TABLE I

ESTERS OF TYPE I

R	B. p. °C.	B. p. Mm.	$n^{25}D$	d^{25}_{25}	MD Calcd.	MD Obs.	Sulfur, % Calcd.	Sulfur, % Found
Ethyl	140–145	0.8	1.4646	1.1498	70.5	70.4	10.96	10.82
n-Butyl	161–163	0.2	1.4606	1.0517	98.2	98.6	8.54	8.92
Octadecyl	50 (melting point, uncor.)						3.43	3.43

TABLE II

Compound	Formula	M. p., °C.	Analyses, % Calculated S	Analyses, % Calculated Na	Analyses, % Found S	Analyses, % Found Na
(Carboxymethylmercapto)-butyl-succinate[a]	$C_{14}H_{23}O_6SNa$	148	9.37	6.72	9.51	6.49
(Carboxymethylmercapto)-benzyl-succinate[a]	$C_{20}H_{19}O_6SNa$	156–157	7.81	...	8.10	...
(Carbobutoxymethylmercapto)-succinate[b,d]	$C_{10}H_{14}O_6SNa_2$	.....	10.39	...	9.98	...
(Carboctoxymethylmercapto)-succinate[b,d]	$C_{14}H_{22}O_6SNa_2$	.....	8.80	12.62	9.01	12.50
(Carbododecoxymethylmercapto)-succinate[c,d]	$C_{18}H_{30}O_6SNa_2$	.....	7.62	...	7.32	...

[a] Purified by dissolving in methanol and precipitating with ether. [b] Purified by dissolving in methanol–water (1:1) and precipitating with acetone. [c] Purified by dissolving in water and precipitating with acetone. [d] White, waxy solids. The octyl and dodecyl compounds have surface-active properties.

The compounds prepared, all as their sodium salts, are listed in Table II.

The (carboctoxymethylmercapto) disodium succinate was converted to the free acid by acidifying an aqueous solution with hydrochloric acid. The oil that separated was dissolved in ether and washed with water. The ether then was evaporated and the oil dried in vacuum. Alkali titration gave an equivalent weight of 165 (theory 160.3) $n^{25}D$ 1.4840, d^{25}_{25} 1.146.

Acknowledgment.—The authors wish to express their appreciation to Miss Lillian Weiss and Mr. J. W. Veale for assistance in the experimental work.

Summary

1. Three tri-esters, two di-esters and three mono-esters of (carboxymethylmercapto)-succinic acid (the latter two types as sodium salts) have been prepared and some of their physical constants determined.

2. An indirect method for the preparation of certain of the mono-esters and di-esters of (carboxymethylmercapto)-succinic acid is reported.

NEW YORK, N. Y. RECEIVED FEBRUARY 28, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Mechanism for the Reaction of Dioxane Sulfotrioxide with Olefins. II. Sulfonation of Styrene

BY F. G. BORDWELL AND CHRISTIAN S. RONDESTVEDT, JR.[1]

In a continuation of the attempt to elucidate the mechanism[2] of the reaction of dioxane sulfotrioxide with olefins,[3] the sulfonation of styrene has been investigated. Styrene was chosen because of its ready availability in a pure state and because preliminary studies[4] indicated that a variety of products are formed in its sulfonation.

To ensure uniformity in the sulfonating agent and a fixed ratio of dioxane to sulfur trioxide the dioxane sulfotrioxide was prepared by adding an equimolar quantity of dioxane to a solution of sulfur trioxide in ethylene dichloride. In this way a fine suspension of dioxane sulfotrioxide was obtained.

In most of the experiments of the present investigation the sulfonation mixture, prepared at −5 to 0° by dropwise addition of a solution of styrene in ethylene dichloride to the sulfonating agent, was hydrolyzed without allowing the temperature to rise above 5°. When the aqueous layer was neutralized with sodium hydroxide, the water-soluble products were sodium 2-phenylethene-1-sulfonate[4] (I), sodium 2-phenyl-2-hydroxy-1-ethanesulfonate (II) and sodium sulfate. The identity of II was established by separation from I and sodium sulfate by fractional crystallization using alcohol–water mixtures,[5] and comparison of the S-*p*-chlorobenzylthiouronium salt[6] with an authentic sample.[7] From the ethylene dichloride layer 2,4-diphenyl-1,4-butanesultone (III) was obtained.[4,8] At higher reaction temperatures the amount of I increased at the expense of II.

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[1] National Research Council Predoctoral Fellow, 1946–1947. Present address: University of Michigan, Ann Arbor, Michigan. This material was abstracted from the Ph.D. Dissertation of Christian S. Rondestvedt, Jr., October, 1947.

[2] Bordwell, Suter and Webber, THIS JOURNAL, **67**, 827 (1945).

[3] Suter and co-workers, *ibid.*, **60**, 538 (1938); **63**, 978, 1594 (1941); **65**, 507 (1943); **66**, 1105 (1944).

[4] Bordwell, Suter, Holbert and Rondestvedt, *ibid.*, **68**, 139 (1946).

[5] Kharasch, Schenk and Mayo, *ibid.*, **61**, 3092 (1939).

[6] Suter and Milne, *ibid.*, **65**, 582 (1943).

[7] We wish to thank Frank Colton for carrying out this experiment.

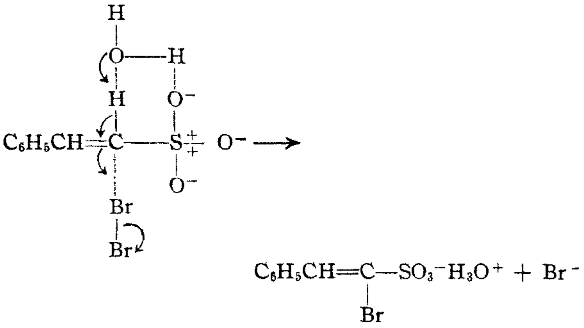
[8] This structure is assigned on the basis of unpublished results.

In order to follow conveniently the variation in the proportions of products with changing experimental conditions it was necessary to devise an analytical method for determining the relative amounts of I and II in the aqueous portions of the hydrolysis mixture. Oxidation of I with potassium permanganate has been reported to be quantitative, but not suitable for the analysis of this mixture since the presence of II interferes with the determination.[5] No reaction occurred when I was treated with hydrogen peroxide and formic acid.[9] However, titration with aqueous bromine using the bromate–bromide method was found to be rapid and quantitative. The presence of II did not affect the analytical results.

The product formed in the reaction of I with bromine water was found to be identical with that obtained in the sulfonation of β-bromostyrene with dioxane sulfotrioxide,[10] as shown by comparison of the corresponding sulfonamides. Truce[10] designated this compound as sodium 2-phenyl-1-bromoethene-1-sulfonate on the basis of its reduction to sodium 2-phenylethene-1-sulfonate under conditions similar to those used by Kohler[11] for the reduction of sodium 1-bromoethene-1-sulfonate to sodium ethene-1-sulfonate. The assigned structure[10] was substantiated in the present investigation by preparation of sodium 1-bromo-2-phenylethene-1-sulfonate from sodium 2-phenylethene-1-sulfonate in a manner comparable to Kohler's preparation of sodium 1-bromoethene-1-sulfonate by bromination of sodium ethene-1-sulfonate, and by the fact that benzaldehyde was obtained on oxidation.

It is of interest to compare the very rapid substitution reaction of sodium 2-phenylethene-1-sulfonate (I) with bromine in aqueous solution to the relatively slow addition of bromine to the double bond of 2-phenylethene-1-sulfonamide and 2-phenylethene-1-sulfonyl chloride. In acetic acid solution 2-phenylethene-1-sulfonamide decolorized an equimolar portion of bromine in about three hours (in the dark about twenty-four hours was required) to give 1,2-dibromo-2-phenyl-1-ethanesulfonamide. In the dark, carbon tetrachloride solutions of 2-phenylethene-1-sulfonyl chloride required about fifteen days for decolorization of an equimolar portion of bromine. The reaction in acetic acid was somewhat faster. When exposed to sunlight and oxygen complete decolorization in carbon tetrachloride solutions occurred in an hour. Hydrogen bromide was not evolved.

The slow rate of electrophilic addition of bromine to 2-phenylethene-1-sulfonamide and 2-phenylethene-1-sulfonyl chloride in acetic acid and carbon tetrachloride solutions is not unexpected in view of the well-known retarding effect of electron-attracting groups on the addition of bromine to olefins. The rapid attack of bromine in aqueous solution on the *alpha* carbon of the ethenesulfonate[11] and 2-phenylethene-1-sulfonate ions is undoubtedly facilitated by the negative charge on the ions. Kohler[11] showed that potassium 1,2-dibromo-1-ethanesulfonate did not undergo dehydrobromination in aqueous solutions, thus ruling out the addition of a molecule of bromine as a preliminary step in the formation of potassium 1-bromoethene-1-sulfonate in this reaction.[12] Further evidence on this point is the observation of Suter and Truce[3] that the 1-methyl-2-phenylethene-1-sulfonate ion which could react by addition but not by comparable substitution, fails to react with bromine under these conditions. A mechanism involving a molecule of water in the transition state is shown for the bromination of I.



$C_6H_5CH{=}C(Br){-}SO_3^-H_3O^+ + Br^-$

Analysis by the isolation technique[5,7] showed that the only water-soluble products present in significant amounts in hydrolysis mixtures from sulfonations carried out below 5° were I, II and

TABLE I

SULFONATION OF STYRENE AT TEMPERATURES BELOW 5°

			Mole per cent. of products (based on SO_3)				
Expt.	Time,[a] hours	Temp., °C.	I	II	III[b]	Na_2SO_4	% SO_3 accounted for
1	1.3[c]	0	33	48	7	8	96
	1.3[d]	0	26	55	7	8	96
2	0	0	15	72	5	5	98
3	2.25	−25	7	53	20	21	101
4	0	0	20	72	6	5	103
	1.5	2	19	74	6	4	103
	3	2	20	76	6	3	105
	4.5	2	20	74	6	4	104
	6.0	2	20	73	8	4	105
	17.5	2	21	69	9	4	103
	50	2	26	66	10	4	106

[a] Time interval from completion of addition of styrene to hydrolysis of the sulfonation mixture. [b] Yield of crude sultone. One crystallization from acetone–water usually gave a 60% recovery of reasonably pure material. [c] In this experiment the quantities were estimated by isolation of the products.[5,7] [d] The same mixture as for *c* analyzed by titration.

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[9] Swern, Findley and Scanlan, THIS JOURNAL, **67**, 1786 (1945); Swern, *ibid.*, **69**, 1692 (1947).

[10] Truce, Doctoral Dissertation, Northwestern University, 1944.

[11] Kohler, *Am. Chem. J.*, **21**, 349 (1899).

[12] Ingold and Smith, *J. Chem. Soc.*, 2742 (1931), found that iodine chloride reacts with ethenesulfonic acid to give 1-iodoethene-1-sulfonic acid. Apparently they misinterpreted Kohler's work since they suggested that 2-chloro-1-iodo-1-ethanesulfonic acid was an intermediate in this reaction.

sodium sulfate. In subsequent work, therefore, I was determined by bromate–bromide titration, sulfate was determined gravimetrically and the quantity of II was taken as the difference between the total acids present and the amounts of I and sulfate determined. To complete the analysis an approximation of the quantity of III was made by evaporation of the ethylene dichloride layer and isolation of the solid product.

The results of the sulfonations carried out below 5° are summarized in Table I. Table II shows the results obtained when the sulfonation mixture was heated to 54.4° prior to hydrolysis.

TABLE II

SULFONATION OF STYRENE AT 54.4°

	Mole per cent. of products (based on SO_3)				
Time,[a] minutes	I	II[c]	III[b]	Na_2SO_4	% SO_3 accounted for
0[d]	28	66	5	3	102
0[d]	28	64	6	4	102
12	33	58	7	3	101
15	44	45	8	3	100
23	54	36	7	2	99
33	61	31	7	1	100
48	68	27	6	1	102
72	72	25	6	0.4	101
104	74	22	5	1	102
143	74	22	5	1	102
210	74	22	4	1	101
1020	75	24	3	0.2	102

[a] Time for which sulfonation mixture was kept at 54.4°. [b] Yield of crude product. One crystallization from acetone–water gave a 60% recovery of reasonably pure material. [c] It seems probable that after a short period of heating the figures in this column also include the percentages of substances other than II (see Discussion). [d] Control taken after completion of the addition of styrene and after the reaction mixture had been allowed to stand for fifteen minutes at 10°.

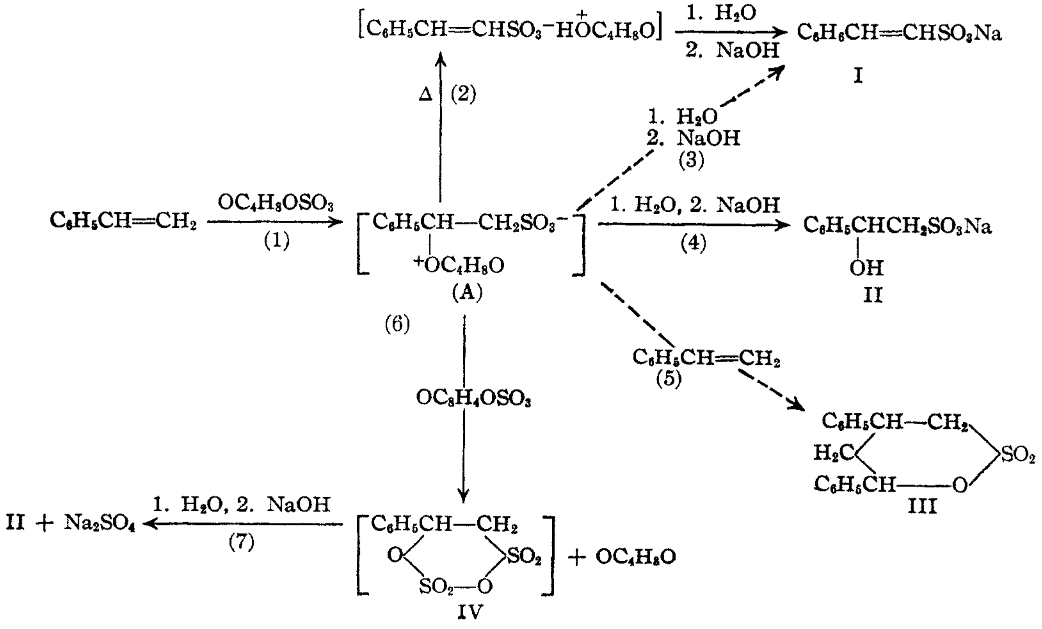
Discussion

The mode of formation previously suggested[2] for the products isolated on hydrolysis and neutralization of sulfonation mixtures obtained from the reaction of dioxane sulfotrioxide and olefins, as applied to the sulfonation of styrene, is represented on the accompanying diagram by solid-shafted arrows (reactions 1, 2, 6, 7). The arrows with broken shafts illustrate new reaction possibilities disclosed by the present investigations (reactions 3, 4, 5). Whether reactions 3, 4 and 5 are peculiar to styrene or applicable to olefins in general is yet to be determined.

At elevated temperatures I is the principal product, and reaction 2 is believed to be the primary route by which it is formed. However, at temperatures below 5° amounts of I varying from 7% to 26% were formed. Since reaction 2 is slow under these conditions (Table I), the formation of as much as 26% of I is surprising. An experiment at 2° utilizing rapid stirring and a slow addition of a more dilute solution of styrene, conditions designed to minimize local heating, resulted in 13% of I. Even at −25° (hydrolysis at 0°) 7% of I was formed. For this reason reaction 3 is tentatively suggested as an additional source of I, but this point requires further investigation.

It has been postulated[2] that the β-hydroxysulfonic acids formed on hydrolysis of these sulfonation mixtures are derived from substituted-ethionic anhydrides (reactions 6 and 7). The fact that equimolar quantities of II and sodium sulfate are not formed in the sulfonation of styrene below 5° eliminates this as the sole source of II. The bulk of II is believed to be formed by reaction 4.

Of the three species (A, III and IV) postulated as being present in the sulfonation mixture at temperatures below 5° only III has been isolated.



Isolation of alkylethionic anhydrides analogous to IV from sulfonation mixtures has been accomplished on a few occasions, but our attempts to isolate such a compound in the present investigation were unsuccessful. The presence of IV is assumed since it appears to be a logical source of the sulfuric acid obtained on hydrolysis.[13]

If (A) is the major source of II, as is suggested, it must possess surprisingly great stability since the amount of II formed on hydrolysis is not changed appreciably when the sulfonation mixture was allowed to stand at 2° for fifty hours (Table I). This stability is probably made possible by solvation with dioxane, since, in the absence of dioxane, styrene is polymerized by sulfur trioxide in ethylene dichloride solution.

If reactions 1, 5 and 6 alone are occurring below 5° prior to hydrolysis, reactions 5 and 6 should be interdependent when equimolar quantities of styrene and sulfur trioxide are used. The molar quantities of III and sulfuric acid should, therefore, be equal. This is only approximately true (Table I), but the amounts are at least of comparable magnitudes. The relatively small quantities of II and sulfuric acid obtained at −5 to 5° indicates that reaction 1 is faster under these conditions than either 5 or 6, since it does not seem likely that either of the latter is reversible. The increased quantity of sulfuric acid obtained at −25° is probably due to incompleteness of reaction 1. The resulting relative increase in the ratio of styrene to (A) leads to an increase in the proportion of III.

Previously[4] a 60% yield of practically pure I was isolated from the first three crops of the hydrolysis and neutralization products of a sulfonation carried out at temperatures above 5°. Using the analytical procedure developed for determination of I the quantity of I present in these crops was found to be 94, 98 and 96%, respectively. The residue was found to contain 56% of I, bringing the total yield of I in this experiment to 75%. A more detailed study of the formation of I at elevated temperatures has now been made (Table II). The increase in the quantity of I is explained by an acceleration of reaction 2. Under these conditions (A) should be converted completely to the dioxane salt corresponding to I, and, in time, the quantity of II should drop to low values. The minimum figure of 22% for II recorded in Table II after extended heating is probably accounted for by the formation of products other than those included in the diagram. Since II was determined only by difference the figures could represent, for example, disulfonation products.

The elimination of the proton in reaction 2 is most likely accomplished with the aid of either an extraneous dioxane molecule or the uncoördinated oxygen of the dioxane molecule incorporated in (A).[14] It was hoped that kinetic data would allow a choice between these two possibilities, but the complexity of the reaction at elevated temperatures discouraged further attempts along these lines.

Acknowledgment.—We wish to thank the National Research Council for the Predoctoral Fellowship which supported this work.

Experimental[15]

Dioxane Sulfotrioxide.—The method of Suter and Evans[3] was used in some experiments, but the following method was preferred. Sulfur trioxide was distilled from an all-glass distillation apparatus containing 60% fuming sulfuric acid or "Sulfan B"[16] into dry ethylene dichloride contained in a tared flask cooled by a cold water-bath. The weight of sulfur trioxide was determined by difference to 0.05 g. An equimolar quantity of dioxane, purified by refluxing with sodium and distilling, was then added with rapid stirring. The internal temperature of the flask must be maintained below 5° in this operation to prevent charring. Since the coördination of sulfur trioxide with dioxane is very exothermic, the permissible rate of addition depends on the efficiency of cooling. For large runs it is advantageous to use a cooling bath temperature of about −40°. The reagent was obtained as fine granules.

Hydrolysis of the reagent with cold water gave 99.6% of the theoretical quantity of sulfuric acid, as determined by titration. No unsaturated material was detectable by a bromate–bromide titration.

Sulfonation of Styrene below 5° (Isolation of the Products[7]).—An equimolar quantity of styrene, dissolved in about an equal volume of ethylene dichloride, was added dropwise to dioxane sulfotrioxide suspended in ethylene dichloride. The mixture was stirred and the temperature kept below 5° (usually below 0°) during the addition. Hydrolysis was effected by pouring the reaction mixture into ice water. The ethylene dichloride layer was separated (the use of ether was helpful in overcoming the emulsions sometimes encountered) and washed; after drying, the solvent was removed at room temperature leaving crude 2,4-diphenyl-1,4-butanesultone[8] (III) as the residue. The aqueous portions were combined and neutralized with barium carbonate, and the barium sulfate was collected and determined gravimetrically. The filtrate was evaporated and three successive crops of barium sulfonates collected. A portion of the sulfonates from each crop was converted to the sodium salts by metathesis. Five grams of the sodium sulfonates from the first crop were refluxed with 50 ml. of 90% alcohol for forty-five minutes, the mixture was allowed to cool to room temperature and filtered. This process was repeated with further portions of 90% alcohol until the residue gave a negligible test for unsaturation with cold aqueous potassium permanganate solution. The residue weighed 2.0 g. and gave an 80% yield of S-*p*-chlorobenzylthiouronium 2-phenyl-2-hydroxy-1-ethanesulfonate, m. p. 179–180°, which gave no depression in melting point when mixed with an authentic sample.[6] The salt obtained by evaporating the alcohol filtrates was largely sodium 2-phenylethene-1-sulfonate (I), as shown by converting it to its S-benzylthiouronium salt[4] in 80% yield. The second and third crops were analyzed in a similar fashion. The percentages of crude I isolated from the three crops were 60, 43 and 0%, respectively. Titration of these samples by the bromate–bromide method showed 49, 36 and 2% of I. The mean values are given in Table I.

The analytical method used for subsequent sulfonations, the results of which are summarized in Table I, was similar to that described below for the analysis of the sulfonation run at 54.4°. To make certain that the determination for

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[13] An alternative representation would be $C_6H_5C^+HCH_2\text{-}SO_2OSO_3^-$. Other types of anhydrides may also be present.

[14] Models show that this oxygen can approach the α-hydrogen atom closely.

[15] The microanalyses were performed by Miss Patricia Craig and Miss Margaret Hines.

[16] The γ-form of sulfur trioxide containing an inhibitor to prevent polymerization. This material was kindly furnished by the General Chemical Company, 40 Rector Street, New York, N. Y.

the experiments carried out over long periods of time was valid, the water-soluble products from a sulfonation mixture kept at 2° for fifty hours prior to hydrolysis were partially separated by the fractional crystallization technique described above. The formation of 2-phenyl-2-hydroxy-1-ethanesulfonic acid and 2-phenylethene-1-sulfonic acid as the principal products was confirmed.

Sodium 1-Bromo-2-phenylethene-1-sulfonate.—A solution of 1.05 g. (0.005 mole) of sodium 2-phenylethene-1-sulfonate was treated with bromine water until a permanent yellow color remained. The solution was evaporated to dryness on a steam-bath with the aid of a current of air. The residue, after crystallization from 90% alcohol, weighed 1.20 g. (87%).

Anal. Calcd. for $C_8H_6O_3SBrNa$: Na, 8.07; Br, 28.03. Found: Na, 8.13; Br, 27.33.

A portion was converted to the sulfonamide (m. p. 130–131°) by the procedure used by Truce,[10] and this showed no depression in melting point when mixed with a sample of his 1-bromo-2-phenylethene-1-sulfonamide, m. p. 130–131°.

1,2-Dibromo-2-phenyl-1-ethanesulfonamide.—A solution of 1.0 g. of 2-phenylethene-1-sulfonamide[4] in about 50 ml. of acetic acid was treated with an equimolar quantity of bromine, and the solution kept in sunlight for three hours. Oxygen appears to catalyze the reaction since decolorization occurs first at the surface. Concentration of the acetic acid at room temperature to about 15 ml. gave 1.0 g. (55%) of crystalline material. After two crystallizations from benzene, colorless needles, m. p. 161–162°, were obtained.

Anal. Calcd. for $C_8H_9O_2Br_2NS$: C, 27.96; H, 2.73. Found: C, 28.00; H, 2.79.

Triethylammonium bromide precipitated immediately when 0.1 g. of 1,2-dibromo-2-phenyl-1-ethanesulfonamide in a warm benzene solution was treated with excess triethylamine. Evaporation of the benzene and crystallization from water gave 1-bromo-2-phenylethene-1-sulfonamide.[10]

Sulfonation of Styrene at 54.4°.—Dioxane sulfotrioxide was prepared from 76.1 g. (0.951 mole) of sulfur trioxide, 83.7 g. (0.951 mole) of dioxane and 150 ml. of dry ethylene dichloride. A solution of 99.0 g. (0.951 mole) of styrene in 30 ml. of ethylene dichloride was added to this reagent in the course of two and one-third hours, the temperature being maintained at 5–7°. After an additional fifteen minutes at 10° two aliquots were withdrawn (by means of a 10-ml. pipet), weighed and hydrolyzed. The remaining solution was heated on the steam-bath to 55° as rapidly as possible, whereupon it was placed in a thermostat at 54.4°. Further aliquots were withdrawn at intervals. The fraction of sulfur trioxide present in each aliquot was determined from the weight of the reaction mixture and the weight of the aliquot. The aliquots were quenched immediately in ice-water, the weight of the aliquot being determined by the increase in weight of the flask holding the ice-water. Ether was added to each aliquot and the layers separated, using sodium chloride to break emulsions where necessary. After washing thoroughly the organic layer was dried and evaporated to dryness at room temperature, the weight of the residue being taken as an approximation of the quantity of 2,4-diphenyl-1,4-butanesultone[8] (III). The water layer was titrated (to phenolphthalein) with standard sodium hydroxide, then acidified and treated with 0.1 mole of barium chloride per mole of sulfur trioxide in the aliquot. The barium sulfate was determined gravimetrically (analysis reproducible to within 1% of the total sulfur trioxide). The filtrate was titrated by the bromate–bromide method to determine the amount of sodium 2-phenylethene-1-sulfonate present. The results are summarized in Table II.

Summary

1. Sulfonation of styrene at temperatures below 5° gave (after hydrolysis and neutralization) sodium 2-hydroxy-2-phenyl-1-ethanesulfonate (II) as the major product. β-Phenylethionic anhydride was ruled out as the principal precursor of II.

2. Titration with aqueous bromine using the bromate–bromide method was used to determine sodium 2-phenylethene-1-sulfonate (I) in the presence of II. A mechanism is given for the rapid reaction of I with bromine in aqueous solution.

3. The olefin–sulfur trioxide intermediate complex previously postulated[2] was useful in accounting for the various products formed in the sulfonation of styrene.

EVANSTON, ILLINOIS RECEIVED MARCH 29, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Formation of Ethers in the Preparation of Pentaerythritol

BY STANLEY WAWZONEK AND DONALD A. REES[1,2]

The preparation of pentaerythritol from acetaldehyde and formaldehyde is always accompanied by the formation of dipentaerythrityl ether.[3]

Attempts[3] to arrive at a mechanism by increasing the amount of dipentaerythrityl ether formed in this condensation proved unsuccessful. The only conclusion made was that pentaerythritol was not necessary for the formation of dipentaerythrityl ether.

One possible mechanism for the formation of dipentaerythrityl ether is outlined in the following series of reactions

$$\mathrm{CH_3CHO + HCHO \overset{OH^-}{\rightleftharpoons} CH_2OHCH_2CHO} \quad (1)$$

$$\mathrm{CH_2OHCH_2CHO \rightleftharpoons CH_2{=}CHCHO + H_2O} \quad (2)$$

$$\mathrm{CH_2{=}CH{-}CHO + HOCH_2CH_2CHO \rightleftharpoons O(CH_2CH_2CHO)_2} \quad (3)$$

$$\mathrm{O(CH_2CH_2CHO)_2 + 6HCHO + 2OH^- \longrightarrow O(CH_2C(CH_2OH)_3)_2 + 2HCOO^-} \quad (4)$$

The existence of an equilibrium between acrolein and β-hydroxypropionaldehyde in aqueous and acid solutions has already been demonstrated by Lucas.[4] Addition of an alcohol to acrolein in

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[1] A. C. S. Pre-Doctoral Fellow, 1946–1947.

[2] Abstracted from a thesis by Donald A. Rees, submitted to the Graduate Faculty of the State University of Iowa in partial fulfilment of the requirements for the degree of Doctor of Philosophy, August, 1947.

[3] Friederick and Brun, *Ber.*, **63**, 2681 (1930).

[4] Lucas and Pressman, THIS JOURNAL, **64**, 1953 (1942).