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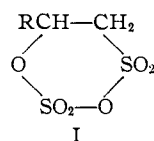
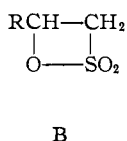
Sulfonation of Olefins. VI. Stereochemistry of the Reaction with Cyclopentene and Cyclohexene

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Sulfonation of cyclopentene with an equimolar quantity of dioxane-sulfur trioxide gave, on hydrolysis, *trans*-2-hydroxycyclopentanesulfonic acid (III). The formation of III is consistent with the presence of a β -sultone intermediate, indicated by previous work, and this hypothesis is strengthened by the formation of the dipolar ion, *trans*-2-(1-proto-1-pyridyl)-cyclopentanesulfonate (IV), on treatment of the sulfonation mixture with pyridine. Use of a double molar quantity of sulfonating agent gave, on hot acid hydrolysis, *cis*-2-hydroxycyclopentanesulfonic acid (V). Sulfation of V gave *cis*-2-hydroxysulfatocyclopentanesulfonic acid (VI), which was also obtained by cautious hydrolysis of the sulfonation solution, which is believed to contain the cyclic sulfonate-sulfate anhydride intermediate VII. From previous work it is clear that only sulfur-oxygen bonds are cleaved in the hydrolysis of VII to VI, and of VI to V, so VII must also have a *cis* structure. Sulfonation of cyclohexene with a double molar amount of sulfonating agent gave, on hydrolysis, *cis*-2-hydroxysulfatocyclohexanesulfonic acid and, from this, *cis*-2-hydroxycyclohexanesulfonic acid. Salts of these acids were previously prepared in a similar manner by Sperling, but assigned a *trans* configuration. The significance of these results with regard to the mechanism of the sulfonation reaction is discussed.

Previous papers in this series have established that the sulfonations of unbranched olefins, such as styrene² and 1-hexene³ give, on hydrolysis, β -hydroxysulfonic acids, which may have been formed by the hydrolysis of a β -sultone intermediate (B)^{2,3} or a cyclic sulfonate-sulfate anhydride intermediate (I).³



In order to learn more concerning the formation and reactions of these intermediates the stereochemical nature of the β -hydroxysulfonic acids from the sulfonation of cyclopentene and cyclohexene has been investigated.

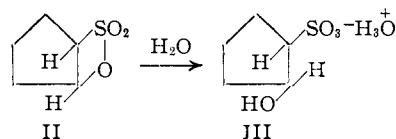
Sperling⁴ reported that the dioxane-sulfur trioxide complex reacts with cyclohexene to form 2-cyclohexene-1-sulfonic acid, and, after hydrolysis and neutralization, barium "*trans*"-2-bariosulfate-1-cyclohexanesulfonate. On further hydrolysis the latter gave barium "*trans*"-2-hydroxy-2-cyclohexanesulfonate. The "*cis*" isomer of the β -hydroxysulfonate was reported as being formed by the reaction of cyclohexene oxide and ammonium sulfite. The structure assignments were made on the basis of the relative solubility of the isomeric barium salts in water, and the "inability" of the less soluble barium salt to form an S-benzylthiuronium derivative. The formation of isomeric products from these two sources has been confirmed in the present study, but the configurations of the compounds are just the opposite of those assigned by Sperling,⁴ as will be brought out in the discussion which follows.

Sulfonation of Cyclopentene.—Since the major product from the sulfonation of cyclohexene was found to be the unsaturated sulfonic acid, 2-cyclohexene-1-sulfonic acid, we turned our attention to the cyclopentane series, where elimination reactions are frequently not so dominant. Sulfona-

tion of cyclopentene with an *equimolar quantity* of dioxane-sulfur trioxide reagent gave, after hydrolysis, 3% of sulfuric acid and 8% of unsaturated sulfonic acids (by bromate-bromide titration). The remainder of the product (79% based on the total acids in the aqueous layer) was presumably a β -hydroxycyclopentanesulfonic acid. Crystallization of the sodium salt from 95% alcohol gave a salt free of unsaturated sulfonates. *p*-Toluidine and S-*p*-chlorobenzyl-thiuronium derivatives failed to form from even concentrated solutions of this salt, but addition of equivalent amounts of *p*-toluidine or aniline to the aqueous solution from hydrolysis of the sulfonation mixture gave the *p*-toluidine and aniline salts on evaporation. The *p*-toluidine salt was converted to the barium salt, an equivalent amount of an aqueous solution of S-(*p*-chlorobenzyl)-thiuronium sulfate added, and the derivative obtained by evaporation of the filtrate.

A β -hydroxycyclopentanesulfonate identical to that described above was obtained by the reaction of either cyclopentene oxide or *trans*-2-chlorocyclopentanol with ammonium sulfite, as shown by mixed melting point comparison of the *p*-toluidine salts in each instance with the *p*-toluidine salt of the sulfonation product. There appears to be no doubt but what this is a salt of *trans*-2-hydroxycyclopentanesulfonic acid (III), since *trans* opening of epoxide rings in the reaction with nucleophilic reagents has been firmly established.⁵ *Trans* products are also the rule for displacement reactions of cyclic halohydrins, the reaction proceeding either by way of the oxide or a cyclic bromonium ion.

The formation of *trans*-2-hydroxycyclopentanesulfonic acid (III) from the hydrolysis of the sulfonation solution is consistent with the presence of a β -sultone intermediate (II), analogous to B.



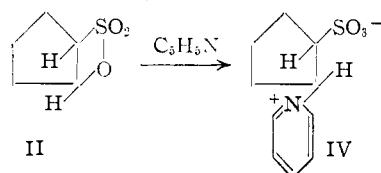
The fusion of the four- and five-membered rings in II must of necessity be *cis*. Ring opening of II by

(1) Procter and Gamble Research Fellow, 1948-1951.
 (2) F. G. Bordwell, M. L. Peterson and C. S. Rondstedt, *THIS JOURNAL*, **76**, 3945 (1954).
 (3) F. G. Bordwell and M. L. Peterson, *ibid.*, **76**, 3952 (1954).
 (4) R. Sperling, *J. Chem. Soc.*, 1925 (1949).

(5) (a) C. E. Wilson and H. J. Lucas, *THIS JOURNAL*, **58**, 2396 (1936); (b) W. E. Grigsby, J. Hind, J. Chanley and F. H. Westheimer, *ibid.*, **64**, 2606 (1942).

attack of a water molecule would be expected to lead to inversion no matter whether the hydrolysis proceeds by an SN1 or SN2 type mechanism, although the presence of some of the *cis* isomer would be anticipated from an SN1 reaction. A minimum of 57% of the *trans* isomer is present by isolation. It is improbable that more than a small amount of the *cis* isomer is present, since derivatives of the *cis* isomer are less soluble than those of the *trans* isomer, and would have separated first.

The formation of the dipolar ion, *trans*-2-(1-proto-1-pyridyl)-cyclopentanesulfonate (IV),⁶ by addition of pyridine to the sulfonation solution is considered, by analogy with previous work,^{2,3} to be additional evidence for the presence of a β -sultone intermediate (II).

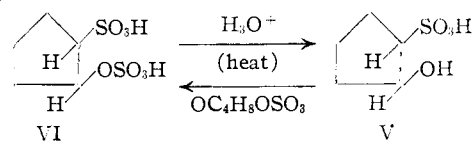
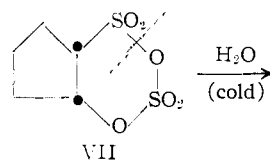
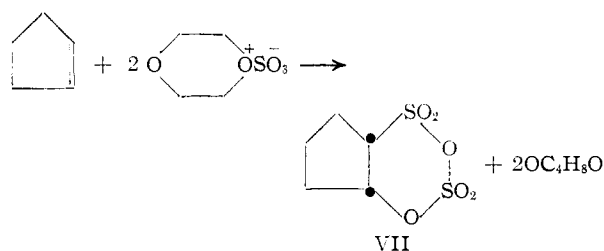


Reaction of cyclopentene with a *two molar quantity* of dioxane-sulfur trioxide reagent gave different results. The sulfonation products were hydrolyzed by pouring into water and *heating* the aqueous solution for several hours. The acids were neutralized with barium carbonate, barium sulfate was removed and the filtrate was evaporated to yield 85% of a barium salt containing only 3% of unsaturated sulfonates. The *p*-toluidine salt was prepared by treating an aqueous solution of the barium salt with equivalent amounts of sulfuric acid and *p*-toluidine. This *p*-toluidine salt was different from, but isomeric with, that obtained from cyclopentene and one mole of sulfonating agent, and must be the *p*-toluidine salt of *cis*-2-hydroxycyclopentanesulfonic acid (V). The S-(*p*-chlorobenzyl)-thiuronium salt of the *cis* isomer (V), unlike that of the *trans* isomer (III), was prepared directly from the barium salt in concentrated aqueous solution and was crystallized from small quantities of water. The aniline salt of V also was prepared and shown to differ from that of III.

Hydrolysis of a sulfonation reaction, involving one mole of cyclopentene and two of the sulfonating agent, with *cold* water and neutralization with barium carbonate gave, on evaporation, the barium salt of the hydrogen sulfate ester of V. This barium salt of a 2-hydrosulfatocyclopentanesulfonic⁷ acid (VI) could be refluxed in aqueous solution for several hours without hydrolysis, but in the presence of 1 *N* hydrochloric acid, barium sulfate began to precipitate within 5 to 10 minutes. A sample of the pure sodium salt of VI gave 98.9% of the theoretical yield of sulfate ion on hydrolysis for 2 hr. with 1 *N* hydrochloric acid.

Acid-catalyzed hydrolysis of alkyl hydrogen sulfate esters is known to proceed by cleavage of the sulfur-oxygen rather than the carbon-oxygen bond since, (1) optically active 2-butyl hydrogen sulfate hydrolyzes in acid medium to 2-butanol

with retention of configuration (albeit with some racemization),^{8a} and (2) aryl hydrogen sulfates may be hydrolyzed readily in acidic solutions.^{8b} Therefore, the fact that VI hydrolyzes to *cis*-2-hydroxycyclopentanesulfonic acid (V) shows that VI must also have a *cis* configuration. This assignment was confirmed by showing that VI could be produced by sulfation of anilinium *cis*-2-hydroxycyclopentanesulfonate with dioxane-sulfur trioxide. Burwell has shown^{8a} that sulfation of optically active 2-butanol proceeds with retention of configuration, and with very little loss of optical purity. Also, the sulfation of primary and secondary alcohols with sulfuric acid is known to involve sulfur-oxygen rather than carbon-oxygen fission.⁹



The representation of the fission of VII during hydrolysis as involving the sulfonate-oxygen rather than the sulfate-oxygen link is based on the behavior of aniline in a similar instance.³

Sulfation of the aniline salt of *trans*-2-hydroxycyclopentanesulfonic acid (III) with dioxane-sulfur trioxide gave a hydrogen sulfate ester isomeric with VI, which must be *trans*-2-hydrosulfatocyclopentanesulfonic acid. The same *trans*-hydrogen sulfate ester also was obtained by sulfation of the barium salt of III.

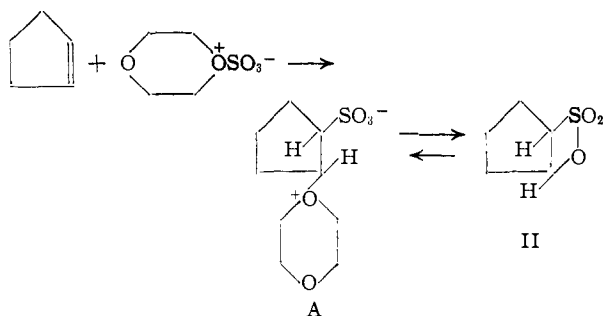
Sulfonation Mechanism.—Unbranched alkenes generally react rapidly at 0° with an equimolar quantity of dioxane-sulfur trioxide in ethylene chloride solution to give a soluble sulfonation intermediate. On the basis of the reaction of this intermediate with water, aniline, pyridine, excess sulfonating agent, etc., either a β -sultone structure (B or II) or a dioxane-solvated-carboniumsulfonate ion (such as A) may be used to represent the intermediate. For styrene the β -sultone structure is favored because a substance agreeing with this formula may be precipitated from the solution by addition of pentane.² For 1-hexene the formation of a structure comparable to (A) from the β -sultone in the presence of excess dioxane has been suggested

(6) See ref. 3 for a discussion of the nomenclature of dipolar ions of this type.

(7) The prefixes hydrosulfato, sodiosulfato and bariosulfato are used for the groups HO_2SO^- , $\text{Na}^+ \text{O}_2\text{SO}^-$ and $\text{Ba}^{+2} \text{O}_2\text{SO}^-$.

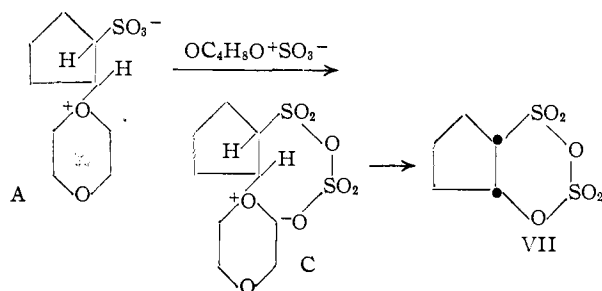
(8) (a) R. L. Burwell, Jr., *THIS JOURNAL*, **67**, 220 (1945); **71**, 1769 (1949); (b) G. N. Burkhardt, W. K. Ford and E. Singleton, *J. Chem. Soc.*, 17 (1936).

(9) M. S. Newman, *THIS JOURNAL*, **72**, 3853 (1950).



to explain the role of dioxane in increasing the rate at which a cyclic sulfonate-sulfate anhydride, comparable to VII, is formed.³

It is very difficult to interpret the stereochemistry of the cyclopentene sulfonation in terms of intermediate (A) without also assuming the presence of II. Thus, (A) would be expected to exchange with the dioxane present in the solution, and mixtures of *cis* and *trans* products would be obtained on hydrolysis, and in the reaction with excess sulfonating agent. If it is assumed that exchange with dioxane and hydrolysis can only occur by way of II (participation of the sulfonate group), then the presence of (A) is not inadmissible. If, by analogy with the sulfonation of 1-hexene, dioxane is given a role in the formation of VII, (A) may be considered as an intermediate in this reaction.



Alternatively, C might be formed directly by the reaction of the β -sulfone II with dioxane-sulfur trioxide. This can be visualized as occurring by coordination of sulfur trioxide with oxygen in II and attack by dioxane with inversion. In any event the stereochemistry of the sulfonation of cyclopentene appears to be best interpreted by assuming a prominent role for a β -sulfone intermediate.

Sulfonation of Cyclohexene.—Sulfonation of cyclohexene with an *equimolar* quantity of dioxane-sulfur trioxide gave about 60% of unsaturated sulfonic acids,¹⁰ and no β -hydroxysulfonic acid was isolated from the products. A sulfonation carried out at -20° with a *two molar* quantity of sulfonating agent gave 29% of unsaturated sulfonic acids (by titration), and 40% of sulfate ester (from the amount of sulfate ion obtained on acid hydrolysis). From the mixture obtained by hydrolysis (without heating) and treatment with aniline a small amount of the dianilinium salt of *cis*-2-hydroxysulfatocyclohexanesulfonic acid (VIII) was obtained. Hydrolysis in acidic medium gave sulfuric acid and *cis*-2-hydroxycyclohexanesulfonic acid (IX), from which

(10) R. S. Schiefelbein, Doctoral Dissertation, Northwestern University, 1951.

the aniline salt was prepared. In agreement with Sperling⁴ it was found that no S-benzylthiuronium salt was precipitated by addition of a saturated aqueous solution of S-benzylthiuronium chloride to a concentrated solution of the sodium salt of IX. The salt was obtained, however, by using the barium salt of IX and S-benzylthiuronium sulfate, removing the barium sulfate, and concentration of the solution.

The salts of IX were shown to be different from those of the *trans* isomer, which were prepared from the product obtained in the reaction of cyclohexene oxide or 2-chlorocyclohexanol and ammonium sulfite.¹⁰ It is clear, then, that the cyclic sulfonate-sulfate anhydride from cyclohexene also has a *cis* configuration (analogous to VII).

Sperling⁴ obtained similar results in the cyclohexane series, but designated his compounds as having the opposite configuration. He apparently did not take into consideration the evidence for *trans* ring openings of epoxides⁵ in making this choice.

Experimental¹¹

Salts of *trans*-2-Hydroxycyclopentanesulfonic Acid (III) from the Sulfonation of Cyclopentene.¹²—To the sulfonating reagent prepared from 25.6 g. (0.320 mole) of sulfur trioxide, 28.2 g. (0.320 mole) of dioxane and 200 ml. of ethylene chloride, 23.8 g. (0.320 mole) of cyclopentene¹² was added dropwise at 0° , and the mixture allowed to stand for one hour. The resulting solution was stirred with water for an hour, the layers separated and the ethylene chloride layer washed free of acids with small portions of water. The aqueous layer and washings contained 0.308 equivalent of acid including 0.0098 mole (3%) of sulfuric acid (determined as barium sulfate) and 0.0256 mole (8%) of unsaturated sulfonic acids (based on bromate-bromide titration). These acids account for 93% of the sulfur trioxide used. The aqueous solution was neutralized with sodium carbonate and evaporated under reduced pressure to give a tan salt. Extraction of a 12-g. portion of this salt with 95% alcohol for 10 hr. in a Soxhlet extractor gave 6.0 g. of colorless crystalline salt (from the solution), which was saturated to bromine water. A 2.0-g. sample of this salt in 20 ml. of water gave no derivative with aqueous saturated S-(*p*-chlorobenzyl)-thiuronium chloride, a few crystals of the reagent itself being eventually obtained from the solution.

The aqueous solution from a comparable reaction using 0.205 molar quantities of reagents was treated with 18.5 g. (0.173 mole) of *p*-toluidine. The red plastic mass obtained by evaporation of the water under reduced pressure was decolorized with activated carbon and crystallized twice from acetone to give 10.8 g. (27%) of nearly colorless crystals, m.p. $153-156^\circ$. Several more crystallizations gave an analytical sample of *p*-toluidinium *trans*-2-hydroxycyclopentanesulfonate, m.p. $157-159^\circ$. The yield of *p*-toluidine salt obtained in a comparable experiment was 32%.

Anal. Calcd. for C₁₂H₁₉O₄NS: C, 52.72; H, 7.01; neut. equiv., 273. Found: C, 52.38; H, 7.01; neut. equiv., 267.

In a similar experiment with 0.220 mole of reagents the aqueous solution was treated with 0.220 mole of aniline. The crude salt obtained on evaporation under reduced pressure was pulverized and dissolved in 400 ml. of 20% alcoholic acetone solution; on cooling 25.5 g. of tan crystals, m.p. $159-166^\circ$, were obtained. Ten grams crystallized from 175 ml. of 20% alcoholic acetone in the presence of 0.5 g. of activated charcoal gave 7.7 g. of slightly yellow crystals, m.p. $166-170^\circ$. Further crystallization gave colorless anilinium *trans*-2-hydroxycyclopentanesulfonate,

(11) Melting points are uncorrected. Microanalyses were by Miss Joyce Sorenson.

(12) We wish to thank Mr. Fred Frey of the Phillips Petroleum Co., Bartlesville, Oklahoma, for making available to us a sample of cyclopentene of 91 mole per cent. purity (the major impurity was cyclopentane). The quantities used in these experiments were based on the 91%.

m.p. 166–170°. By working up the filtrates the total yield of anilinium salt melting from 160–170° was 57%.

Anal. Calcd. for $C_{11}H_{17}O_4SN$: C, 50.94; H, 6.61; neut. equiv., 259. Found: C, 51.06; H, 6.47; neut. equiv., 258.

Four grams (0.0147 mole) of the *p*-toluidine salt dissolved in 30 ml. of water was treated with 2.3 g. (0.0073 mole) of barium hydroxide octahydrate. The *p*-toluidine formed was removed by filtration and extraction of the filtrate with 50 ml. of ether. The aqueous solution was treated with 3.6 g. (0.0147 mole) of *S*-(*p*-chlorobenzyl)-thiuronium sulfate and, after digestion for 30 min. on the steam-bath, the barium sulfate was removed with the aid of Celite, and the filtrate evaporated under reduced pressure to give 4.5 g. (0.0123 mole, 84%) of colorless crystals. Crystallization from alcohol-acetone gave *S*-(*p*-chlorobenzyl)-thiuronium *trans*-2-hydroxycyclopentanesulfonate, m.p. 151.5–152°.

Anal. Calcd. for $C_{13}H_{19}O_4N_2S_2Cl$: C, 42.55; H, 5.22. Found: C, 42.73, 43.11; H, 5.02, 5.34.

Salts of *trans*-2-Hydroxycyclopentanesulfonic Acid (III) from 2-Chlorocyclopentanol and from Cyclopentene Oxide.—2-Chlorocyclopentanol was prepared in 53% yield by the method described by Coleman and Johnstone¹³ for 2-chlorocyclohexanol. A solution consisting of 8.0 g. (0.069 mole) of ammonium sulfite, 8.1 g. (0.0675 mole) of 2-chlorocyclopentanol and 50 ml. of 50% aqueous alcohol was refluxed for 24 hr. The solution was concentrated to a small volume, 50 ml. of water was added and barium hydroxide added until ammonia ceased to be evolved. Carbon dioxide was bubbled into the mixture, the barium carbonate and sulfate were removed, and the filtrate evaporated under reduced pressure to give 10.2 g. (65%) of barium *trans*-2-hydroxycyclopentanesulfonate. An aqueous solution of 6.0 g. of the barium salt was treated with an equivalent amount of sulfuric acid and 2.8 g. (0.026 mole) of *p*-toluidine added to the filtrate from removal of the barium sulfate. The brown solid obtained on evaporation of the resulting solution was crystallized from acetone to yield 3.0 g. (42%) of salt, which after another crystallization gave a salt, m.p. 155–158°. A mixed m.p. with the *p*-toluidine salt of III gave no depression.

Using essentially the same procedure in a 0.059-mole experiment with cyclopentene oxide the yield of barium salt was 8.7 g. (62%) and the yield of crude *p*-toluidine salt of III, m.p. 142–153°, was 78%. Recrystallization gave material of m.p. and mixed m.p. 157–159°.

trans-2-(1-Proto-1-pyridyl)-cyclopentanesulfonate (IV).—A sulfonation solution prepared from 0.245 molar quantities of reagents was allowed to stand for 45 min. at 0° and then treated with 35.0 g. (0.440 mole) of dry pyridine. On cooling in an ice-bath a dark brown solid was obtained, which was collected and washed with ethylene chloride leaving 27.0 g. (49%) of a tan solid. This material was very soluble in water but was insoluble in acetone. Recrystallization in the presence of activated charcoal from 95% alcohol gave a colorless salt (77% recovery) decomposing above 310°.

Anal. Calcd. for $C_{10}H_{13}O_3NS$: C, 52.84; H, 5.76. Found: C, 52.89, 53.39; H, 5.56, 5.68.

The remainder of the ethylene chloride solution was evaporated under reduced pressure, and the resulting oil dissolved in water and digested for 12 hr. on the steam-bath with barium carbonate. The precipitate was digested with dilute hydrochloric acid to give a residue of 5.62 g. (10%) of barium sulfate. Evaporation of the filtrate left 10.2 g. of tan crystals containing 52% of unsaturated sulfonates as determined by titration. Four recrystallizations of a *S*-(*p*-chlorobenzyl)-thiuronium salt prepared from this product gave a sample melting at 179–180°, which did not depress the m.p. of an authentic sample of the salt of 1-cyclopentene-1-sulfonic acid.¹⁴

Salts of *cis*-2-Hydroxycyclopentanesulfonic Acid (V).—To the sulfonating agent prepared from 51.4 g. (0.643 mole) of sulfur trioxide, 56.6 g. (0.643 mole) of dioxane and 100 ml. of ethylene chloride was added by dropwise addition at 0°, 21.8 g. (0.321 mole) of cyclopentene.¹² After standing for 2 days at 10° the mixture was stirred vigorously with 200 ml. of water, and the aqueous solution was refluxed for 4 hr. and heated on the steam-bath for 18 hr. The solution

was neutralized with barium carbonate and digested for several hours in the presence of activated charcoal. The solid was removed and extracted with 200 ml. of hot water. The aqueous solutions were combined and evaporated to dryness under reduced pressure to yield 63.0 g. (0.272 mole, 85%) of a light yellow barium salt. Titration indicated the presence of 3% of unsaturated sulfonate. A 10.0 g. (0.043 mole) portion of the barium salt was treated with an equivalent amount of sulfuric acid, barium sulfate was removed, and 4.6 g. (0.043 mole) of *p*-toluidine added. The aqueous solution was evaporated on the steam-bath under reduced pressure and the resulting salt was dissolved in 50 ml. of refluxing acetone. On cooling, 7.2 g. (62%) of pink crystals, m.p. 125–131°, were obtained. After several recrystallizations in the presence of activated charcoal *p*-toluidinium *cis*-2-hydroxycyclopentanesulfonate, m.p. 132–133.5°, was obtained. The mixed m.p. of this *p*-toluidine salt with that of III (m.p. 157–159°) was 112–137°.

Anal. Calcd. for $C_{12}H_{19}O_4NS$: C, 52.72; H, 7.01. Found: C, 53.19; H, 6.90.

Addition of 3.2 g. (0.013 mole) of *S*-(*p*-chlorobenzyl)-thiuronium sulfate to 3.0 g. (0.013 mole) of the barium salt of V in 20 ml. of water gave 2.1 g. of colorless crystals, after removal of the barium sulfate and concentration of the solution to 10 ml. On concentration, the filtrate yielded 1.4 g. more of salt bringing the total yield to 73%. Recrystallization from small amounts of water gave *S*-(*p*-chlorobenzyl)-thiuronium *cis*-2-hydroxycyclopentanesulfonate, m.p. 152–153°.

Anal. Calcd. for $C_{13}H_{19}O_4N_2S_2Cl$: C, 42.55; H, 5.22. Found: C, 42.71; H, 5.25.

A mixed m.p. of this *cis* compound with an equal amount of the *S*-(*p*-chlorobenzyl)-thiuronium salt of the *trans* isomer, m.p. 151–152°, was 150–153°. However, a mixture of about three-fourths *trans* derivative and one-fourth *cis* derivative melted at 146–152°.

Anilinium *cis*-2-hydroxycyclopentanesulfonate was prepared by a procedure comparable to that used for the *p*-toluidine salt. Crystallization of the crude aniline salt gave a 69% yield of material in four crops melting between 150–162°. Recrystallization gave colorless material, m.p. 159–162°. The mixed m.p. with the *trans*-aniline salt, m.p. 166–170°, was 144–155°.

Anal. Calcd. for $C_{11}H_{17}O_4NS$: C, 50.94; H, 6.61; neut. equiv., 259. Found: C, 50.79; H, 6.33; neut. equiv., 259.

Salts of *cis*-2-Hydrosulfatocyclopentanesulfonic Acid (VI).—A sulfonation mixture was prepared from 37.2 g. (0.465 mole) of sulfur trioxide, 40.9 g. (0.465 mole) of dioxane, 100 ml. of ethylene chloride and 15.8 g. (0.233 mole) of cyclopentene,¹² and the solution allowed to stand at 5° for 48 hr. An aliquot of the red-brown solution amounting to 6.9% by weight was neutralized with sodium carbonate for sulfate analysis. Addition of barium chloride to the solution and digestion on the steam-bath gave 0.581 g. (8%) of barium sulfate; after making the filtrate 2 *N* in hydrochloric acid and digesting for 24 hr. on the steam-bath an additional 3.02 g. (41%) of barium sulfate was obtained. From this value it would appear that 82% of the hydrogen sulfate ester was formed.

The remainder of the sulfonation solution was neutralized with barium carbonate, digested for 2 hr. on the steam-bath and filtered. Concentration of the filtrate gave four successive crops of barium salts, the first two containing no unsaturated sulfonate, the last, 25% of unsaturated sulfonate. The barium salt was recrystallized by dissolving in a minimum amount of hot water and adding of alcohol to the saturation point.

Anal. Calcd. for $C_8H_9O_7S_2Ba$: Ba, 35.99. Found: Ba, 35.67.

The sodium salt of VI was prepared from the barium salt and an equivalent quantity of sodium sulfate. The salt was crystallized by dissolving it in hot 75% alcohol and adding 95% alcohol to the saturation point. The yield of crystalline sodium salt was 81%. A 0.734-g. (0.00253 mole) quantity was hydrolyzed by refluxing for 2 hr. in 100 ml. of 1 *N* hydrochloric acid containing barium chloride. The barium sulfate formed weighed 0.583 g. (98.9%).

To a hot solution of 0.5 g. (0.0017 mole) of sodium *cis*-2-sodiosulfatocyclopentanesulfonate in 10 ml. of water 0.8 g. (0.0034 mole) of *S*-(*p*-chlorobenzyl)-thiuronium chloride was

(13) G. H. Coleman and H. F. Johnstone, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 158.

(14) Unpublished results from this Laboratory.

added. After cooling, 1.1 g (100%) of colorless salt, m.p. 170–180° was formed. After crystallization from water the bis-*S*-(*p*-chlorobenzyl)-thiuronium salt of *cis*-2-hydro-sulfatocyclopentanesulfonic acid, m.p. 194–196°, was obtained.

Anal. Calcd. for $C_{21}H_{23}O_7N_4S_2Cl_2$: C, 38.94; H, 4.36. Found: C, 38.96; H, 4.43.

Addition of an equivalent amount of aniline (27.6 g., 0.296 mole) to a sulfonation product which had been treated with ice-water gave 39.0 g. (38%) of the aniline salt of VI, m.p. 190–201°. Recrystallization from alcohol to a constant m.p. gave the dianilinium salt of *cis*-2-hydro-sulfatocyclopentanesulfonic acid, m.p. 202–203°.

Anal. Calcd. for $C_{17}H_{24}O_7N_2S_2 \cdot H_2O$: C, 45.32; H, 5.81. Found: C, 45.64, 44.88; H, 6.06, 6.11.

Further crops of aniline salt were obtained from the filtrate. Hydrolysis of 0.733 g. (0.00170 mole) of pure aniline salt in 25 ml. of 2 *N* hydrochloric acid for 18 hr. in the presence of barium chloride gave 0.387 g. (0.00166 mole, 97.9%) of barium sulfate.

Sulfation of Anilinium *cis*-2-Hydroxycyclopentanesulfonate.—Six and three-tenths grams (0.026 mole) of anilinium *cis*-2-hydroxycyclopentanesulfonate was rapidly added at 0° with stirring to a mixture of 2.1 g. (0.026 mole) of sulfur trioxide, 3.0 g. (0.034 mole) of dioxane and 50 ml. of ethylene chloride. After 15 min., 2.5 g. (0.027 mole) of aniline was added, which caused a colorless gelatinous precipitate to form. Part of the ethylene chloride was removed from this material by suction filtration, and the residue was washed with 50 ml. of acetone. The salt was recrystallized from 125 ml. of alcohol in the presence of activated charcoal giving 5.8 g. (0.014 mole, 54%) of colorless product, m.p. 201–202°, which did not depress the m.p. of the dianilinium salt of *cis*-2-hydro-sulfatocyclopentanesulfonic acid.

Sulfation of Salts of *trans*-2-Hydroxycyclopentanesulfonic Acid (III).—The sulfation of the aniline salt of III was carried out as described above for the *cis* isomer; 9.9 g. of tan solid was precipitated by the addition of 2.4 g. (0.026 mole, an equimolar portion) of aniline. Sulfate analysis before and after acid hydrolysis indicated that this material consisted of 20% of anilinium sulfate and 70% of the dianilinium salt of *trans*-2-hydro-sulfatocyclopentanesulfonic acid. The salt was too soluble in acetone, alcohol or water to allow purification from these solvents (in contrast to the lower solubility of the *cis* isomer). Addition of aqueous *S*-(*p*-chlorobenzyl)-thiuronium chloride solution gave a derivative which melted at 158–160° after recrystallization from water in the presence of activated charcoal. Recrystallization from water gave the bis-*S*-(*p*-chlorobenzyl)-thiuronium salt of *trans*-2-hydro-sulfatocyclopentanesulfonic acid, m.p. 161–162°.

Anal. Calcd. for $C_{21}H_{23}O_7N_4S_4Cl_2$: C, 38.94; H, 4.36. Found: C, 39.04; H, 4.39.

Five grams (0.021 mole) of barium *trans*-2-hydroxycyclopentanesulfonate was added to 0° to a solution of 3.0 g. of 60% oleum and 6 g. of sulfuric acid. After the dark brown mixture had stood for 5 min., it was poured onto ice. The solution was neutralized with barium carbonate, the insoluble salts removed, and the filtrate evaporated to dryness under reduced pressure yielding 6.6 g. (82%) of slightly yellow barium salt of *trans*-2-hydro-sulfatocyclopentanesulfonic acid. The *S*-(*p*-chlorobenzyl)-thiuronium derivative prepared from this salt was identical with that obtained from the aniline salt.

Dianilinium Salt of *cis*-2-Hydro-sulfatocyclohexanesulfonic acid (VIII).—A mixture of 49.3 g. (0.616 mole) of sulfur trioxide, 54.5 g. (0.620 mole) of dioxane and 200 ml. of ethylene chloride was cooled to –20° in an acetone–Dry Ice-bath, and 31.6 g. (0.386 mole) of cyclohexene was added at such a rate that the temperature of the reaction mixture remained below –15°. The mixture stood at temperatures

below –10° for 1 hr., at 0° for 6 hr., and was allowed to warm up to 25° during the next 9 hr. The resulting clear yellow solution was poured onto ice. Analysis of the aqueous layer showed the presence of 0.459 equivalent of acids, 0.110 mole (29% of the cyclohexene) of unsaturated sulfonic acids and 0.0354 mole (5.7% of the sulfur trioxide) of sulfuric acid. A sample of the aqueous solution, from which free sulfate ions had been precipitated from neutral solution, was digested with 1 *N* hydrochloric acid at steam-bath temperature for 5 hr. From this solution an additional 0.122 mole (40% of the cyclohexene) of barium sulfate was precipitated. These products accounted for only 67% of the sulfur trioxide used. Evaporation of the ethylene chloride layer gave a dark oil.

The greater portion of the aqueous solution was neutralized with barium hydroxide. After removal of barium sulfate, sulfuric acid was added to the filtrate until no more barium sulfate was formed. To the filtrate from this reaction mixture 42.6 g. (0.459 mole) of aniline was added. The solution was concentrated to 150 ml. and allowed to stand for 24 hr., whereupon 14.2 g. of yellow crystals, m.p. 170–193°, precipitated. When a sample of 0.466 g. of this material was refluxed for 2 hr. in 50 ml. of hydrochloric acid containing barium chloride, 0.203 g. of barium sulfate precipitated. This indicates the presence of 83% of the dianilinium salt of *cis*-2-hydro-sulfatocyclohexanesulfonic acid in the sample, which places the yield of this material at 7%. A 10-g. portion of the salt was recrystallized from 100 ml. of 95% alcohol to give 6.0 g. of white crystals, m.p. 201–205°. Several more crystallizations gave material melting at 201–203°.

Anal. Calcd. for $C_{18}H_{26}O_7N_2S_2 \cdot H_2O$: C, 46.53; H, 6.08; neut. equiv., 232. Found: C, 45.82, 46.16; H, 6.04, 6.49; neut. equiv., 238.

Salts of *cis*-2-Hydroxycyclohexanesulfonic Acid (IX).—A solution of 5.0 g. of the dianilinium salt of *cis*-2-hydro-sulfatocyclohexanesulfonic acid in 20 ml. of 1 *N* sulfuric acid was refluxed for 2 hr., and then neutralized with barium carbonate. After removal of barium sulfate the filtrate was evaporated under reduced pressure to give 2.6 g. (94%) of barium salt of IX. A solution of 1.2 g. (0.0048 mole) of the barium salt in 15 ml. of water was treated with 0.23 g. (0.0023 mole) of sulfuric acid and 0.5 g. (0.0054 mole) of aniline. After removal of the barium sulfate, the filtrate was evaporated to dryness under reduced pressure and the resulting salt crystallized from 25 ml. of 20% alcoholic acetone to give 0.7 g. (0.0026 mole, 55%) of colorless crystals, m.p. 203–205° dec. Further crystallization gave material, m.p. 205–206°, the m.p. of which was depressed to 160–179° when mixed with the dianilinium salt of *cis*-2-hydro-sulfatocyclohexanesulfonic acid, and was depressed to 164–183° when mixed with anilinium 1-cyclohexene-1-sulfonate.

Anal. Calcd. for $C_{12}H_{19}O_4NS$: C, 52.73; H, 7.01; neut. equiv., 273. Found: C, 52.64; H, 6.91; neut. equiv., 279.

A solution of 1.2 g. (0.0048 mole) of the barium salt of IX in 15 ml. of water was treated with 1.0 g. (0.0048 mole) of *S*-benzylthiuronium sulfate, the mixture digested for 15 min. on the steam-bath, the barium sulfate removed and the filtrate concentrated to 10 ml. On cooling, 1.4 g. (0.0037 mole), 75%, of colorless crystals, m.p. 150–153°, were formed. After two crystallizations, each from 4 ml. of water, *S*-benzylthiuronium *cis*-2-hydroxycyclohexanesulfonate, m.p. 151–152.5°, was obtained.

Anal. Calcd. for $C_{14}H_{22}O_4N_2S_2$: C, 48.52; H, 6.40. Found: C, 48.80; H, 6.57.

These salts of IX differed in physical properties from those of the *trans* isomer which were prepared from the product of the reaction cyclohexene oxide or 2-chlorocyclohexanol with ammonium sulfite.¹⁰

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