfonate without separation of the crude mixtures into their components. Accurately weighed samples were treated with cold neutral permanganate in excess, the solution freed from precipitated manganese dioxide, and added to excess acid potassium iodide solution. By titrating the liberated iodine with thiosulfate a measure of the unreacted permanganate was obtained. Under such conditions the substitution product is quickly and completely oxidized. The reaction, however, does not follow any predictable stoichiometric course, and as a result it is necessary to standardize the permanganate against a sample of unsaturated sulfonate or sulfonamide of known purity rather than against any of the usual inorganic standards. As a further qualification, it was found that while pure hydroxysulfonate (III) is not attacked by the oxidizing agents employed, it does react to a varying extent when present in a mixture of products and thus leads to extremely inconsistent results. Its removal is very conveniently effected, fortunately, leaving only addition and substitution products in the remainder. These are nearly impossible to separate, but since the former, unlike the hydroxy derivative, is uniformly inert, assay of the latter with permanganate standardized as described gives highly reproducible results.

Mechanism

The data herein presented are entirely in accord with the thesis of Kharasch, May, and Mayo[1] that the reaction proceeds through a free-radical intermediate. The evidence for this hypothesis lies in the facts that reagents capable of oxidizing bisulfite are necessary for any interaction to occur and that the products (aside from the benzoic acid arising probably from the direct oxidation of styrene) are exclusively those ac-

countable for by "abnormal" addition to the double bond. Our observations furthermore provide a more quantitative basis for the conclusion that the favored reactions between bisulfite and styrene are unlike those which occur with other olefins in that chains are apparently not important in this particular case. It is true that a chain reaction best accounts for the simple addition products (I), but this class of compound, which constitutes the main product of most unsaturated hydrocarbons, is formed to only a very limited extent from styrene. Reference to the footnotes to Table I will show the comparatively large amounts of oxidant consumed in the addition of bisulfite to the latter olefin, indicating a stoichiometric rather than a chain reaction. In addition, the proportion of sulfite lost as sulfate is not compatible with a self-propagating reaction.

The first steps, wherein a bisulfite free radical, produced by the oxidant[4] capturing an electron from a bisulfite ion, is absorbed by a styrene molecule, have previously been postulated by Kharasch, May, and Mayo.[1] They are reproduced below as equations 1 and 2.

$$R:\overset{..}{\underset{.}{C}}:\overset{H}{\underset{\overset{..}{H}:\overset{..}{O}:}{C}}:\overset{H}{\underset{..}{S}}:\overset{:\overset{..}{O}:}{\underset{..}{O}}:H + \text{oxidant} \longrightarrow \quad (\text{see figure}) \quad (1)$$

The resulting free-radical complex is then subject to three types of further change, each giving rise to a different product.

1. The simplest case is that in which a hydrogen atom is acquired by collision with another bisulfite ion, as in equation 3, with the formation of 2-phenylethanesulfonic acid and regeneration of sulfite-ion free radical.
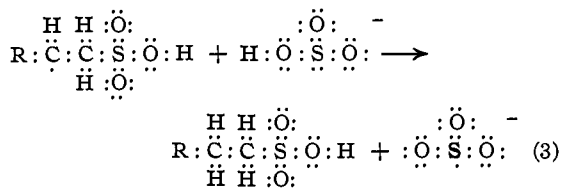
2. The intermediate may collide with the oxidant and in doing so lose to the latter its unpaired electron. The positively charged molecule thus created readily combines with a negative ion from the solution to form 2-hydroxy-2-phenylethanesulfonic acid.

$$\text{(equation 4)} \qquad (4)$$
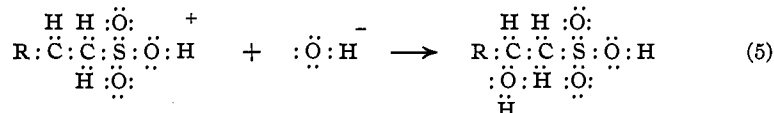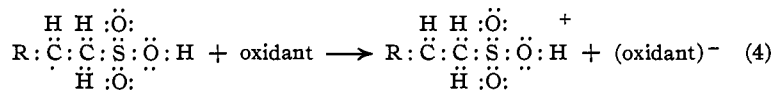
$$\text{(equation 5)} \qquad (5)$$

3. The third type of impact, that which is responsible for the substitution reaction and the formation of 2-phenethylenesulfonic acid, occurs only in the presence of oxygen. For this reason the nature of the oxidant in equation 6 is specified.
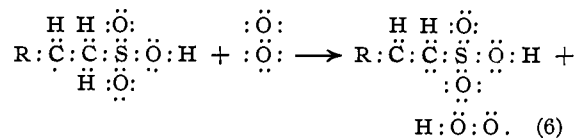
$$\text{(equation 6)} \qquad (6)$$

Finally, bisulfite free radicals are transformed to sulfate by a second collision with oxidant, before they can effect combination with styrene, as in equation 7.

$$\text{(equation 7)} \qquad (7)$$
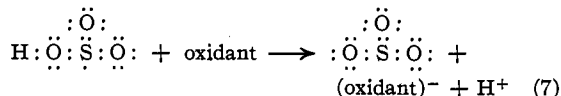
The loss of the second electron to the oxidant has been written, when it takes place (reactions 4 and 6), as a separate step for several reasons. In the first place the removal of both charges at once from sulfite ion results in molecular sulfur trioxide, which in aqueous solution would at once stabilize itself as totally unreactive sulfate ion. Furthermore, if it were possible for sulfur trioxide to exist in dilute solution long enough for it to share the free-electron pair of styrene, the ensuing formation of hydroxysulfonates would be a general property of bisulfite addition instead of being peculiar to styrene, as observed. Lastly, the method employed permits each equation to follow in simple sequence from a common foundation, whereas the introduction of a two-electron transfer would require the retention of both species of inorganic free radical.

It is significant that the apparent relative stabilities of the substituted ethanesulfonate

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(4) The term "oxidant" as used in this paper refers to any molecule, atom or free radical capable of accepting an electron or a hydrogen atom from either bisulfite ion, bisulfite free radical, or the organic free-radical complex.

free radicals fall in the same order as those of the corresponding substituted methyl free radicals. The latter, arranged according to increasing ability to independent existence, are methyl, phenylmethyl, diphenylmethyl, and triphenylmethyl. Of the former, the alkylethanesulfonate free radicals are relatively short-lived and are the most reactive with the result that practically every collision with bisulfite is effective, and the products are mainly simple addition compounds. Arylethanesulfonate free radicals, on the other hand, are probably of much greater stability. Reaction of these with bisulfite may be assumed to require an appreciable activation energy. Consequently, fruitful impacts are largely with the oxidant and lead to substitution or the introduction of hydroxyl groups in a large proportion of the intermediate free radicals. The observed phenomena thus follow predictions based on consideration of the probable electron patterns as defined by the theory of electronegativity.[5]

Experimental

Materials.—Styrene, obtained through courtesy of Bakelite Corp., was used both as received (containing small amounts of hydroquinone) and freshly distilled *in vacuo*. No difference between the two kinds was perceptible in any bisulfite addition. Baker monohydrated ammonium sulfite of 71% purity and General Chemical Co. ammonium bisulfite solution, 25% sulfur dioxide, were employed, together with Merck Reagent sodium bisulfite and Mallinckrodt Analytical sodium sulfite, anhydrous, assaying 79% sodium bisulfite and 86% sodium sulfite, respectively. Ethylenediamine sulfite was prepared by diluting the Eastman Kodak Co. Technical base (60% $(CH_2NH_2)_2$ in water) with two volumes of alcohol and saturating with sulfur dioxide. The granular white precipitate, after collection on a filter, an alcohol and ether wash, and air-drying, melted at 176°. Iodine titration of a sample for sulfur dioxide showed the material to be 99% pure $(CH_2NH_3)_2SO_3$. The yield was nearly quantitative. Concentrated stock solutions of substituted ammonium bisulfites were made up by absorbing the maximum of sulfur dioxide in 25–35% solutions of base in water as supplied by Commercial Solvents Corp. Pyridine was diluted with one-fourth its weight of water and sulfur dioxide introduced until its concentration was approximately molar. This reagent was used without further dilution. Dimethylaniline was suspended in water and treated with sulfur dioxide until the mixture became homogeneous. More water was added to the resulting solution to reduce its sulfite content to molar before use.

Procedure for Reaction

Buffered solutions of highly reproducible *p*H for oxygen-promoted runs were prepared by mixing weighed quantities of sulfite and bisulfite, or of solutions of bisulfite and free

(5) Kharasch and Reinmuth, *J. Chem. Educ.*, **8**, 1703 (1931); Kharasch and Flenner, THIS JOURNAL, **54**, 674 (1932).

base, and diluting until molar in total sulfurous acid salts. Reaction was carried out on a high-speed shaker in ordinary round-bottomed flasks with wired-in rubber stoppers, pierced by inlet tubes leading to a graduated reservoir of pure oxygen collected over water. The oxygen tension in the atmosphere over the reaction mixture in the vessel was fixed by using the undiluted gas, air, or a mixture of air with four volumes of nitrogen. In any case the concentration of the promoter was automatically kept constant by replacement with pure oxygen from the reservoir as fast as consumed. Over-all pressure was maintained at atmospheric within narrow limits by never permitting the water level to rise far inside the cylinder. Back diffusion was negligible because of the steady flow of oxygen into the flask. Oxygen runs were continued until iodine titration of an aliquot showed that only a negligible quantity of bisulfite remained, or until extreme *p*H changes greatly reduced the rate of reaction.

Solutions of bisulfite alone were used in nitrite-catalyzed, of sulfite alone in persulfate-catalyzed additions. The sole change necessary in the apparatus was substitution for the gas inlet tube of two stopcocks. Air was displaced from the flask and liquid by passing in carbon dioxide rapidly for fifteen to twenty minutes before shaking was commenced and excluded thereafter, within the limitations of the method, by introducing the oxidant through the stopcocks. The oxidant was added as a 2.5–5 M solution at the rate of 10 mmole. per mole of sulfite or bisulfite every half-hour. Samples for assay of unreacted sulfite were withdrawn in a capillary pipet from time to time by the same route without permitting ingress of appreciable oxygen. This type of run was stopped when the sulfite concentration had fallen to such a point (0.15 M) that fresh portions of oxidant caused a much smaller drop in the reducing power of the solution than at the start of the experiment.

The proportion of styrene present was in all instances the same: mole for mole with the total sulfurous salts. Since even at best a large part of the latter are oxidized to sulfate, the styrene is always actually in excess.

Among the solvents tested, two, 95% alcohol and liquid ammonia, failed to produce any evidence of reaction whatever. Dimethylaniline was the base employed in the former trial, and in the latter the solvent itself functioned as proton acceptor. This second run was made by bubbling through air under stirring in place of the usual technique of shaking in a closed system. The action of nitrite on either of these mixtures was not investigated. Water proved to be a generally reliable medium. The most desirable results were obtained in 80% aqueous pyridine, in which a much more nearly homogeneous solution is attainable than with water. Even under high oxygen pressures the ratio of sulfonate to sulfate formed in such a run is unusually favorable.

Analysis of Reaction Mixture.—Completed reaction mixtures were separated and the aqueous portion clarified by ether extraction or filtration through a little carbon. After potentiometric *p*H determination and iodine titration of an aliquot to measure the unused sulfite, the salt solution was evaporated to dryness in an open dish on the steam-bath: directly if from an oxygen- or persulfate-sodium sulfite addition, and after mixing with 0.55 mole of sodium carbonate for every gram atom of

nitrogen contained if from any other type, whether the nitrogen as originally added was contained in the base or in nitrite or nitrate ion (which are reduced by bisulfite to ammonia or hydroxylamine). Heating of the residue, when nitrogen was present, was continued as long as escape of any ammoniacal fumes could be detected. Small variations in this procedure were desirable in several special cases: for instance, pyridine was not evaporated off freely but was recovered by distilling from the salts *in vacuo*, after addition of aqueous sodium carbonate solution to cause separation of excess styrene. Dimethylaniline was separable mechanically from the alkalinized solution.

The salt residues from these evaporations were finely ground and extracted with 1 liter of boiling 70% alcohol per mole of sulfite consumed. The solution was filtered from the inorganic insolubles and the filtrate taken to dryness as before. The organic residue was then treated with 10 cc. of 90% alcohol per gram, the mixture boiled, cooled to room temperature, and filtered. The residue from this step consists of nearly pure hydroxyphenethyl sodium sulfonate, which may be efficiently recrystallized from 70% alcohol as pearly white platelets. From the filtrate may be obtained, by evaporation to dryness, a mixture of phenethyl and phenethylene sodium sulfonates. These may be recrystallized from 85–90% alcohol or from saturated aqueous salt solutions, but the former solvent often leads to difficultly filterable pastes and the latter to products contaminated with inorganic salts. A much more satisfactory procedure is to convert the sodium to the barium salts by metathesis with barium bromide and recrystallize from water. The sodium salts of both these compounds are obtained as small, shiny white plates from alcohol or as coarse, thin, transparent plates from brine. The barium salts crystallize from water as tiny, white scales, containing one molecule of water of crystallization. Either of the materials may be obtained in a pure state by any of the above methods from a mixture with the other in which it preponderates. The saturated sulfonate also may be freed from any proportion of the unsaturated by destroying the latter with potassium permanganate. No scheme has yet been devised for the separation of both components of an approximately equimolar mixture, or for the isolation of small amounts of unsaturated sulfonate from a mixture rich in the saturated.

Preparation of Sulfonamides.—Sulfonamides were prepared from both the saturated and unsaturated salts in the manner described by Kharasch, May and Mayo.[1] That obtained from the former melted at 124° and from the latter at 143° as they reported. In neither case did a mixed melting point with an authentic specimen show any depression.

Anal. (1) Sodium 2-phenylethanesulfonate. Calcd. for $C_8H_9SO_3Na$: C, 46.15; H, 4.36; Na, 11.05. Found: C, 45.80; H, 4.26; Na, 11.01.

Anal. (2) Barium 2-phenylethylenesulfonate monohydrate. Calcd. for $(C_8H_7SO_3)_2Ba \cdot H_2O$: C, 36.83; H, 3.09; Ba, 26.32. Found: C, 37.00, H, 3.27, Ba, 26.64.

Anal. (3) Sodium 2-hydroxy-2-phenylethanesulfonate. Calcd. for $C_8H_9SO_4Na$: C, 42.85; H, 4.05; Na, 10.26. Found: C, 42.69; H, 4.05; Na, 10.24.

Establishment of Structure of Sodium 2-Hydroxy-2-phenylethane Sulfonate.—The analytical data reproduced

above for this salt correspond to those calculated for sodium 2-phenethylenesulfonate containing one molecule of water per mole. We have never been able to prepare such a hydrate, however (it is only the barium salt which forms a stable hydrate). Furthermore, a sample of the material was observed to have lost no weight after standing for a week over phosphorus pentoxide *in vacuo*. The stability of the compound to cold permanganate shows the material to be saturated, and the fact that when it is oxidized under more vigorous conditions only benzoic acid (identified by its mixed melting point of 123° with a known sample) can be isolated in high yield, indicates that all substituents are in the side-chain. Treatment with phosphorus pentachloride in the cold resulted in a vigorous exothermic reaction, accompanied by the evolution of much hydrogen chloride and yielding a sulfonyl chloride which was transformed by the action of ammonia into the unsaturated amide of melting point 143°. The over-all conversion of the salt into amide was about 70%. This reaction, together with the stability of the salt to both acid and base (no inorganic sulfur was liberated even on long boiling), demonstrated the absence of sulfate ester and the position of the sulfonic group as beta to the phenyl. The hydroxyl cannot also be beta to the phenyl group, since compounds having a hydroxyl on the same carbon atom as a sulfonic acid group are known to be easily decomposed by either acid or base into sulfur dioxide and an aldehyde. The configuration thus arrived at has been shown to be correct by synthesis from styrene bromohydrin (see below).

The hydroxyl group here present exhibits none of the reactions characteristic of its class. All attempts to esterify it uniformly failed. No treatment with reagents designed to replace it with halogen was successful: either the salt was recovered unchanged or only the unsaturated derivative was obtained.

Styrene bromohydrin was prepared according to Read and Reid,[6] although it was not found possible to reproduce the high (95–98%) yield reported. Under the best circumstances only 80 to 85% of the bromine employed added as hypobromous acid, the remainder forming styrene dibromide, while as little as 60% of the theoretical quantity of bromohydrin was isolated from larger runs. The two products were efficiently separated by thoroughly cooling the crude oil in the icebox and filtering the still-liquid bromohydrin from the crystallized dibromide.

Styrene iodohydrin was prepared by the method of Brunel.[7]

Styrene dibromide was obtained both as a by-product in the manufacture of the bromohydrin and in the manner of Evans and Morgan.[8]

Sodium 2-hydroxy-2-phenylethanesulfonate . resulted from treatment of styrene bromo- or iodohydrin with aqueous sodium sulfite according to the procedure of Houlton and Tartar[9] for alkyl halides in general. It was found to be identical in all its properties, physical and chemical, with that fraction of the reaction products analytically identified as such.

Phenylhydrazinium 2-hydroxy-2-phenylethanesulfonate

(6) Read and Reid. *J. Chem. Soc.*, 1487 (1928).

(7) Brunel, *Ann. chim.*, (viii) **6**, 219 (1905).

(8) Evans and Morgan, THIS JOURNAL, **35**, 56 (1913).

(9) Houlton and Tartar. *ibid.*, **50**, 544 (1938).

was prepared by the method of Latimer and Bost[10] from samples of hydroxysulfonate resulting from both addition to styrene and metathesis of the bromohydrin. It crystallized from alcohol as small yellowish plates, very soluble in water and melting sharply at 180–181° with decomposition. Mixtures from the several sources showed no depression of the melting point.

Sodium 2-phenethylenesulfonate was produced in high yield from the hydroxysulfonate by grinding with excess phosphorus pentachloride, drowning in water and refluxing the resulting water-insoluble sulfone chloride with excess saturated aqueous sodium carbonate solution to complete disappearance of the oily layer. On cooling the unsaturated salt separated as a loose mass of large, thin, transparent plates.

Sodium Benzoylmethanesulfonate.—This salt was prepared also according to Houlton and Tartar,[9] and crystallized from 85% alcohol as soft, asbestos-like fibers. No amide could be obtained from this material, nor was any fraction even remotely resembling it in any of its properties ever isolated from our various reaction products.

Addition of Sodium Bisulfite to Substitution Product.— Ten grams (0.05 mole) of sodium 2-phenethylenesulfonate, from either direct substitution or the hydroxysulfonate as above, was dissolved in a solution of 10.5 g. (0.1 mole) of sodium bisulfite and 25 g. (0.2 mole) of sodium in 250 cc. of water and shaken with oxygen in the same apparatus used for styrene additions until absorption of the gas ceased. The solution was evaporated to dryness on the steam-bath and the residue finely ground. It was then exhaustively extracted with boiling 70% alcohol and the soluble salts isolated by evaporation of the filtrates. The product separated from smaller volumes of dilute alcohol as a pulpy mass of soft, silky needles grouped in rosets. This material no longer gave a positive permanganate test for unsaturation, but was still oxidizable by more powerful reagents to benzoic acid, showing that the additional molecule of bisulfite indicated by the analysis had added to the double bond to form a side-chain disulfonate. Treatment with phosphorus pentachloride eliminates a sulfonic group and causes extensive decomposition. The only amide isolable, and that in extremely small yield, proved to be the β-phenethylene sulfonamide of melting point 143°.

Anal. Disodium 2-phenylethane-1,1-disulfonate dihydrate. Calcd. for $C_8H_8S_2O_6Na_2 \cdot 2H_2O$: Na, 13.28; H_2O, 9.54. Found: Na, 13.12; H_2O, 9.22.

Disodium 2-phenylethane-1,2-disulfonate was prepared from styrene dibromide by Houlton and Tartar's[9] procedure. It crystallized from 70% alcohol as small, elongated prisms totally unlike the needles described immediately above. The action of phosphorus pentachloride and ammonia, however, on this disulfonate was practically

(10) Latimer and Bost, THIS JOURNAL, **59**, 2500 (1937).

identical with that on the addition compound, only a very small quantity of the same unsaturated amide resulting.

Phenylhydrazinium 2 - phenylethane - 1,2 - disulfonate, synthesized according to the instructions of Latimer and Bost,[10] melted sharply at 187–188° with decomposition. It crystallizes from alcohol as microscopic yellowish scales, very soluble in water.

Phenylhydrazinium 2-phenylethane-1,1-disulfonate was prepared in the same manner as the above from the addition product disulfonate. This salt possesses the lowest water solubility of any organic phenylhydrazinium derivative thus far studied by us. It may be recrystallized from water as tiny yellowish scales, and melts at no definite temperature. In a slowly heated bath it darkens at 173° and sinters at 180–185° with decomposition to brownish-black products which thereafter are infusible. When introduced into a pre-heated bath at 195–200°, it visibly melts with evolution of gas and transformation into the same dark residue.

We have been unable to prepare by unambiguous synthesis the β,β-disulfonate we assume the above addition product to be. However, we have shown (1) that both groups are in the chain, (2) that one at least must be terminal, and (3) that the compound is not identical with the α,β-disulfonate of known structure. By elimination, then, the configuration must be that represented by formula (IV), 2-phenylethane-1,1-disulfonic acid.

Summary

1. Previous findings on the production of 2-phenylethanesulfonic acid and 2-phenethylene-sulfonic acid by the oxygen- or nitrite-promoted reaction of styrene with bisulfite have been qualitatively confirmed.

2. The interaction of styrene with bisulfite yields mainly 2-hydroxy-2-phenylethanesulfonic acid.

3. A mechanism involving oxygen has been proposed to explain the substitution of bisulfite in styrene, and one independent of the nature of the oxidant to account for the formation of the hydroxy derivative.

4. Four new sulfonic acids, namely, 2-hydroxy-2-phenylethanesulfonic acid, 2-phenylethane-1,2-disulfonic acid, 2-phenylethane-1,1-disulfonic acid, and benzoylmethanesulfonic acid have been prepared, together with derivatives of each of the first three named.