tion, four fractions were obtained by slow concentration under slightly reduced pressure. Molecular weights (Rast) of the different fractions were 748, 750, 573 and 612.

Anal. (Mol. wt. 748) Calcd. for $(C_{20}H_{16})_n$: C, 93.71; H, 6.29. Found: C, 93.59; H, 6.38.

Summary

1. In the presence of halides of cobalt or chromium, aromatic Grignard reagents react with vinyl halides and substituted vinyl halides to yield normal condensation products.
2. The effect which substituents in the vinyl halide molecule exercise on the yield of the condensation product has been determined.
3. Phenylmagnesium bromide and triphenylbromoethylene react to give an equilibrium mixture of two Grignard reagents.

CHICAGO, ILLINOIS RECEIVED OCTOBER 15, 1942

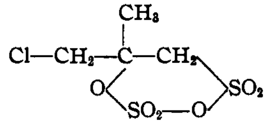
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Sulfonation of Methallyl Chloride. Mobility of the Olefinic Linkage in Unsaturated Sulfonic Acids

BY C. M. SUTER AND FREDERICK G. BORDWELL

It has long been known[1] that the action of sulfur trioxide upon ethylene gives a cyclic anhydride, carbyl sulfate. More recently it has been shown[2] that dioxane sulfotrioxide reacts readily with propylene and other straight-chain *alpha* olefins resulting in similar products.[3] On the other hand, isobutylene[4] and styrene[5] give for the most part olefinic mono and disulfonic acids through substitution reactions. Because of these varied results it seemed of interest to investigate the sulfonation of methallyl chloride in order to determine the influence of the chlorine on the nature of the reaction products. The major part of the investigation has dealt with the dioxane sulfotrioxide sulfonation, but the behavior of sodium chlorosulfonate[6] and a solution of sulfur trioxide in ethylene chloride received some study.

The sulfonation of methallyl chloride by dioxane sulfotrioxide in ethylene chloride solution proceeds smoothly at 0°. In contrast to isobutylene, no polymerization was observed and the products were substantially the same whether the methallyl chloride was added to the sulfonating agent or the reverse. Since the addition of water and alkali (even at a low temperature) to the reaction mixture resulted in the formation of chloride ion, a better method of isolating the components of the mixture was sought. The best results were obtained by the addition of aniline which precipitated a mixture of anilinium chloroisobutylenesulfonates, anilinium sulfate, and probably anilinium phenylsulfamate. The yield of this mixture is practically quantitative based on the sulfur trioxide. The probable presence of anilinium sulfate and anilinium phenylsulfamate in this product was indicated by the fact that about 18% of the total sulfur present was precipitated, after acid digestion, as barium sulfate. This sulfate seemed most logically to be derived from products of the anilinolysis of an intermediate of the carbyl sulfate type, I. Fortunately it was possible to isolate this intermediate, β-chloromethyl-β-methylethionic anhydride (I), in crystalline form by using sulfur trioxide dissolved in ethylene chloride as a sulfonating agent. When methallyl chloride was added to this reagent in the ratio of one mole of olefin to two of sulfur trioxide at 0°, the reaction was almost exclusively addition of the sulfur trioxide to the double bond, as indicated by the amount of sulfate ion formed by the hydrolysis of the product. Treatment of a solution of I in chloroform with aniline gave about a 25% yield of anilinium sulfate, and small amounts of a compound which has been tentatively identified as anilinium phenylsulfamate, thus confirming


(I)

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(1) Regnault, *Ann. chim. phys.*, **46**, 98 (1838); *Ann.*, **27**, 11 (1838); **25**, 32 (1838); Michael and Weiner, THIS JOURNAL, **58**, 294 (1936).

(2) Suter, Evans and Kiefer, *ibid*, **60**, 538 (1938).

(3) It has been observed by Mr. Kaplan in this Laboratory that some unsaturated sulfonic acid is formed when propylene is sulfonated.

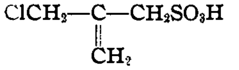
(4) (a) Suter and Malkemus, THIS JOURNAL, **63**, 978 (1941): (b) Suter, Malkemus and Archer, *ibid.*, **63**, 1594 (1941).

(5) J. M. Holbert, Ph.D. Thesis, Northwestern University, 1941.

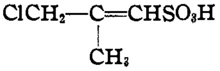
(6) We are indebted to Dr. S. Archer of this Laboratory for the report on experiments with this reagent.

the view that these products had their origin from the reaction of I with aniline. As determined by the amount of sulfate formed on acid digestion the aniline sulfate and the phenylsulfamate make up about 20% by weight of the aniline salt mixture.

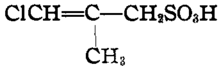
On the basis of halogen analysis of the aniline salt mixture the aniline salts of chloroisobutylenesulfonic acids of the type II, III, and IV make up 80% of the total. This composition for the mixture would require a total sulfur content of about 32%, which checks well with the observed value. The neutral equivalent of the salt mixture is about 245, which can be readily correlated with the other analytical data. The composition of the mixture is not in accord with the presence of more than a trace of a chloroisobutylenedisulfonate. The fact that about 20% of the sulfur in the aniline salt mixture is hydrolyzable must mean that approximately 40% of the sulfur trioxide adds to the olefin whereas the other 60% reacts to replace a hydrogen atom.


$\mathrm{ClCH_2{-}C({=}CH_2){-}CH_2SO_3H}$

(II)


$\mathrm{ClCH_2{-}C(CH_3){=}CHSO_3H}$

(III)


$\mathrm{ClCH{=}C(CH_3){-}CH_2SO_3H}$

(IV)

If dry gaseous ammonia is passed into a methallyl chloride sulfonation mixture, heat is evolved and precipitation of a mixture of ammonium salts occurs. The gel-like mass cannot be separated from the solvent by centrifuging or filtering, but upon treatment with ethyl or *n*-butyl alcohol the salt can be filtered. Ammonia could be added until the weight of ammonium salts was 40–50% of the theoretical before ammonium chloride began to be formed. Analysis of the ammonium salt mixture for sulfate and halogen, as for the aniline salt, gave results which could be readily correlated with the conclusions reached as to the composition of the aniline salt mixture.

The presence of chloroisobutylenesulfonates in these salt mixtures was confirmed by isolation of their aniline and ammonium salts and preparation of benzylthiuronium salts, a sulfonamide, a phenoxy derivative, and an isobutylenedisulfonate, all of which analyzed for salts or other derivatives of a chloroisobutylenesulfonic acid, $C_4H_7ClSO_3$.

The aniline and ammonium salts obtained by fractional crystallization both gave tests for halide when their aqueous solutions were warmed with silver nitrate solution indicating that they have either structure II or III. Samples of each salt were obtained, however, which on oxidation with potassium permanganate gave no test for sulfate ion indicating that they are salts of II and not III. There is evidence, nevertheless, that salts of III are present in the original salt mixture. Thus, oxidation of the ammonium salt mixture with potassium permanganate converts about 20% of the sulfonate sulfur to sulfate. This indicates that III may constitute as much as 25% or more of the chloroisobutylenesulfonates.[7] The presence of the salts of IV is suggested by the fact that digestion of either the aniline or ammonium salt mixtures at 100° in aqueous solutions acidified with nitric acid and in the presence of silver nitrate liberates only about 65% of the total halogen present. This must mean that about 35% of the chlorine is present in an inert form, presumably in the salts of IV. No salts or other derivatives of IV have as yet been isolated, however. These results indicate that the relative amounts of the salts of II, III and IV present in the mixture are roughly 40, 25 and 35%.

Beautifully crystalline benzylthiuronium salts of chloroisobutylenesulfonic acids could be obtained directly from the ammonium or aniline salt mixtures. From the ammonium salt mixture two apparently different salts were thus obtained, but it seems doubtful that the isomeric salts were prepared in an entirely pure state. Both salts gave a positive test for active halogen, and were further shown to correspond in structure to salts of II or III rather than IV by comparison with a synthetic sample of the benzylthiuronium salt of IV.

By treatment of the mixture of ammonium salts with phosphorus pentachloride or phosphorus oxychloride, followed by ammonia, a sulfonamide, $C_4H_8O_2SNCl$, was obtained. Since this derivative was found not to be identical with a synthetic sample of the sulfonamide of IV, it must be a derivative of II or III. Ozonolysis of this sulfonamide of II or III in glacial acetic acid solution gave only 2% of the theoretical amount of formaldehyde indicating the absence of a

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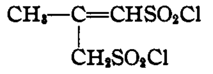
(7) Ethylenesulfonic acid gives a quantitative yield of sulfate ion on oxidation (Kohler, *Am. Chem. J.*, **20**, 680 (1898)), but tests on the few other alpha-beta unsaturated sulfonates available indicate that this quantitative oxidation is not general, the amount of sulfate formed sometimes being as low as 65%. The formation of sulfate ion on oxidation with permanganate has thus far proved to be a valid qualitative test for distinguishing between alpha-beta and other unsaturated sulfonates, however.

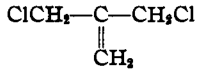
terminal methylene group in the compound. During the ozonolysis about 40% of the theoretical amount of sulfate ion was formed showing that the sulfonamide must correspond to structure III. The presence of the salt of III in the sulfonation mixture is thus confirmed.

Attempts to further confirm the presence of II and III and to determine the relative amounts of each present through derivatives formed by replacement of the chlorine atom have not been conclusive because of the rearrangement of double bonds during the formation of these derivatives. Thus it was found that heating the ammonium chloroisobutylenesulfonate mixture with sodium sulfite in aqueous solution, and treatment of the salt thus obtained with phosphorus pentachloride gave 2-methylpropene-1,3-disulfonyl chloride, V, in small yields. Of the three isomeric ammonium chloroisobutylenesulfonates present, only the salt of III could give rise to V in this series of reactions if no shift of the double bond took place. It was found, however, that V could also be obtained from 2-chloromethyl-3-chloro-1-propene, VI, by its reaction with two moles of sodium sulfite followed by treatment of the residue with phosphorus pentachloride. That the structure of the product did actually correspond to V and not to the alternate structure VII was shown by the fact that treatment of the compound in question with ozone gave no formaldehyde, but did give 82% of the theoretical amount of sulfate ion assuming that one sulfonate group is removed in the oxidation.[8] In contrast with this behavior sodium 2-methyl-2-propene-1-sulfonate, VIII, for example, gives a 69% yield of formaldehyde, as determined by its formaldimethone derivative, and only 9% of the theoretical amount of sulfate ion. Therefore an allylic shift of the double bond must have occurred either in preparing the disulfonate IX (or X) from VI, or in the conversion of this disulfonate to the disulfonyl chloride. That the rearrangement actually occurred in the sodium sulfite treatment of VI was shown by the identity of a benzylthiuronium salt prepared from this product with the benzylthiuronium salt prepared from the dioxane salt of X.[4a,9] The ease with which this rearrangement occurs indicates that either the ammonium salt of II or III could give rise to 2-methylpropene-1,3-disulfonyl chloride in the reaction with sodium sulfite and subsequent reaction with phosphorus pentachloride.



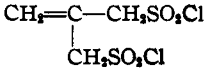
$CH_3-\underset{\substack{|\\ CH_2SO_2Cl}}{C}=CHSO_2Cl$

(V)



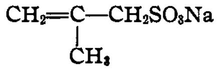
$ClCH_2-\underset{\substack{\|\\ CH_2}}{C}-CH_2Cl$

(VI)



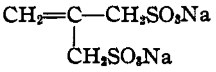
$CH_2=\underset{\substack{|\\ CH_2SO_2Cl}}{C}-CH_2SO_2Cl$

(VII)



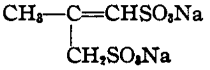
$CH_2=\underset{\substack{|\\ CH_3}}{C}-CH_2SO_3Na$

(VIII)



$CH_2=\underset{\substack{|\\ CH_2SO_3Na}}{C}-CH_2SO_3Na$

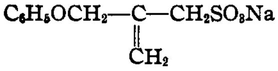
(IX)



$CH_3-\underset{\substack{|\\ CH_2SO_3Na}}{C}=CHSO_3Na$

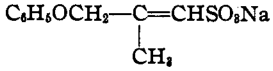
(X)

Treatment of the ammonium salt mixture so as to replace the chlorine atom in the salts of II or III by a phenoxy group leads to an interesting derivative, but again the rearrangements occurring during the formation of the derivative make this reaction of little value in determining the relative amounts of II, III and IV. Treatment of the ammonium salt mixture with phenol and an excess of sodium hydroxide gave about a 20% yield of a crystalline phenoxy derivative which was at first assumed to be XI or XII.



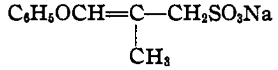
$C_6H_5OCH_2-\underset{\substack{\|\\ CH_2}}{C}-CH_2SO_3Na$

(XI)



$C_6H_5OCH_2-\underset{\substack{|\\ CH_3}}{C}=CHSO_3Na$

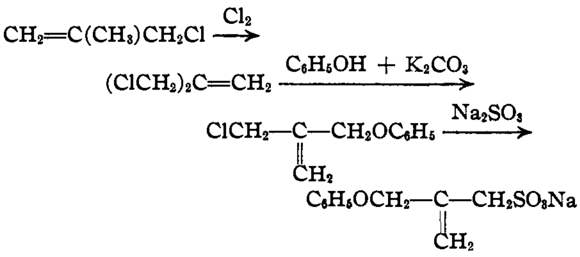
(XII)



$C_6H_5OCH=\underset{\substack{|\\ CH_3}}{C}-CH_2SO_3Na$

(XIII)

Oxidation with permanganate gave no sulfate ion, eliminating structure XII. However, oxidation of a compound with structure XI should give a keto sulfonate, $C_6H_5OCH_2COCH_2SO_3Na$, which with alkali would undergo cleavage to sodium methanesulfonate and sodium phenoxyacetate, but such products were not obtained. The phenoxy compound XI was then synthesized independently by the following steps.



$$CH_2=C(CH_3)CH_2Cl \xrightarrow{Cl_2} (ClCH_2)_2C=CH_2 \xrightarrow{C_6H_5OH\ +\ K_2CO_3} ClCH_2-\underset{\substack{\|\\ CH_2}}{C}-CH_2OC_6H_5 \xrightarrow{Na_2SO_3} C_6H_5OCH_2-\underset{\substack{\|\\ CH_2}}{C}-CH_2SO_3Na$$

This phenoxy compound was not identical with the one obtained from the ammonium salts, the

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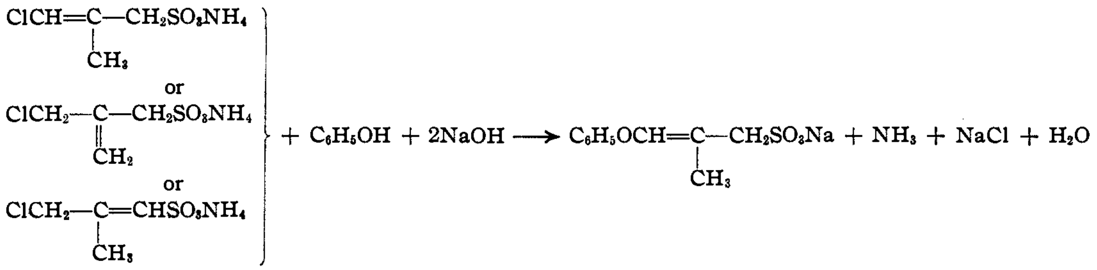
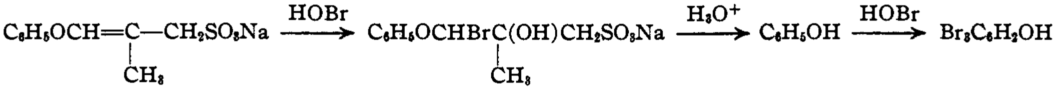
(8) See also reference (4a) in regard to the structure of this compound.

(9) We are indebted to Dr. E. C. Campaign of this Laboratory for a sample of this benzylthiuronium salt.



$$\left.\begin{array}{c} ClCH{=}\underset{CH_3}{\underset{|}{C}}{-}CH_2SO_3NH_4 \\ \text{or} \\ ClCH_2{-}\underset{CH_2}{\underset{\|}{C}}{-}CH_2SO_3NH_4 \\ \text{or} \\ ClCH_2{-}\underset{CH_3}{\underset{|}{C}}{=}CHSO_3NH_4 \end{array}\right\} + C_6H_5OH + 2NaOH \longrightarrow C_6H_5OCH{=}\underset{CH_3}{\underset{|}{C}}{-}CH_2SO_3Na + NH_3 + NaCl + H_2O$$



$$C_6H_5OCH{=}\underset{CH_3}{\underset{|}{C}}{-}CH_2SO_3Na \xrightarrow{HOBr} C_6H_5OCHBr\underset{CH_3}{\underset{|}{C}}(OH)CH_2SO_3Na \xrightarrow{H_3O^+} C_6H_5OH \xrightarrow{HOBr} Br_3C_6H_2OH$$

melting points, solubilities and melting points of derivatives differing greatly. Furthermore, on oxidation and treatment of the product with alkali, phenoxyacetic acid *was* formed. Even more conclusively ozonization gave a 45% yield of formaldehyde determined as formaldimethone. The phenoxy compound obtained from the ammonium chloroisobutylenesulfonates was then shown to have the vinyl structure XIII by treatment with bromine in aqueous solution. A 90% yield of tribromophenol resulted. No tribromophenol was obtained when the compound with structure XI was brominated. Heating the phenoxy compound XI with aqueous alkali resulted in the formation of XIII indicating further the relationship between these isomers, and confirming the assigned position of the carbon–sulfur linkage in the chloroisobutylenesulfonates. There is evidence indicating that XIII could have been formed from the ammonium salt of IV as well as from II or III, for treatment of a synthetic sample of the sodium salt of IV with an equivalent amount of sodium phenoxide in aqueous solution gives a mixture of phenoxy derivatives of which about 40% is XIII, judging from the amount of tribromophenol formed on treatment with bromine water. Some of XII is also present in the mixture from the appreciable test for sulfate ion given after oxidation with potassium permanganate.

It was necessary to explain one further observation. Ozonization of the phenoxy compound XIII gave a 33% yield of formaldehyde. However, in this reaction the salt was heated with glacial acetic acid to get it partially dissolved before ozone was added. It seems likely that this treatment is conducive to migration of the olefin linkage, especially in view of the fact that XIII and also sodium 2-methyl-2-propene-1-sulfonate when heated in glacial acetic acid for fifteen minutes rearrange partially to the vinyl compounds as indicated by the formation of sulfate ion on oxidation after, but not before, this treatment.

Although no method is as yet available to determine the equilibrium amounts of alpha-beta and beta-gamma unsaturated sulfonates, some qualitative observations on the rearrangement of some beta-gamma unsaturated sulfonates have been made which it is believed may be indicative of the behavior of these compounds. Although too few compounds have been studied to give much exactness to the statement, it seems that, in contrast to beta-gamma unsaturated carboxylic acids,[10] the rearrangement of beta-gamma unsaturated sulfonates to the corresponding alpha-beta isomers takes place only slowly and to a limited extent. Although there seems to be no marked tendency for this rearrangement to take place, the double bonds in beta-gamma sulfonates are nonetheless mobile as is illustrated by the behavior of the phenoxy derivatives described in this paper. Sodium 2-methyl-2-propene-1-sulfonate, as reported by Suter, Archer and Malkemus,[4b] shows little tendency to rearrange to the alpha-beta isomer, but the fact that some rearrangement does occur is indicated by the formation of small amounts of sulfate ion on oxidation *after* heating with 5% alkali, and by the formation of about 9% of the theoretical amount of sulfate ion on ozonolysis in glacial acetic acid solution. Substitution of a chlorine atom in the terminal methylene group markedly affects the tendency toward rearrangement. Thus sodium 1-chloro-2-methyl-1-propene-3-sulfonate rearranges readily in 5% alkali as evidenced by the liberation of appreciable amounts of chloride ion in a few minutes of heating at 100°. The

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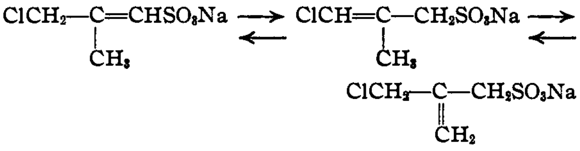
(10) Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 819.

rearrangement proceeds very slowly, however, in acid or neutral solution in the presence of silver nitrate, or in slightly alkaline solution (sodium sulfite or sodium acetate). It seems unlikely that the easy rearrangement of this compound can be attributed to a tendency to form a more stable alpha-beta isomer for the product formed in the presence of phenoxy ion consists of about 40% of XIII and the remaining product probably contains XI as well as XII. It seems more probable that the rearrangement in alkaline solution is readily effected because the equilibrium shown above is shifted either to the right or to the left by the rapid replacement of the chlorine atom by hydroxyl. Evidently this equilibrium is established only very slowly in absence of a high concentration of hydroxyl ions for otherwise the rearrangement would also occur in acid or neutral solution in the presence of silver nitrate.



$$ClCH_2\text{—}\underset{|\atop CH_3}{C}{=}CHSO_3Na \rightleftarrows ClCH{=}\underset{|\atop CH_3}{C}\text{—}CH_2SO_3Na \rightleftarrows ClCH_2\text{—}\underset{\|\atop CH_2}{C}\text{—}CH_2SO_3Na$$

The unsaturated disulfonate IX must contain a very mobile double bond for the formation of the sodium salt of X from VI by reaction with sodium sulfite exhibits an allylic rearrangement of the double bond under only mildly alkaline conditions. The product of this rearrangement is the sulfur analog of β-methylglutaconic acid, a compound which is well known to contain an especially mobile system.

The sulfonation of methallyl chloride with sodium chlorosulfonate[6] gives about a 40% yield of sulfonation product which, from the few observations made, is evidently similar to the product obtained with dioxane sulfotrioxide. Thus Archer was able to prepare the disulfonyl chloride V from this product, and it gives XIII on treatment with sodium hydroxide and phenol.

The sulfonation of methallyl chloride with a solution of sulfur trioxide in ethylene chloride gives somewhat different results than does dioxane sulfotrioxide in that, if the sulfur trioxide solution is added to the olefin, addition to the olefin bond is the chief reaction, almost to the exclusion of substitution, and β-chloromethyl-β-methylethionic anhydride, I, crystallizes from the reaction mixture in about 50% yield. This compound is of particular interest in two respects. Although many olefins have been sulfonated by one means or another since the discovery of carbyl sulfate, no other compound of this type seems to have been isolated in a state of purity.

Furthermore, I is, in effect, an anhydride of a tertiary alkyl ester of sulfuric acid and no tertiary ester of sulfuric acid is known. Its properties were therefore studied with some care.

The anhydride decomposes slowly at room temperature even when kept in a vacuum desiccator. At −5°, however, it may be kept over long periods with apparently little decomposition. Hydrolysis of I with water gave an acidic solution and a compound saturated to bromine and permanganate. Titration of the solution with standard alkali gave a neutral equivalent somewhat low for the compound $ClCH_2\text{-}C(CH_3)(OSO_3H)\text{-}CH_2SO_3H$, and sulfate ion was present, hence the tertiary ester linkage is readily cleaved. Digestion on the steam-bath followed by addition of barium chloride gave the theoretical amount of barium sulfate. Alkaline hydrolysis, however, produces a highly unsaturated substance, and spontaneous decomposition of I by standing in the air also gives an unsaturated material. When the anhydride was heated with phenol and an excess of alkali the unsaturated phenoxy compound XIII, $C_6H_5OCH{=}\underset{|\atop CH_3}{C}\text{—}CH_2SO_3Na$, was formed.

Experimental

Sulfonation of Methallyl Chloride with Dioxane Sulfotrioxide.—To 170 ml. (1.73 moles) of methallyl chloride in 90 ml. of ethylene chloride at 0° was added with stirring a suspension of dioxane sulfotrioxide[4] in 300 ml. of ethylene chloride equivalent to 170 g. (2.13 moles) of sulfur trioxide. The rise in temperature during this addition was negligible, and a clear light-yellow solution resulted. This stock solution was used in the preparation of the aniline and ammonium salts. Treatment of a little of this solution with a dilute solution of barium hydroxide at 0° caused the immediate formation of chloride ion.

Formation of the Aniline Salts.—To 100 ml. of the sulfonation mixture was added gradually 40 ml. of aniline (about 3 moles of aniline for every 2 moles of sulfur trioxide). Heat was evolved, and after the first few portions had been added a salt began to separate. Two hundred milliliters of ether was added, and the light-yellow aniline salt mixture was collected on a filter and washed with further portions of ether. The yield was almost quantitative. The salt mixture was readily soluble in water giving a clear light-yellow solution. Addition of silver nitrate solution gave no immediate turbidity showing the absence of aniline hydrochloride; on warming a copious precipitate of silver chloride was formed. The salt melted over a wide range from about 130–145°. The following analyses were run on the mixture: total chloride, 10.8%; sulfate after acid digestion (as SO_3), 5.5%; chloride precipitated by digestion on the steam-bath for twelve hours in the presence of silver nitrate, 6.3%; neutral equivalent, 242, 245; total SO_3, 30.1%. Fractional crystallization of the aniline salt mixture from chloroform was partially successful. The residue from extraction with chloroform was found to contain anilinium sulfate, and from the soluble fraction there was also obtained a crystalline product. This material was crystallized once more from chloroform and then twice from acetone. From the latter solvent the salt separates as long transparent needles, m. p. 185–195° with decomposition.

Anal. Calcd. for $C_{10}H_{14}O_3NClS$: n. e., 263.5. Found: n. e., 259, 259. The solutions obtained from the neutral equivalent determinations were evaporated to dryness to obtain the sodium salt. An aqueous solution of the latter gave no sulfate ion on oxidation with permanganate, showing that the product was free of the salt of III. The aniline salt gave a test for halogen on warming with silver nitrate, showing that it is the aniline salt of II, rather than IV (it is possible that the salt is contaminated with IV, however).

In view of the ready solubility of the aniline salt mixture in water it seems unlikely that diphenylsulfamide, which has been reported to be only slightly soluble in water,[11] can be present in more than very small amounts. No more than a trace of a disulfonate can be present or the percentage of sulfur trioxide in the salt would be much higher than the observed value. On the whole all our results are consistent with the view that the halogen content represents approximately the amount of anilinium chloroisobutylenesulfonates and that the amount of sulfate formed by acid digestion represents the amount of anilinium sulfate and anilinium phenylsulfamate present in the mixture.

The aniline salt mixture from neutralization of a sulfonation in which the methallyl chloride was *added to* the dioxane sulfotrioxide gave analyses almost identical with those shown for the aniline salt mixture above. Thus: total chloride, 10.7%; sulfate after acid digestion (as SO_3), 5.5%; total SO_3, 29.7%; chloride precipitated by digestion on the steam-bath for twelve hours in the presence of silver nitrate, 6.6%. The reversal of the mode of addition of the methallyl chloride and dioxane sulfotrioxide therefore had little effect on the nature of the product.

Reaction of β-Chloromethyl-β-methylethionic Anhydride, I, with Excess Aniline.—Two grams of the crystalline anhydride dissolved in 100 ml. of chloroform was treated with 7 ml. of aniline. The mixture was allowed to stand overnight, and the small amount of salt that separated collected on a filter. There was thus obtained 0.5 g. of colorless product. Recrystallized from alcohol the material separated as fine needles, stable at 250° in a melting point bath. The crystalline material was moderately soluble in water and its aqueous solution gave a copious precipitate when treated with barium chloride solution. These properties are consistent with those of anilinium sulfate.

Anal. Calcd. for $C_{12}H_{16}N_2SO_4$: n. e., 142.1. Found: n. e., 143.0, 142.6. On standing 0.15 g. more of solid material separated from the solution. This material differed from the anilinium sulfate first isolated in that it was very readily soluble in water and gave only a slight test for sulfate with barium chloride solution; warming the solution caused a heavy precipitate of barium sulfate. The neutral equivalent of this material was 230. It melted and then seemed to evaporate from the melting point tube at 148–150°, and gave no test for halide when heated with silver nitrate solution. These properties, except the neutral equivalent, are consistent with what might be expected of anilinium phenylsulfamate (n. e., 266), but this salt was undoubtedly contaminated with some anilinium sulfate. Complete evaporation of the chloroform left a red oil from which no solid material has as yet been obtained.

Formation of Ammonium Salts.—When dry gaseous ammonia was passed into a portion of the sulfonation mixture, heat was evolved and a solid salt soon began to separate. After one-half to one hour the contents of the flask were practically solid and the ammonia was being taken up but slowly. The solid material could not be separated from the solvent by filtration or centrifuging, but if the whole was dissolved in hot ethyl or *n*-butyl alcohol, a colorless ammonium salt was obtained on cooling which could be collected on a filter. The yields of this salt depended on the length of time the ammonia was passed in, but if the addition was continued over a period of much over one hour, ammonium chloride began to be formed. The maximum yield of product free of ammonium chloride was about 55%. The ammonium salt was very soluble in water. The aqueous solution gave no immediate precipitate with silver nitrate, showing that no ammonium chloride was present, but on warming the solution a copious precipitate of silver chloride was obtained. Further qualitative tests showed that the aqueous solution contained sulfate ion and was very unsaturated to permanganate solution or bromine water. The composition of the mixture was indicated by the following analyses: total chloride, 17.8. 18.1%; sulfate (as ammonium sulfate), 3.5, 3.8%; sulfate after oxidation with permanganate (as ammonium salt of III), 20.3%; chloride formed on digestion on steam-bath in the presence of silver nitrate, 11.9%. These analyses are consistent with the view that this mixture consists chiefly of ammonium chloroisobutylenesulfonates, ammonium sulfate, and probably a little ammonium sulfamate. Apparently a relatively high proportion of the ammonium sulfamate remains in the solvent, so that about 95% of the salt mixture is made up of the ammonium chloroisobutylenesulfonates. As with the aniline salts, about 65% of the total chloride was precipitated by digestion with silver nitrate, indicating that about 35% of the chloroisobutylenesulfonates corresponds to the ammonium salt of IV. The ammonium salt does not give a crystalline product readily from any of the solvents tried, but a sample crystallized twice from *n*-butyl alcohol, once from dioxane–water, and finally once again from *n*-butyl alcohol seemed to be reasonably pure. The sample of salt thus obtained was not contaminated with sulfate and gave no sulfate ion on oxidation so it was free of ammonium sulfate and the ammonium salt of III. An aqueous solution heated with silver nitrate gave an appreciable precipitate of silver chloride, indicating that the compound was a salt of II (small amounts of the ammonium salt of IV may be present, however).

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[11] Audrieth, Sveda, Sisler and Butler, *Chem. Rev.*, **26**, 49 (1940).

Anal. Calcd. for $C_4H_{10}O_3NClS$: N, 7.47. Found: N, 7.59.

Preparation and Properties of Sodium 1-Chloro-2-methyl-1-propene-3-sulfonate.—Chlorination of methallyl chloride at room temperature yields, along with the addition product, a fraction boiling at 132°, which has been shown to contain about equal parts of 2-chloromethyl-3-chloro-1-propene and 1,3-dichloro-2-methyl-1-propene.[12] Twenty-four grams of this dichloride fraction was refluxed and stirred for two hours with a solution of 36 g. of sodium sulfite dissolved in 100 ml. of water. The hot solution was filtered and allowed to cool slowly. About 11 g. of crystalline material separated, which proved to be mostly sodium 1-chloro-2-methyl-1-propene-3-sulfonate. This material was separated from the disulfonate and inorganic salts by crystallization from 95% alcohol. Four grams of pure sodium salt was thus obtained, decomp. 305–310°. *Anal.* Calcd. for $C_4H_6ClSO_3Na$: Na, 11.94. Found: Na, 11.83. Only a trace of silver chloride was formed when either a neutral or acidic aqueous solution of the salt was heated with silver nitrate, but if the salt was heated in 5% sodium hydroxide solution, and after acidification with nitric acid, silver nitrate was added, appreciable amounts of silver chloride were formed. This behavior indicates that the salt is a vinyl chloride. Oxidation with potassium permanganate in the cold gave no sulfate ion, but appreciable amounts of chloride ion, again pointing to a vinyl chloride, and not a vinyl sulfonate. After treatment with alkali some vinyl sulfonate was present, for oxidation with permanganate now gave sulfate ion (there was no cleavage of the sulfonate linkage on heating with alkali). The rearrangement does not take place readily in slightly alkaline solution (sodium acetate solution) or in glacial acetic acid solution, as shown by the absence of chloride ion in these solutions after heating for fifteen minutes.

Evaporating the original reaction mixture gives further quantities of solid material from which more sodium 1-chloro-2-methyl-1-propene-3-sulfonate was obtained by alcoholic extraction. The insoluble portion was used in the preparation of 2-methylpropene-1,3-disulfonyl chloride.

The benzylthiuronium salt of 1-chloro-2-methyl-1-propene-3-sulfonic acid was prepared in the usual manner. This derivative melted sharply at 76–78°; but further crystallization from 50% alcohol widened this melting point range. After three recrystallizations from 50% alcohol a sample was obtained which separated on slow cooling as large plates. This sample melted when an attempt was made to dry it in an Abderhalden drying pistol at 56°, but when dried over phosphorus pentoxide at room temperature melted sharply at 123.5–125°. *Anal.* Calcd. for $C_{12}H_{17}O_3N_2ClS$: N, 8.32. Found: N, 8.67.

Treatment of sodium 1-chloro-2-methyl-1-propene-3-sulfonate with phosphorus pentachloride gave the sulfonyl chloride, which was treated (without purification) with ammonia in chloroform solution to give the sulfonamide. The sulfonamide came out as a yellow oil, but when the solution was allowed to stand in the icebox, crystals formed. After two crystallizations from benzene the derivative melted at 68–69°. A sample gave no test with boiling aqueous-alcoholic silver nitrate. *Anal.* Calcd. for $C_4H_8O_2NClS$: N, 8.26. Found: N, 8.26.

Benzylthiuronium Salts.—The ammonium salt mixture yielded a beautifully crystalline benzylthiuronium salt which, however, melted over a wide range from 72–90°. Samples of this salt recrystallized from alcohol came out as beautiful plates, but still melted over a wide range. From chloroform or benzene the salt separated as fine needles, m. p. 107–109°. A sample of this higher melting material recrystallized from 50% alcohol again showed the wide melting range of the original sample, but when dried under vacuum for five hours melted from 103–105°. Apparently hydrates of the salts were responsible for the wide melting point range. For analysis the sample was crystallized once from 50% alcohol, then from chloroform, and finally twice more from 50% alcohol. The final crystals were very large flat plates, m. p. (after drying) 103–105°. *Anal.* Calcd. for $C_{12}H_{17}O_3N_2ClS_2$: N, 8.32. Found: N, 8.18.

A benzylthiuronium salt prepared from the second crop obtained in the crystallization of the ammonium salt from *n*-butyl alcohol exhibited somewhat different properties on melting. Like the first salt it crystallized beautifully from 50% alcohol and melted over a wide, albeit somewhat higher, range, m. p. 82–120°. After drying, the material melted at 123–128°. The sample for analysis was crystallized three times from 50% alcohol. *Anal.* Calcd. for $C_{12}H_{17}O_3N_2ClS_2$: N, 8.32. Found: N, 8.08.

A mixture of the two salts melted at 110–119°. Benzylthiuronium salts prepared from subsequent samples of ammonium salt or from the aniline salts were found to have, after drying, melting points intermediate between those mentioned above with ranges of three to five degrees. Mixtures of any two of the salts were furthermore found to melt at temperatures intermediate between those of the salts in question. From these data it seems probable that the isomeric benzylthiuronium salts form mixed crystals, and it is doubtful that either of the salts analyzed was entirely free of the other. Both salts gave a test for halide when heated with aqueous silver nitrate. A synthetic sample of the benzylthiuronium salt of IV was found to melt sharply at 123–124.5°. A mixture of this sample with the sample melting at 123–128° melted at 105–113°.

3-Chloro-2-methyl-1-propene-1-sulfonamide.—The sulfonamide was made by treating the dried ammonium salt mixture with phosphorus pentachloride or phosphorus oxychloride and an ether solution of the resulting sulfonyl chloride treated (without purification) with ammonia. Addition of petroleum ether gave a turbid solution which after several days in the icebox gave nice crystalline needles, m. p. 64–72°. After two recrystallizations from benzene the sulfonamide melted at 75.5–77°. *Anal.* Calcd. for $C_4H_8O_2NClS$: N, 8.26. Found: N, 8.17.

The sulfonamide gave a test for chloride with alcoholic silver nitrate indicating that it was either a derivative of II or III. A mixed melting point with a synthetic sample of the sulfonamide of IV (m. p. 68–69°) was found to be 49–56°, thus definitely eliminating this structure for the sulfonamide. Ozonolysis in glacial acetic acid solution of 218 mg. of the sulfonamide gave only 7 mg. (2% of the theoretical) of the dimethone derivative of formaldehyde, m. p. and mixed m. p. with an authentic sample, 189–191°. Digestion of the filtrate from collecting the dimethone derivative in acid solution in the presence of barium chlo-

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[12] Burgin, Hearne and Rust, *Ind. Eng. Chem.*, **33**, 385 (1941).

ride gave about 40% of the theoretical amount of barium sulfate.

Preparation of 2-Methylpropene-1,3-disulfonyl Chloride, V, from the Ammonium Salts.—Ten grams of the ammonium salt mixture and 10 g. of sodium sulfite were dissolved in about 50 ml. of water, and the resulting solution refluxed for twenty-four hours. The salts were precipitated by adding a large volume of alcohol, and were then dried thoroughly at 110°. The dried salts were refluxed with 15 ml. of phosphorus oxychloride for seven hours and then poured into water. After a short time the aqueous mixture was extracted with chloroform. After drying over sodium sulfate, the chloroform was evaporated down somewhat and petroleum ether added. On cooling 0.55 g. of almost colorless needles separated, m. p. 78–79°. A mixture of this sample with an authentic sample of V previously prepared by Suter and Malkemus[4a] melted at 78–79°.

2-Methylpropene-1,3-disulfonyl Chloride from 2-Chloromethyl-3-chloro-1-propene, VI.—The alcohol insoluble residue obtained in the preparation of sodium 1-chloro-2-methyl-1-propene-3-sulfonate was dried in an oven at 100°. Five grams of this residue was then ground in a mortar with 8 g. of phosphorus pentachloride. The mixture was then heated on the steam-bath for twenty-four hours, and the dark material thus obtained added to ice water. The aqueous mixture was extracted with chloroform and the chloroform extract dried over sodium sulfate. Evaporation of the chloroform and addition of petroleum ether gave 1.1 g. (about 33% over-all yield from methallyl chloride) of long needles, m. p. 78.5–80°. A mixed melting point of this sample with an authentic sample of V previously prepared by Suter and Malkemus[4a] showed no depression. To make sure that this disulfonyl chloride was a derivative of X rather than of IX its reaction with ozone was investigated. The previous evidence for distinguishing between these structures[4a] was based solely on the fact that the disulfonate obtained in the sulfonation of isobutylene gave sulfate ion on oxidation, which the allyl sulfonate, IX, would not be expected to do. The formation of this disulfonyl chloride from 2-chloromethyl-3-chloro-1-propene pointed, however, to a derivative of IX assuming no rearrangements. Further substantiation of structure V for the disulfonyl chloride was therefore deemed necessary. For this purpose a 0.500-g. sample of V was dissolved in 45 ml. of acetic acid and a rapid stream of ozone passed through the solution for one hour. The solution was then poured into water and after standing for two hours the acid was neutralized with 10% sodium hydroxide. The neutral solution was divided into two portions, and to one was added 0.25 g. of methone dissolved in 5 ml. of alcohol. No derivative separated. About 10 ml. of 5% barium chloride solution was added to the other portion and the amount of barium sulfate determined. The yield of barium sulfate was 82% of the theory assuming that one of the sulfonate groups was cleaved off by the ozone. In contrast with this behavior sodium 2-methyl-2-propene-1-sulfonate, a compound with a terminal double bond and no vinyl sulfonate linkage, gives a 69% yield of formaldimethone and only 9% of the theoretical amount of barium sulfate.

Benzylthiuronium Salt of 2-Methylpropene-1,3-disulfonic Acid.—One gram of the residue containing the disulfonate was used for the preparation of a benzylthiuronium salt. After two crystallizations from 50% alcohol this derivative melted over a range from about 126–131° with sintering before this point. After drying under vacuum at 100° for several hours, however, it melted sharply at 157–158°. A benzylthiuronium salt prepared from the dioxane salt of 2-methylpropene-1,3-disulfonic acid[4a,9] melted at 139–141°, but a mixture of the two salts melted sharply at 157–158°. A sample of the low melting solid was dissolved in 50% alcohol and the cooled solution seeded with a little of the higher melting salt. The crystalline salt thus obtained, after drying for several hours at 100° under vacuum, melted sharply at 158–159°. This is evidently an example of the formation of dimorphous crystals.

Sodium 2-Methyl-3-phenoxy-2-propene-1-sulfonate, (XIII)

(1) **From the Ammonium Salt Mixture.**—Twenty grams of the ammonium salt mixture was dissolved in 25 ml. of water and to this solution was added 10 g. of phenol dissolved in 35 ml. of 33% sodium hydroxide solution. After refluxing this solution for about one hour a crystalline salt began to separate. After refluxing for three hours, the solution was diluted to about twice its original volume and the crystalline salt collected on a filter. The filtrate was acidified, extracted twice with ether, and then evaporated down until solid began to separate. The two batches of crystals were combined and recrystallized from water. The salt is only slightly soluble in 95% alcohol. In all about 5.5 g. of crystalline phenoxy derivative was obtained, about a 20% yield. For analysis the salt was crystallized three times from distilled water. From this solvent it separates as either long needles or flat plates. On heating, the salt darkens slightly up to 340° and decomposes for the most part at 345–350°. *Anal.* Calcd. for $C_{10}H_{11}O_4SNa$: S, 12.80. Found: S, 13.36.

The benzylthiuronium salt was prepared in the usual manner, m. p. 145–146°. *Anal.* Calcd. for $C_{18}H_{22}O_4N_2S_2$: N, 7.11. Found: N, 7.27, 7.11.

(2) **From β-Chloromethyl-β-methylethionic Anhydride (I).**—Ten grams of the anhydride (crude) was added to a solution of 3.7 g. of phenol and 6.4 g. of sodium hydroxide. This mixture was heated on the steam-bath for about two hours. The solid which had separated during this time was filtered off, but qualitative tests indicated that it consisted chiefly of sodium sulfate. After digesting overnight a second crop was collected, which was shown by qualitative tests to be a phenoxy derivative contaminated with sodium chloride and large amounts of sodium sulfate. Recrystallization of this second crop from about 12 ml. of water gave a crystalline material only slightly contaminated with inorganic salts. On heating in a melting point bath it showed only slight darkening up to 335°, and decomposed for the most part from 340–345°. The benzylthiuronium salt prepared from 0.25 g. of this salt, after two crystallizations from 50% alcohol, melted at 145–146.5°, and showed no depression in melting point when mixed with a sample of the benzylthiuronium salt described above. Some further amounts of phenoxy derivative were obtained in succeeding crops, but these were contaminated with inorganic salts and were not further purified.

(3) **From the Sulfonation Product Formed from Methallyl Chloride and Sodium Chlorosulfonate.**—Sulfonation

of methallyl chloride was carried out with sodium chlorosulfonate as described by Archer[6] and the solid material obtained was extracted with 95% alcohol. Only a small amount of alcohol soluble material was obtained, but reaction of this material with sodium phenoxide gave a small yield of a phenoxy derivative, which from qualitative tests and its decomposition point (345–350°), was identical with compound (XIII).

Ozonization of Sodium 2-Methyl-3-phenoxy-2-propene-1-sulfonate (XIII).—A 0.25-g. sample of XIII was heated on the steam-bath for fifteen minutes with 25 ml. of glacial acetic acid. About one-third of the solid did not dissolve so 10 ml. more of acetic acid was added; the amount of solid remaining undissolved did not change appreciably. A rapid stream of oxygen containing about 6% of ozone was passed through the solution for twenty minutes. The solid did not dissolve during this time, so the reaction was stopped and the reaction vessel shaken to effect solution. The ozone–oxygen mixture was passed in for fifteen minutes longer, and then the solution poured into about 35 ml. of warm water and this solution was allowed to stand for an hour. The solution was then neutralized with 15% sodium hydroxide, heated on the steam-bath, and 0.5 g. of methone (dimethyldihydroresorcinol) in 10 ml. of alcohol was added. The derivative separated after a few seconds and after an hour was collected in a sintered glass crucible. After drying in a vacuum desiccator the colorless derivative weighed 0.093 g., which corresponds to a 33% yield of formaldimethone (assuming one mole of formaldehyde is liberated). The melting point of this crude material was low for formaldimethone, but after one recrystallization from alcohol the derivative melted sharply at 191–192°. The melting point of a mixture of this derivative with a known sample of formaldimethone was also 191–192°.

Aqueous solutions of XIII reduced potassium permanganate rapidly. The amount of sulfate ion formed in these oxidations was negligible since addition of barium chloride, after the solution had been acidified with acetic acid and cleared of manganese dioxide with a drop of 30% hydrogen peroxide, gave no turbidity. When a sample of XIII was heated with glacial acetic acid for about one-half hour to effect solution, and then oxidized with potassium permanganate, sulfate ion is formed as shown by a slight though definite turbidity with barium chloride. Sodium 2-methyl-2-propene-1-sulfonate behaves exactly as does XIII when subjected to similar tests.

Sodium 2-Methyl-3-phenoxy-2-propene-1-sulfonate with Bromine Water.—A 0.5-g. sample of XIII was treated with bromine water until a faint yellow color persisted. The colorless, flocculent precipitate was collected on a filter and washed with water. After drying in a vacuum desiccator the product weighed 0.6 g. and melted after previous sintering at 89–91°. After crystallization from a small amount of petroleum ether (60–90°), the product melted at 92.5–93.5°. A mixed melting point with a known sample of tribromophenol was 92.5–93.5°. The yield of crude product was 90%, of crystalline material 60%.

Sodium 2-(Phenoxymethyl)-2-propene-1-sulfonate, XI.—Forty-two milliliters (48 g. or 0.38 mole) of the dichloride fraction, b. p. 125–137°, obtained in the chlorination of methallyl chloride, was dissolved in 75 ml. of acetone, and 36 g. (0.38 mole) of phenol and 53 g. (0.38 mole) of potassium carbonate were added. This mixture was heated under reflux for twenty-four hours. The mixture was then filtered, and the solid material washed several times with acetone. The acetone was distilled off from the filtrate on the steam-bath. To the liquid remaining was added 24 g. (0.19 mole) of sodium sulfite, and about 100 ml. of water. This mixture was refluxed for seven hours, and then allowed to stand overnight. The crystalline material that separated was collected on a filter. The crystalline product was dissolved in water and the solution extracted twice with ether to remove the water-insoluble material. The water layer was evaporated down, but the salt is so soluble in water that it does not separate out until the solution has been evaporated practically to dryness. About 1.5 g. of product was thus obtained. Evaporation of the water layer of the original reaction mixture (after ether extraction) yields second and third crops of the derivative. In all about 6.2 g. of the crude product was obtained, 13% yield, based on methallyl chloride. The product was recrystallized from 95% alcohol; after three crystallizations it melted at 226–230°. The salt crystallizes as either long needles or shiny plates. *Anal.* Calcd. for $C_{10}H_{11}O_4SNa$: S, 12.80. Found: S, 13.28.

The benzylthiuronium salt was prepared in the usual manner and crystallized several times from 50% alcohol. It melted sharply at 117–118°. *Anal.* Calcd. for $C_{18}H_{22}O_4S_2N_2$: N, 7.11. Found: N, 7.07.

Oxidation of XI with Permanganate.—One gram of XI dissolved in 100 ml. of water was oxidized at 0° with 250–300 ml. of an aqueous solution containing 1.7 g. of potassium permanganate. The mixture was heated to boiling, and then filtered The filtrate was boiled down somewhat, and then allowed to evaporate to dryness on the steam-bath. The brown residue was dissolved in water, the solution acidified with hydrochloric acid, and then extracted twice with ether. The ether layer was dried over sodium sulfate, and then the ether evaporated. An oily residue remained, which crystallized on scratching. The very small amount of solid material thus obtained was found to be slightly soluble in water, but immediately soluble in dilute sodium bicarbonate solution (carbon dioxide was evolved). It melted over a wide range, mostly from 85–95°. Part of the material dissolved in petroleum ether (60–90°). The clear solution was decanted from the residue and on evaporation yielded a few colorless crystalline plates, m. p. 96–98°. A mixture of this material with an authentic sample of phenoxyacetic acid melted at 97–98°.

Ozonization of XI.—A 0.25-g. sample of XI was dissolved in 25 ml. of glacial acetic acid; in contrast with XIII, 0.25 g. of XI dissolves readily in 15 ml. of acetic acid at room temperature. The ozonization was carried out as for XIII. Treatment with methone gave 0.126 g. of formaldimethone, a 45% yield of formaldehyde based on the formation of one mole of formaldehyde.

Reaction of XI with Bromine Water.—A 0.5-g. sample of XI was treated with bromine water until a light yellow color persisted for some time. Only about 0.1 g. of solid was obtained by filtration. This solid was light tan in color and melted over a wide range from about 60–85°. Only part of this material was soluble in petroleum ether (tribromophenol is very soluble in this solvent). Evaporation of the petroleum ether almost to dryness gave a small amount of crystals, which melted at 70–80°. This may be crude tribromophenol, but the amount was insufficient to purify further.

Rearrangement of XI to XIII by Alkali.—A 1.0-g. sample of XI was dissolved in 5 ml. of 10% sodium hydroxide and the mixture digested on the steam-bath for twenty-four hours. The solution was neutralized with hydrochloric acid and evaporated. The solid which crystallized on cooling was collected on a filter and then dried in a vacuum desiccator, dry weight 0.8 g. This salt was dissolved for the most part by refluxing with about 40 ml. of 95% alcohol. On cooling 0.1 g. of a salt separated as fine plates This salt is much higher melting than the starting material, showing no change up to 280°, then gradually darkening until at about 330° it is very dark. With bromine water the salt shows the characteristic behavior of XIII rather than of IX for, from 0.095 g. of the salt, there was obtained 0.11 g. (an 87% yield) of tribromophenol as identified by mixed melting points. The alcohol filtrate from which XIII was obtained was evaporated down to about 20 ml. On cooling a salt separated as long, colorless needles. This salt is evidently unchanged XI contaminated with some XII and probably also some XIII for it melted over a range from about 226–240°, and gave an appreciable test for sulfate ion after oxidation with potassium permanganate. Repetition of this rearrangement gave a further quantity of high melting phenoxy derivative. The benzylthiuronium salt of this material was prepared by dissolving it in about 2 ml. of water and adding this warm solution to 1 ml. of 15% benzylthiuronium chloride solution. The solid thus obtained was recrystallized once from 2 ml. of 95% alcohol. The derivative then melted with slight sintering at 145–146°. When this material was mixed with an equal amount of a sample of the benzylthiuronium salt of the phenoxy derivative XIII the melting point was 145–146°.

Sulfonation of Methallyl Chloride with Sodium Chlorosulfonate.[6]—In a one-liter three-necked flask equipped with a mercury-seal stirrer, a Friedrichs condenser and a dropping funnel was placed 200 ml. of ethylene chloride and 58 g. of sodium chloride. The stirrer was started and 58 g. of practical chlorosulfonic acid was added rapidly. There was a violent evolution of hydrogen chloride and the salt first became gummy and then crystalline again. After one hour of stirring 45 g. (0.5 mole) of redistilled methallyl chloride was added during fifteen minutes. The mixture became warm, turned dark, and hydrogen chloride was evolved. The mixture was heated for six hours to complete the reaction. The solvent was then removed under reduced pressure and the dark residue extracted repeatedly with alcohol. Upon concentrating and cooling the alcohol deposited 38 g. of sodium chloroisobutylenesulfonate, a 40% yield based upon the sodium chlorosulfonate used. A sample was recrystallized twice from alcohol for analysis. *Anal.* Calcd. for $C_4H_6ClO_3SNa$: Na, 11.96. Found: Na, 12.21.

From this sodium chloroisobutylenesulfonate there was obtained by successive treatment with sodium sulfite and phosphorus oxychloride, as already described for the ammonium salt, a small yield of the disulfonyl chloride, V.

Reaction of the sodium chloroisobutylenesulfonate with sodium hydroxide and phenol gave the phenoxy derivative, XIII.

Sulfonation of Methallyl Chloride with Sulfur Trioxide in Ethylene Chloride.—Twenty-four grams of sulfur trioxide was distilled into about 70 ml. of ethylene chloride at room temperature, with slight cooling. The clear and colorless solution thus obtained was cooled to 0° and a solution of 14 ml. of methallyl chloride in 45 ml. of ethylene chloride added over a period of about two hours. The addition was slow enough so that the temperature of the reaction mixture never rose above 0°. The reaction mixture gradually turned dark, but with the addition of the last few drops of olefin suddenly became noticeably lighter due to the sudden deposition of a light-colored solid. The solid material was collected on a filter. It was light tan in color, but contaminated with small amounts of dark colored material; the yield was about 18 grams or 50%. More solid separated when the filtrate was allowed to stand in the cold-room for several days. The solid obtained was soluble in alcohol, chloroform, benzene, or ether, insoluble in petroleum ether, and moderately soluble in ethylene chloride. It was recrystallized from ethylene chloride by gently warming the mixture, decanting the light yellow solution away from the dark-colored insoluble oil always formed, and allowing the solution to cool. The crystalline material thus obtained was only slightly colored; after several recrystallizations it separated as colorless rosets, m. p. 66–68° with decomposition. The solid decomposed slowly on standing at room temperature in a vacuum desiccator, but may be kept for long periods in an ice-box. It dissolved slowly in cold water, rapidly in warm water or cold aqueous alkali. An aqueous solution of the solid had the following properties: (1) very acidic toward litmus, (2) on warming with barium chloride solution a marked turbidity develops, (3) gives no immediate turbidity with silver nitrate solution, but on warming gives an appreciable test for halide, (4) is only very slightly unsaturated to permanganate or bromine water. In contrast to the behavior of the solutions prepared by dissolving the compound in water, the solution resulting from addition of the solid to aqueous alkali was very unsaturated toward permanganate or bromine water. The above properties of the solid isolated, are all consistent with those to be expected of β-chloromethyl-β-methylethionic anhydride. This structure was borne out by analytical tests. A 0.1192-g. sample of the anhydride was dissolved in distilled water and titrated to methyl red with 0.01 *N* sodium hydroxide. The neutral equivalent found was 121.5 as compared to the theoretical value of 126 for $ClCH_2C(CH_3)(OSO_3Na)CH_2SO_3Na$, but the solution was found to contain sulfate ion already, indicating that some of the sulfate ester had been cleaved. Five milliliters of 5% barium chloride solution was then added and the mixture digested on the steam-bath for twenty-four hours, enough alkali being added from time to time to keep the mixture alkaline to phenolphthalein. After this digestion the mixture was acidified with hydrochloric acid and the barium sulfate determined quantitatively. *Anal.* Calcd. for $C_4H_7O_6S_2Cl$: hydrolyzable SO_3, 31.70; Cl, 14.0. Found: hydrolyzable SO_3, 31.70; Cl, 13.7.

Summary

1. The sulfonation of methallyl chloride by dioxane sulfotrioxide gives a complex mixture of products. About 40% of the sulfur trioxide reacts by addition to the double bond to give a cyclic anhydride of the carbyl sulfate type. The remainder reacts by substitution to give three isomeric chloroisobutylenesulfonic acids.

2. In contrast to isobutylene, methallyl chloride is neither polymerized nor disulfonated by the dioxane sulfotrioxide.

3. It has been found that the olefinic linkage in a variety of unsaturated sulfonic acids is mobile in the presence of alkali.

4. The ozonization of 2-methylpropene-1,3-disulfonyl chloride confirmed the structure previously assigned to this compound. An attempt to prepare sodium 2-methylenepropane-1,3-disulfonate was unsuccessful, the double bond shifting into the chain.

5. The sulfonation of methallyl chloride by a solution of sulfur trioxide in ethylene chloride yields chiefly the carbyl sulfate type of compound. The hydrolysis reactions of this were studied in some detail.

6. The sulfonation of methallyl chloride with sodium chlorosulfonate gives a mixture of unsaturated sulfonic acids.

7. Numerous compounds have been prepared from the chloroisobutylenesulfonic acids during attempts to determine their structures.

EVANSTON, ILL. RECEIVED DECEMBER 10, 1942

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Polymerization of Styrene in the Presence of 3,4,5-Tribromobenzoyl Peroxide

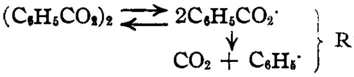
BY CHARLES C. PRICE AND BRYCE E. TATE

Samples of polystyrene, prepared by heating solutions of styrene and 3,4,5-tribromobenzoyl peroxide in benzene and purified by repeated reprecipitation from ether or dioxane by pouring into alcohol have been found to contain as much as 15% bromine. On the basis of the average molecular weights of the samples, as measured repeatedly by both the cryoscopic and viscometric methods, the bromine content of each sample corresponded to approximately one tribromophenyl radical per polymer molecule.

Since the polymers were of relatively low molecular weight, in the range of one to three thousand, fairly reliable estimates of the molecular weight were obtained by cryoscopic determinations, using *p*-nitrotoluene and, in a few instances, benzophenone for the solvent. These cryoscopic values for the molecular weight were found to agree satisfactorily with the viscometric measurements, using the revised[1] value for the constant of the Staudinger equation relating viscosity of polymer solutions to the molecular weight of the polymer.[2]

Using the Kemp and Peters equation, the values for the viscometric molecular weights of various samples of polystyrene prepared in the presence of anisoyl, *p*-bromobenzoyl and chloroacetyl peroxides would be just half those we previously recorded[3] and the average number of end groups per polymer molecule calculated on the basis of the recalculated viscometric molecular weights, 0.93 ± 0.37, now agrees satisfactorily with the average calculated on the basis of the cryoscopic molecular weights, 1.07 ± 0.41 and both these values are in good agreement with the more accurate results reported herein for tri-bromobenzoyl peroxide.

The accumulation of data thus points to the presence of one fragment from the catalyst per polymer molecule. If active growing polymer chains, initiated by a free radical derived from decomposition of the catalyst, were to be stabilized by disproportionation of hydrogen with some other radical in the solution, the polymer molecules so formed would each contain one fragment from the catalyst.

A.


$$(C_6H_5CO_2)_2 \rightleftarrows \left.\begin{array}{c} 2C_6H_5CO_2^{\cdot} \\ \downarrow \\ CO_2 + C_6H_5^{\cdot} \end{array}\right\} R^{\cdot}$$

B. $R^{\cdot} + CH_2{=}CHX \longrightarrow RCH_2CHX^{\cdot} \longrightarrow\longrightarrow R(CH_2CHX)_nCH_2CHX.$

C. $R(CH_2CHX)_nCH_2CHX^{\cdot} + R(CH_2CHX)_mCH_2CHX^{\cdot} \longrightarrow R(CH_2CHX)_nCH{=}CHX + R(CH_2CHX)_mCH_2CH_2X$

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(1) Kemp and Peters, *Ind. Eng. Chem.*, **34**, 1097 (1942).

(2) Staudinger, "Die hochmolekularen organischen Verbindungen," J. Springer, Berlin, 1932.

(3) Price, Kell and Krebs, THIS JOURNAL, **64**, 1103 (1942).