[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Sulfonation of 2-Benzyl-1-propene. Mechanism for the Reaction of Dioxane Sulfotrioxide with Olefins. I[1]

BY F. G. BORDWELL, C. M. SUTER[2] AND A. J. WEBBER[3]

In this Laboratory an extensive study of the reaction of dioxane sulfotrioxide with various types of olefins[4-8] and other unsaturated compounds is under way. Up to the present time the reactions with straight chain α-olefins,[4] α-olefins with a branch in the chain at the number two carbon,[5-7] and olefins with a phenyl group attached to one of the double bond carbon atoms[8] have been reported. Straight chain α-olefins react with two molecules of sulfur trioxide by addition, giving alkylethionic anhydrides.[4] These anhydrides are seldom isolated,[9] but instead are hydrolyzed to sulfuric acid and the corresponding β-hydroxy sulfonic acid, which is isolated in the form of one of its salts. α-Olefins having a branch in the chain at the number two carbon atom undergo this addition reaction only to a minor extent, the chief products being unsaturated sulfonic acids.[5-7] Styrene and its derivatives also give unsaturated sulfonic acids as the principal products.[8] With the completion of the study of the sulfonation of 2-benzyl-1-propene, reported in this paper, enough information has been obtained to formulate a plausible mechanism for these reactions.

Sulfonation of 2-Benzyl-1-propene.—The sulfonation of 2-benzyl-1-propene was accomplished readily by adding the olefin to an equimolar quantity of dioxane sulfotrioxide in ethylene chloride at 0°. Hydrolysis of the sulfonation mixture and neutralization of the sulfonic acids with excess barium carbonate gave a difficultly soluble barium sulfonate, $(C_{10}H_{11}SO_3)_2Ba$, in practically pure state. This salt is barium 2-methyl-3-phenyl-2-propene-1-sulfonate (I), since oxidation with potassium permanganate gave benzaldehyde and no barium sulfate, and ozonolysis gave 65% of the theoretical quantity of benzaldehyde. This structure was confirmed by an independent synthesis starting with 2-methyl-3-phenyl-2-propene-1-ol.[10] The hydroxyl group in this alcohol was replaced by a chlorine atom by means of thionyl chloride and pyridine. The chloride thus obtained gave sodium 2-methyl-3-phenyl-2-propene-1-sulfonate on treatment with aqueous sodium sulfite. The S-benzylthiouronium salt of this synthetic compound was identical with a similar derivative prepared from (I), the identity being established through a comparison of melting points (157–158°) and mixed melting point (no depression). It is of course conceivable that in the transformation of 2-methyl-3-phenyl-2-propene-1-ol to the sulfonate, one or more allylic shifts might occur. A second possible product of this series of reactions is then sodium 2-methyl-1-phenyl-2-propene-1-sulfonate. This structure for (I) is untenable, however, since ozonization would then yield formaldehyde and no benzaldehyde, which is not in agreement with the experimental facts.

Attempts to prepare the sulfonyl chloride from (I) by means of phosphorus halides were unsuccessful. Failure to obtain sulfonyl chlorides in this reaction has been reported for several arylmethane sulfonates, of which (I) is a vinylog. Thus sodium 1-phenylethane-1-sulfonate gives no sulfonyl chloride when treated with phosphorus pentachloride,[11] nor does sodium α-naphthylmethanesulfonate.[12] Phenylmethanesulfonyl chloride is stable at 90° but at somewhat higher temperatures is cleaved to benzyl chloride and sulfur dioxide.[13]

The most interesting reaction of (I) was that with bromine water or aqueous potassium tribromide, the product in either case being a water-insoluble compound, $C_{10}H_{11}O_3SBr$, which has been tentatively identified as 3-phenyl-2-bromo-2-methylpropane-1,3-sultone.[14] The yield of this sultone is practically quantitative, and this reaction proved to be of considerable value in estimating the amounts of (I) present in mixtures in which it appeared as a constituent. Thus, evaporation of the filtrate from which (I) was obtained gave four more crystalline crops and a final small discolored residue. From the amount of sultone formed in the reaction of these crops with potassium tribromide the total yield of (I) is estimated to be fifty per cent., based on the amount of sulfur trioxide used in the experiment.

In addition to (I) there appear to be two other sulfonates present in the sulfonation product. From ten to fifteen per cent. of the sulfur trioxide was recovered as barium sulfate. The sulfate ion

---

[1] Presented in part before the Organic Division of the American Chemical Society at Cleveland, April 4, 1944.

[2] Present address: Winthrop Chemical Company, Rensselaer, N. Y.

[3] Part of the experimental work herein reported was abstracted from a Master's thesis submitted by A. J. Webber. Present address: Cheplin Laboratories, Inc., Syracuse, N. Y.

[4] Suter, Kiefer and Evans, THIS JOURNAL, **60**, 538 (1938); Suter, unpublished results.

[5] Suter and Malkemus, *ibid.*, **63**, 978 (1941).

[6] Suter, Malkemus and Archer, *ibid.*, **63**, 1594 (1941).

[7] Suter and Bordwell, *ibid.*, **65**, 507 (1943).

[8] Suter and Truce, *ibid.*, **66**, 1105 (1944); unpublished results from this Laboratory.

[9] Only one alkylethionic anhydride other than ethionic anhydride itself (carbyl sulfate) has been isolated in a pure state and characterized; see ref. 7.

[10] Stevens, Allen and Du Bois, THIS JOURNAL, **62**, 1424 (1940).

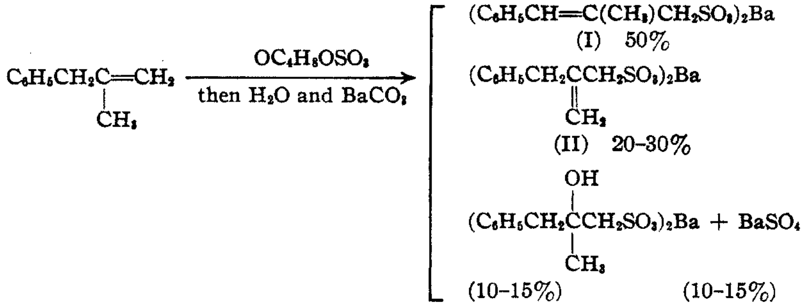
[11] Kharasch, May and Mayo, *J. Org. Chem.*, **3**, 175 (1938).

[12] Johnson and Sprague, THIS JOURNAL, **59**, 1838 (1937).

[13] Johnson and Ambler, *ibid.*, **36**, 381 (1914).

[14] A further account of the structure of this compound and the reaction by which it is formed will be given in a later paper.

is probably formed by hydrolysis of β-benzyl-β-methylethionic anhydride, and it seems reasonably certain that ten to fifteen per cent. of the other hydrolysis product, barium 3-phenyl-2-methyl-2-hydroxypropane-1-sulfonate is present in the mixture of barium salts. We were unable, however, to isolate this hydroxy sulfonate or its derivatives from the mixture. The S-benzylthiouronium salt and p-toluidine salt of 3-phenyl-2-methyl-2-hydroxypropane-1-sulfonic acid were prepared from a synthetic sample of the sodium salt, but these did not agree in physical properties with any of the corresponding salts prepared from the various crops of barium sulfonates.



$$C_6H_5CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 \xrightarrow[\text{then } H_2O \text{ and } BaCO_3]{OC_4H_8OSO_3} \left[\begin{array}{l} (C_6H_5CH=C(CH_3)CH_2SO_3)_2Ba \\ \qquad (I)\ 50\% \\ (C_6H_5CH_2\underset{\displaystyle CH_2}{\underset{\|}{C}}CH_2SO_3)_2Ba \\ \qquad (II)\ 20\text{–}30\% \\ (C_6H_5CH_2\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}CH_2SO_3)_2Ba + BaSO_4 \\ (10\text{–}15\%) \qquad\qquad (10\text{–}15\%) \end{array}\right.$$

The fourth and fifth crops of barium salts consisted chiefly of an unsaturated sulfonate, $(C_{10}H_{11}SO_3)_2Ba$ (II), isomeric with (I). These crops yielded no sultone when treated with aqueous potassium tribromide, yet decolorized a greater volume of this solution. Oxidation gave no barium sulfate indicating that the double bond was not α–β to the sulfonic acid group. The most plausible structure for (II) is then barium 2-benzyl-2-propene-1-sulfonate. This structure was confirmed by an independent synthesis of (II) by the reaction of 3-phenyl-2-chloromethyl-1-propene (from coupling 3-chloro-2-chloromethyl-1-propene[15] with phenylmagnesium bromide) and aqueous sodium sulfite. That the resulting compound had the structure assigned was shown by ozonolysis of the sodium salt to give a 55% yield of formaldehyde. Formaldehyde was also obtained by ozonolysis of crops four and five, and after these crops had been recrystallized from alcohol, they yielded p-toluidine and S-benzylthiouronium salts identical with similar derivatives obtained from the synthetic sodium salt.

The reaction of (II) with an equivalent quantity of phosphorus pentachloride gave a low yield of the corresponding sulfonyl chloride, which was converted without purification to 2-benzyl-2-propene-1-sulfonamide.

A third possible isomeric unsaturated sulfonic acid, 2-benzyl-1-propene-1-sulfonic acid was formed, if at all, in only very small amounts in the sulfonation of 2-benzyl-1-propene, since oxidation of the various crops of barium sulfonates gave no more than a trace of barium sulfate.

The probable composition of the mixture of barium salts obtained by addition of water and barium carbonate to the sulfonation mixture is shown.

Approximately 95% of the sulfur trioxide used was accounted for in the form of these barium salts.

Rearrangement of (II) to (I).—The question as to whether (I) (sulfonic acid) is formed from (II) (sulfonic acid) during the sulfonation is of importance in relation to the mechanism of the sulfonation. Rearrangement of the sodium salt of (II) to (I) was therefore investigated. The amount of (I) present in mixtures of (I) and (II) was determined by measuring the quantity of bromosultone formed on treatment of neutral aqueous solutions of the salts with a slight excess of potassium tribromide solution, and comparing the weight of sultone with that from known mixtures of the two salts. It was found that heating (II) (sodium salt) in five per cent. sodium hydroxide solution on the steam-bath for twenty-four hours gave a nearly complete conversion to (I). Rearrangement was also observed when acid solutions of (II) were heated for twenty-four hours or more at steam-bath temperature. No rearrangement was observed when the heating period in either case was cut to three hours, or when acidic or neutral solutions of salts of (II) were allowed to stand at room temperature as long as seven days.

Since the sulfonation of 2-benzyl-1-propene can be carried out at 0° in one hour to give (I) and (II) (sulfonic acid) in ratios of about two to one, it does not seem probable that (I) (sulfonic acid) was formed from (II) by rearrangement.

Discussion of Mechanism

Addition *vs.* Substitution.—The formation of 2-methyl-2-propene-1-sulfonic acid in the sulfonation of isobutylene[6] raised the question as to whether this product was formed by the direct attack of the sulfonating agent on one of the methyl groups, or by addition of sulfur trioxide to the terminal carbon atom of the double bond (number one carbon), and the shift of a proton from one of the number three carbon atoms to the negative oxygen, with a simultaneous formation of a new double bond.[16] The latter of these mechanisms is more attractive in view of the well-known tendency of alkenes, but not alkanes, to react with ionic type reagents under mild conditions. The substitution mechanism predicts the formation of (II) in the sulfonation of 2-benzyl-1-propene. Actually the products are (II) (25%)

---

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

[16] The same question is raised by the formation of methallyl chloride in the chlorination of isobutylene and as yet remains unanswered. Burgin, Engs, Groll and Hearne, *Ind. Eng. Chem.*, **31**, 1413 (1939), have shown that the mechanism does not involve splitting out of hydrogen chloride from an intermediate dichloride, but addition of a "positive" chlorine atom and elimination of a proton, as suggested by Tishchenko, *J. Gen. Chem.* (U. S. S. R.), **8**, 1232 (1938), remains as a plausible "addition" mechanism.

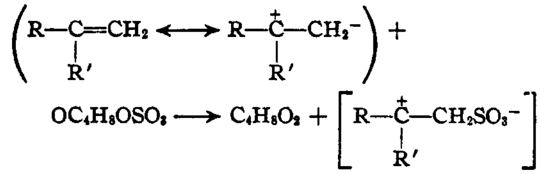
and (I) (50%). Since there is no evidence to indicate that a rearrangement of (II) to (I) can take place under the experimental conditions used, the substitution mechanism appears inadequate. The formation of (I) and (II) by an addition mechanism is, on the other hand, entirely plausible and the preponderance of (I) is understandable in view of the conjugation of double bonds in this molecule. The addition mechanism is, furthermore, capable of explaining the formation of three isomeric unsaturated chloroisobutylene sulfonic acids in the sulfonation of methallyl chloride[7] without recourse to postulated rearrangements. Finally, the addition mechanism alone is capable of explaining the formation of 1-phenyl-1-propene-2-sulfonic acid in the sulfonation of 1-phenyl-1-propene.[8]

Addition Mechanism.—The following facts pertinent to the mechanism of the sulfonation of alkenes with dioxane sulfotrioxide have now been elucidated: (1) in the reaction of one or two molecules of dioxane sulfotrioxide with an α-olefin the sulfur atom always becomes attached to the terminal carbon atom,[4-8] (2) alkylethionic anhydrides are not intermediates in the formation of unsaturated sulfonic acids,[5] and (3) the formation of unsaturated sulfonic acids does not involve the direct attack of the sulfonating agent on an alkyl group (see above).

The preferential attachment of sulfur trioxide to the terminal carbon atom of the double bond in α-olefins is analogous to the selective addition of the likewise electrophilic proton of the hydrohalogen acids to this carbon atom, and is therefore in accordance with an electronic interpretation of Markownikoff's rule. It is not at all certain, however, that sulfur trioxide itself is the active sulfonating agent, since in a mixture containing the electron donors dioxane and ethylene chloride most of the sulfur trioxide will be coördinated with these molecules. These coördination compounds may well be the actual sulfonating agents. If this is the case, the reaction would most likely be initiated by an attack of a "polarized" alkene molecule on the face of the tetrahedral sulfur atom opposite to the position at which the molecule of dioxane (or ethylene chloride) is coördinated, and would therefore be a nucleophilic replacement reaction. At present there seems to be no simple method available by which the true nature of the sulfonating agent can be determined. We prefer to represent all reactions as nucleophilic replacement reactions occurring between dioxane sulfotrioxide and the alkene.

Whatever the nature of the sulfonating agent, we believe that the net result of the first step in the reaction is the addition of a molecule of sulfur trioxide to the terminal carbon atom of the *alpha* olefin.[17]

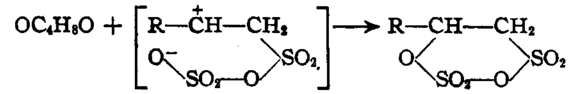
(1)



$$\left(R-\underset{R'}{\underset{|}{C}}=CH_2 \longleftrightarrow R-\underset{R'}{\underset{|}{\overset{+}{C}}}-CH_2^-\right) + OC_4H_8OSO_3 \longrightarrow C_4H_8O_2 + \left[R-\underset{R'}{\underset{|}{\overset{+}{C}}}-CH_2SO_3^-\right]$$

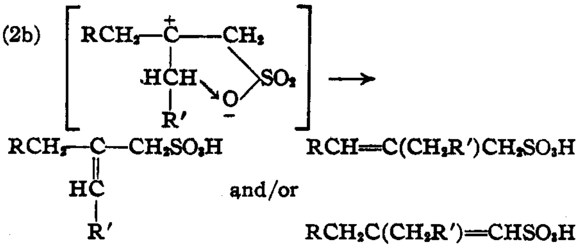
The second step of the reaction depends on the nature of R and R′ of the alkene. If R or R′ is hydrogen the next step is addition of a second molecule of sulfur trioxide[4] to give an alkylethionic anhydride. This addition probably involves coördination of the second molecule of sulfur trioxide with the oxygen of the first, followed by ring closure. These reactions may also be represented as nucleophilic replacement reactions, a solvent molecule being released at each stage.

(2a)



If R and R′ are alkyl groups[5-7] or if R or R′ is a phenyl group[8] the predominant reaction, after the initial addition, is migration of a proton to give unsaturated sulfonic acids, rather than the reaction shown in equation (2a). The proton can be released from any one of the three carbon atoms adjacent to the carbon bearing the positive charge, and α–β and/or β–γ unsaturated sulfonic acids may thus be formed. The reaction is probably intramolecular.[18]

(2b)



Structure of the Intermediate.—The intermediate complex formed by the addition of a molecule of sulfur trioxide to the alkene (equation 1) has been represented as bearing both a positive and negative charge. This first step in the proposed sulfonation mechanism resembles closely the formation of a "positive" bromonium ion in the addition of bromine to alkenes.[19] To explain the formation of only the *trans* isomer in the addition of bromine to *cis*- or *trans*-stilbene,[19] as well as other examples of similar selective addition; Roberts and Kimball[20] suggested that the bromonium ion formed in the first step has a cyclic structure. Recently Winstein and Lucas[21]

---

[17] It seems certain that this reaction is accompanied by coördination of a solvent molecule with the carbon bearing the positive charge. Whenever a carbon atom is shown as being positively charged it is understood that it is solvated.

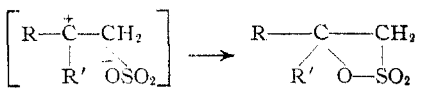
[18] This mechanism is somewhat similar to that proposed recently by Luder and Zuffanti, *Chem. Rev.*, **34**, 345 (1944), for aromatic sulfonations.

[19] Bartlett and Tarbell, THIS JOURNAL, **58**, 466 (1936).

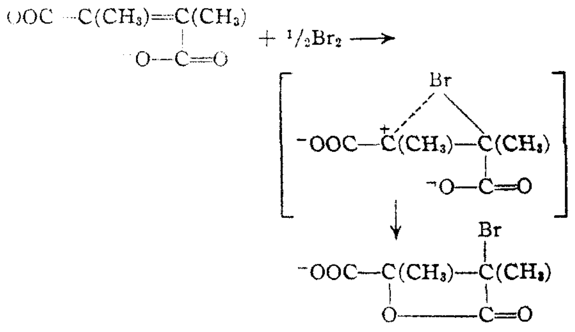
[20] Roberts and Kimball, *ibid.*, **59**, 947 (1937).

[21] Winstein and Lucas, *ibid.*, **61**, 1576 2845 (1939). See also Winstein and Henderson, *ibid.*, **65**, 2196 (1943), and previous papers in this series.

have found the concept of cyclic bromonium ions to serve admirably as an explanation for otherwise unexpected stereochemical configurations resulting from a series of replacement reactions. Roberts and Kimball[20] point out in their arguments for the existence of a cyclic bromonium ion "that a coördinate link will almost certainly be formed by the sharing of one of the pairs of electrons of the halogen with the unoccupied orbital of carbon." The opportunities for such coördination between oxygen and carbon in the sulfur trioxide addition complex would appear to be even greater since the oxygen atoms should be closer to the carbon atom than the halogen to carbon in the bromine addition complex and, furthermore, the oxygen atoms not only have unshared electrons but also a negative charge. If such a ring closure does occur the intermediate would be a β-sultone.



The formation of a *beta* lactone in the bromination of the sodium salt of dimethylmaleic acid[22] is a close analogy to the above reaction. If the sulfonation intermediate is a β-sultone, then this compound in the case of the sulfonation of 2-benzyl-1-propene must be cleaved to unsaturated sulfonic acids at 0° in the non-aqueous acid medium, or when the sulfonation mixture is hydrolyzed with water. The chemical behavior of β-sultones therefore becomes of primary interest. Unfortunately no well substantiated instance of the isolation of a β-sultone appears to be recorded in the literature.[23] The question as to their stability under these conditions cannot therefore be completely answered at this time. However, the following facts make it seem probable that β-sultones would not readily rearrange to unsaturated sulfonic acids: (1) β-lactones are stable under ordinary conditions and have not been reported to rearrange to unsaturated carboxylic acids; (2) N-phenylanhydrotaurine, a β-sultam, is extremely resistant to hydrolysis by either basic or acidic solutions[24]; (3) γ- and δ-sultones are quite stable in acidic and neutral solutions and only slowly hydrolyzed in alkaline solutions. On the basis of these analogies it appears doubtful that the addition complex between sulfur trioxide and an alkene (equation 1) has a ring structure.



Work relative to the proposed mechanism is being continued.

Experimental

Sulfonation of 2-Benzyl-1-propene.—2-Benzyl-1-propene was prepared by coupling methallyl chloride[25] with phenylmagnesium bromide. The product was purified by distillation through a Podbielniak column of about 100 theoretical plate efficiency[26] at a reflux ratio of 120 to 1. The physical constants of the main fraction, b. p. 170.5–171 (753 mm.), d^{25} 0.882, n^{20}_{D} 1.5086, agreed well with those recently published by Whitmore, Weisgerber and Shabica[27] for this compound.

The description of the procedure for the sulfonation given below is typical of a number of such experiments. Thirteen and one-half grams (0.17 mole) of sulfur trioxide was gradually distilled into a mechanically stirred mixture of 25 ml. of dioxane and 25 ml. of ethylene chloride kept at about 0°. To this stirred suspension of dioxane sulfotrioxide was added gradually 25 ml. (0.17 mole) of 2-benzyl-1-propene diluted with an equal volume of ethylene chloride. After standing overnight (in some experiments the mixture was allowed to stand for only one hour) the reaction mixture was poured into about one liter of ice water and the aqueous layer separated and neutralized with excess barium carbonate. The resulting mixture was digested for an hour on the steam-bath and then the filtrate separated from the residue of barium carbonate and barium sulfate. On cooling 15.1 g. of a crystalline organic barium salt separated from the filtrate. Concentration of the filtrate gave further crops of barium salts as follows: crop 2 from 175 ml., 2.1 g. (from hot solution); crop 3 from 175 ml., 5.2 g. (from cold solution); crop 4 from 100 ml., 5.6 g.; crop 5 from 25 ml., 7.3 g. The residue on final evaporation of the filtrate consisted of 3.5 g. of discolored non-crystalline material. Extraction of the residue of barium sulfate and barium carbonate gave 1.3 g. of organic barium salt. The barium sulfate freed of barium carbonate weighed 4.85 g. after ignition (12% yield based on sulfur trioxide).

Barium 2-Methyl-3-phenyl-2-propene-1-sulfonate (I).—The barium salt isolated from crop 1 was crystallized from water. An aqueous solution of the salt reduced aqueous potassium permanganate solution rapidly giving off a strong odor of benzaldehyde. No barium sulfate was formed in the oxidation.

Anal. Calcd. for $C_{20}H_{22}S_2O_6Ba$: Ba, 24.53. Found: Ba, 24.13, 24.05.

The sodium salt prepared by metathesis was found to be appreciably more water soluble.

Anal. Calcd. for $C_{10}H_{11}SO_3Na$: Na, 9.82. Found: Na, 9.59, 10.09.

The S-benzylthiouronium salt[28] was prepared by adding a 15% solution of S-benzylthiouronium chloride to an aqueous solution of the sodium salt. It was crystallized from alcohol–water mixtures, m. p. 157.5–158.5°.

---

[22] Tarbell and Bartlett, This Journal, 59, 407 (1937).

[23] Kohler, *Am. Chem. J.*, 21, 349 (1899), suggested a β-sultone structure for an unstable substance obtained by the reaction of phosphorus pentoxide on 1-bromo-2-hydroxyethanesulfonic acid. His claim that sultone ring closure is accomplished as readily with β-hydroxy as with γ- and δ-hydroxysulfonic acids does not appear to have been supported by subsequent experimental evidence, and recent work, Shriner, Rendleman and Berger, *J. Org. Chem.*, 4, 103 (1939), indicates that ring closure does not occur readily with γ-hydroxysulfonic acids.

[24] Leymann, *Ber.*, 18, 872 (1885).

[25] Supplied through the courtesy of the Shell Development Company, Emeryville, California.

[26] We wish to thank Dr. R. H. Baker for his assistance in carrying out this distillation.

[27] Whitmore, Weisgerber and Shabica, This Journal, 65, 1469 (1943).

[28] Chambers and Watt, *J. Org. Chem.*, 6, 376 (1941).

Anal. Calcd for $C_{18}H_{22}O_3S_2N_2$: S, 16.90. Found: S, 16.85, 16.94.

The *p*-toluidine salt crystallized when a solution of 0.5 g. of the barium salt, 0.2 g. of *p*-toluidine, 1 ml. of concd. hydrochloric acid and 35 ml. of water was allowed to cool, m. p. 226–228° (dec.).

Anal. Calcd. for $C_{17}H_{21}O_3NS$: neut. equiv., 319. Found: neut. equiv., 318.

Oxidation of the barium salt with aqueous potassium permanganate gave a 50% yield of benzaldehyde, isolated as its 2,4-dinitrophenylhydrazone, m. p. 237°. Ozonolysis in glacial acetic acid or water solution gave 65–70% of the theoretical amount of benzaldehyde identified by means of its phenylhydrazone, m. p. 157°. Reaction of the barium salt with bromine water or bromine dissolved in aqueous potassium bromide gave about 80% of the theoretical quantity of 2-bromo-2-methyl-3-phenyl-1,3-propanesultone,[14] m. p. 108–112°. After two recrystallizations from acetone–water this compound melted at 113–114°. From the crystallized sodium salt 95% of the theoretical quantity of bromosultone melting at 113–114° was obtained.

Anal. Calcd. for $C_{10}H_{11}O_3SBr$: Br, 27.4. Found: Br, 28.0, 26.9.

On the basis of the quantity of sultone obtained by treatment with excess potassium tribromide, crops 1 and 2 are practically 100% (I) and crop 3 is about 50% (I). Crops 4 and 5 may contain as much as 10% of (I), since the portion of these crops insoluble in 95% alcohol (about 10% of the total) gives the bromosultone on titration with potassium tribromide. The total yield of (I) is estimated to be 20–23 g. or about 50% based on sulfur trioxide. A rough estimate of the amount of (I) in each of the crops was also obtained by measuring the amount of S-benzylthiouronium salt obtained, using 0.2 g. of the barium salt, 0.2 g. S-benzylthiouronium chloride and 25 ml. of water. The yields of pure derivative obtained were as follows: crop 1, 50%; crop 2, 50%; crop 3, 12%; crop 4, 0%; crop 5, 0%. The yield of derivative using a pure sample of barium salt was about 50% under the same experimental conditions.

Synthesis of sodium 2-methyl-3-phenyl-2-propene-1-sulfonate was accomplished starting with 2-methyl-3-phenyl-2-propene-1-ol, prepared by an aluminum isopropoxide reduction of α-methylcinnamaldehyde.[10] The alcohol was converted to the chloride by the method of Darzens,[29] and the crude chloride (b. p. 140–150° (40 mm.)) was heated with sodium sulfite in the presence of 10% sodium hydroxide. The synthetic salt gave an S-benzylthiouronium salt melting at 157–158°, which showed no depression in melting point when mixed with the corresponding derivative prepared from the barium sulfonate isolated in the first crops obtained from the sulfonation reaction.

Sodium 2-Benzyl-2-propene-1-sulfonate (II).—This compound was synthesized in order to study its properties and reactions, since it was believed to be the chief constituent present in crops 4 and 5 (these crops were very unsaturated to permanganate or bromine water, but yielded no barium sulfate with the former, or bromosultone with the latter). A mixture of 2-chloromethyl-3-chloro-1-propene and 2-methyl-1,3-dichloro-1-propene was prepared by the chlorination of methallyl chloride.[15] One hundred and twenty-three grams (1 mole) of this dichloride fraction (b. p. 131–133°) was added in one portion to an ether solution containing one mole of phenylmagnesium bromide. It was necessary to cool the flask in order to control the resulting reaction. After the reaction had subsided the reaction mixture was poured into ice-water, acidified with dilute hydrochloric acid and extracted with ether. Thirty-eight grams (0.23 mole) of the product obtained (b. p. 140–150° at 25 mm.) was added slowly to a saturated aqueous solution containing 14 g. (0.11 mole) of sodium sulfite, stirred and heated at 100°. The mixture was heated and stirred for a total of five hours and the aqueous layer separated. On cooling 15 g. (58% yield based on sodium sulfite) of crystalline sodium 2-benzyl-2-propene-1-sulfonate separated. The salt was recrystallized from 150 ml. of 95% alcohol.

Anal. Calcd. for $C_{10}H_{11}O_3SNa$: Na, 9.84. Found: Na, 10.00.

The S-benzylthiouronium salt was prepared and recrystallized several times from water containing small amounts of 95% alcohol, m. p. 129–129.5°.

Anal. Calcd. for $C_{18}H_{22}O_3S_2N_2$: N, 7.41. Found: N, 7.08.

The *p*-toluidine salt separated as colorless rectangular plates when a solution containing 0.5 g. of the sodium salt, 0.2 g. of *p*-toluidine, 1 ml. of concd. hydrochloric acid and 9 ml. of water was allowed to stand for several days, m. p. 143–144°.

Anal. Calcd. for $C_{17}H_{21}O_3NS$: neut. equiv., 319. Found: neut. equiv., 323.

An oxygen-ozone mixture was bubbled for thirty minutes into an acetic acid solution (containing about 1% of water) of 0.25 g. of the sodium salt. The solution was diluted to about 200 ml. with water and neutralized with 15% sodium hydroxide solution. Addition of 0.3 g. of methone dissolved in 5 ml. of alcohol yielded 0.17 g. (55%) of formaldimethone. After recrystallization from dilute alcohol the derivative weighed 0.12 g. (38%) and melted at 190–191°. A mixed melting point with an authentic sample of formaldimethone showed no depression.

A comparison of the barium salts obtained in crops 4 and 5 with the synthetic sample established the presence of barium 2-benzyl-2-propene-1-sulfonate as their principal constituent. The crude salts each gave a 20% yield of recrystallized formaldimethone by the ozonolysis procedure described above. Like the synthetic sample these salts could be rearranged to (I) (see below). The S-benzylthiouronium salts and *p*-toluidine salts obtained from these crops melted 10 to 20° below the melting point of similar salts obtained from the synthetic salt and recrystallization was not effective in purifying them. Pure derivatives were obtained, however, from samples of the barium salts which had been recrystallized from 95% alcohol (both salts of (I) and of 3-phenyl-2-methyl-2-hydroxy-propane-1-sulfonate are practically insoluble in this solvent), and these showed no depression in melting point when mixed with the corresponding S-benzylthiouronium salt and *p*-toluidine salt from the synthetic sample of the sodium salt of (II).

2-Benzyl-2-propene-1-sulfonamide.—Mixing equivalent amounts of either barium or sodium 2-benzyl-2-propene-1-sulfonate with phosphorus pentachloride brought about a spontaneous reaction. The reaction mixture was heated at 80° for one hour, poured into ice-water, and the sulfone chloride extracted with ether. Shaking the ether solution with concd. ammonia solution gave about 20% yield of crude amide. The amide was crystallized from water, from benzene and Skellysolve B, and finally from benzene, m. p. 109–110°.

Anal. Calcd. for $C_{10}H_{13}O_2NS$: N, 6.63. Found: N, 6.64.

Attempts to prepare the isomeric sulfonamide, 2-methyl-3-phenyl-2-propene-1-sulfonamide, from the barium or sodium salt, using phosphorus pentachloride or phosphorus oxychloride either in the absence or presence of carbon tetrachloride, followed by treatment with ammonia, were unsuccessful.

Rearrangement of Sodium 2-Benzyl-2-propene-1-sulfonate (II).—The course of the rearrangement was followed by weighing the amount of bromosultone formed from the solution of salts obtained after treatment of (II) (sodium salt) in such a way as to induce rearrangement, neutralizing the resulting solution, and addition of a slight excess of potassium tribromide solution. The weight of bromosultone obtained from known mixtures containing the salts of (I) and (II) was not directly proportional to the amount of (I) present. It was therefore necessary to measure the amount of bromosultone formed from known mixtures of (I) and (II) (sodium salts) and use these as standards in determining the amount of (I) present in re-

---

[29] Darzens, *Comp. rend.*, **152**, 1314 (1911).

arranged mixtures of (II). The weights of bromosultone obtained from 0.2-g. mixtures of (I) and (II) were as follows: 0% (I), very small amount of oil; 10% (I), small amount of oil; 20% (I), 0.10 g.; 30%, 0.12 g.; 40%, 0.13 g.; 50%, 0.14 g.; 60%, 0.16 g.; 70%, 0.19 g.; 80%, 0.21 g.; 90%, 0.22 g.; 100%, 0.235 g. (95% yield). The oil formed from (II) on treatment with potassium tribromide solution contaminates the bromosultone so that all samples from mixtures of the two salts are low melting. A mixture of sodium 2-hydroxy-3-phenyl-2-methylpropane-1-sulfonate with (I) did not alter the quantity or purity of bromosultone obtained from the latter. No solid bromosultone was obtained on addition of potassium tribromide solution to solutions of (II) (sodium salt) which were allowed to stand at room temperature with or without the addition of alkali (5% NaOH solution) or acid (10% HCl solution) for periods of from one to seven days. Heating at 100° caused as much as 70% rearrangement in twenty-four hours in acid or basic solution but no change in neutral solution. No rearrangement was observed after three hours at 100° in acid, basic or neutral solution.

Sodium 2-Hydroxy-3-phenyl-2-methylpropane-1-sulfonate.—3-Phenyl-2-methyl-2-hydroxy-1-bromopropane was prepared from 13 g. (0.1 mole) of 2-benzyl-1-propene according to the directions of Read and Reid.[30] The crude bromohydrin was added slowly to a saturated solution containing 12 g. (0.1 mole) of sodium sulfite in 10% sodium hydroxide. The mixture was stirred and heated on the steam-bath for forty-eight hours. Working up the reaction mixture gave 9 g. (0.035 mole) of organic sodium salt, which was extremely soluble in water and slightly soluble in alcohol (35% yield of crude salt). Separation from inorganic salts was difficult.

The S-benzylthiouronium salt was prepared and crystallized with difficulty from alcohol-water mixtures, m. p. 132.5–133°.

Anal. Calcd. for $C_{18}H_{24}O_4N_2S_2$: N, 7.07. Found: N, 6.66.

The *p*-toluidine salt crystallized from a solution containing 1 g. of hydroxysulfonate, 0.4 g. of *p*-toluidine, 1 ml. of concd. HCl and 5 ml. of water after five days, m. p. 148–149°.

Anal. Calcd. for $C_{17}H_{23}O_4NS$: neut. equiv., 337. Found: neut. equiv., 328.

Acknowledgment.—The authors wish to express their appreciation to Professors C. D. Hurd and R. H. Baker for reading and criticizing the manuscript.

Summary

1. Sulfonation of 2-benzyl-1-propene with dioxane sulfotrioxide gives about 50% of 3-phenyl-2-methyl-2-propene-1-sulfonic acid and 25% of 2-benzyl-2-propene-1-sulfonic acid. It is believed that the remaining 25% of the sulfur trioxide added to the double bond of the olefin to give β-benzyl-β-methylethionic anhydride, which would account for the presence of 12% of barium sulfate in the neutralization products.

2. A mechanism for the reaction of dioxane sulfotrioxide with olefins is proposed, which accounts for the presence of both unsaturated and hydroxy sulfonic acids in the neutralization products. The unsaturated sulfonic acids are believed to be formed by addition of a molecule of sulfur trioxide to the number one carbon of the olefin to give a dipolar intermediate, which stabilizes itself by transfer of a proton from one of the number three carbon atoms to an oxygen atom. Addition of a second molecule of sulfur trioxide to the intermediate accounts for the formation of alkyl ethionic anhydrides, which on hydrolysis give hydroxy sulfonic acids and sulfuric acid.

3. Details of the mechanism and the possibility of a cyclic structure for the intermediate are discussed.

EVANSTON, ILL. RECEIVED MARCH 7, 1945

---

[30] Read and Reid, *J. Chem. Soc.*, 1487 (1928).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE VICK CHEMICAL COMPANY]

The Synthesis of a Clavacin Isomer and Related Compounds[1]

BY BRUNO PUETZER, CYRIL H. NIELD AND RICHARD H. BARRY

In November, 1943, Raistrick and co-workers[1a] described the isolation of a crystalline antibiotic from the culture filtrate of *Penicillium patulum Bainier* which they named patulin. This antibacterial substance was first isolated in an impure state by Wiesner[2] and Waksman, Horning and Spencer[3] from the culture media of *Aspergillus clavatus* and was named clavacin by Waksman. The identity of patulin with clavacin and antibiotic substances isolated from several other mold cultures has been established.[4] On the basis of studies on the chemical degradation of this compound, structure I was assigned[1] to it. The strongest evidence presented by Raistrick in favor of I, was the decomposition of patulin by dilute sulfuric acid to formic acid and in 10% yield to tetrahydro-γ-pyrone-carboxylic acid-2. The Bergel group[4b] state that the proposed formula I does not entirely agree with all the results of their studies on the chemistry of the compound. They also refer to the possibility of tautomerism between I and several isomeric structures (I, II, III and IV), and, on the basis of their results, they conclude that clavacin exists in solution chiefly in forms III and IV.

---

[1] A preliminary report on the subject matter of this paper was published in *Science*, March 23, 1945, **101**, #2621, pp. 307–8, entitled "The Synthesis of a Clavacin Isomer" by Puetzer, Nield and Barry.

[1a] Raistrick, Birkinshaw, Bracken and Michael, *Lancet*, **2**, 625 (1943).

[2] Wiesner, *Nature*, **149**, 356 (1942).

[3] Waksman, Horning and Spencer, *Science*, **96**, 202 (1942).

[4] (a) Bergel, Morrison, Moss, Klein, Rinderknecht and Ward, *Nature*, **152**, 750 (1943); (b) Bergel, Morrison, Moss and Rinderknecht, *J. Chem. Soc.*, 415 (1944); (c) Chain, Florey and Jennings, *Brit. J. Exp. Path.*, **23**, 202 (1942); (d) Chain, Florey and Jennings, *Lancet*, **1**, 112 (1944); (e) Florey, Jennings and Philpot, *Nature*, **153**, 139 (1944); (f) Hooper, Anderson, Skell and Carter, *Science*, **99**, 16 (1944); (g) Anslow, Raistrick and Smith, *J. Soc. Chem. Ind.*, **162**, 236 (1943).