droxy group and the oxygen atoms of the sulfone bridge probably disfavor conformations resembling J and K too, but to a lesser extent. The solvated ionized hydroxy group is most free in conformations of type M. The less strained conformations are energetically favored and the more heavily populated. In order to rearrange, the molecule must rotate from various "non-rearranging" conformations, especially of type M, into "rearranging" conformations of type N, forcing the solvated ionized hydroxy group into a crowded situation against a significant energy differential.

Now when a large 6-substituent is introduced, conformations of type M are strongly disfavored because of steric compressions between the 6-substituent and the carbon atoms of the other ring, conformations of types J and K are disfavored to a lesser extent because of crowding of the 6-substituent with the oxygen atoms of the sulfone bridge, and "rearranging" conformations like N are rendered most favorable insofar as compressions with the 6-substituent are considered. A new energy differential in favor of the "rearranging" conformations is superimposed on the former differential against them. There is a net decrease in the energy differential between "rearranging" and "non-rearranging" conformations, a consequent decrease in the energy of activation, and therefore a higher rate of rearrangement.

Acknowledgments.—Mr. Kenneth M. Pruitt determined many of the titrimetric rate coefficients for sulfones IVa and IVb. We sincerely appreciate his help. Dr. Charles N. Reilley suggested the polarographic method of analysis, and we are grateful to him and to Dr. Rudolf Schmid for advice in connection with its use. We thank the Office of Ordnance Research, U. S. Army, for financial assistance.

CHAPEL HILL, N. C.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

Sulfonation of Olefins. VII. Sulfonation of 1,1-Diphenyl-2-methyl-1-propene

BY F. G. BORDWELL AND G. W. CROSBY[1]

RECEIVED JUNE 7, 1956

Sulfonation with the dioxane–sulfur trioxide complex was observed to occur at a much slower rate with 1,1-diphenyl-2-methyl-1-propene than with styrenes previously studied. Attack occurred in the aromatic nuclei of the substituted styrene rather than in the side chain. Speculation concerning the significance of these results with regard to the mechanism of sulfonation is given. 2-Chloroethyl chlorosulfonate and 2-chloroethyl hydrogen sulfate were identified as products of the reaction of sulfur trioxide with ethylene chloride.

The previous investigations on the sulfonation of olefins with dioxane–sulfur trioxide complex[2] indicate a prominent role in the reaction for a β-sultone intermediate. Hydrolysis of this intermediate on addition of water is believed to be the primary source of the β-hydroxyalkanesulfonic acids formed from equimolar quantities of olefin and sulfonating reagent. The unsaturated sulfonic acids obtained (after hydrolysis) in these reactions also are probably formed, at least in part, from this intermediate.[3] Sulfonation of 1,1-diphenyl-2-methyl-1-propene (I) is of interest in this latter regard, since the expected β-sultone intermediate II should be rapidly hydrolyzed, but cannot give unsaturated products, unless hydrolysis is accompanied by rearrangement.

The rate of sulfonation of I with a solution of the dioxane–sulfur trioxide complex in ethylene chloride at 0° was found to be much slower than that of styrene. Whereas the reaction with styrene was 60% complete within one minute,[4] that with I was only about 25% complete after 15 hours at 0°, judging from the quantity of sulfuric acid obtained on hydrolysis.

In order to effect sulfonation a solution containing equimolar quantities of I and the sulfonating agent was allowed to stand at room temperature for 15 hours. Under these conditions about 50% of a monosulfonic acid III and 30% of a disulfonic acid IV were formed, judging from the quantities of barium salts isolated. The barium disulfonate was contaminated by 10% or more of sulfonation products resulting from reaction of sulfur trioxide with dioxane. About 5% of the sulfur trioxide was recovered as sulfate, and about 5% was converted to a sultone V.

The products of the sulfonation were isolated by hydrolysis and conversion of the acids present in the aqueous layer to barium salts with barium carbonate. The barium salt of the monosulfonic acid III was soluble in water only to the extent of about 1% by weight, and was separated readily from the more soluble barium salt of the disulfonic acid IV. On oxidation with aqueous potassium permanganate the salts of both III and IV gave acetone, which was identified through its 2,4-dinitrophenylhydrazone. Analysis of distillates from the oxidation mixtures for acetone using the iodine–thiosulfate method of Messinger[5] showed the formation of 68% of acetone from the monosulfonic acid and 44% of acetone from the disulfonic acid under these conditions. These results showed conclusively that sulfonation had occurred in the benzene nucleus rather than in the side chain of

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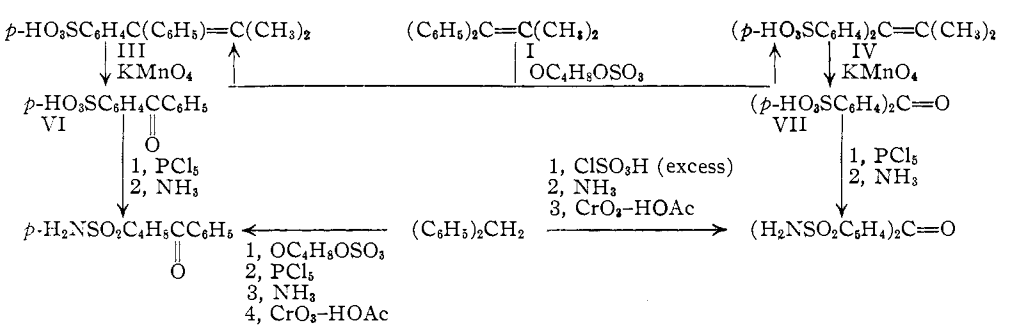
(1) Winthrop–Stearns Chemical Co. Fellow, 1946–1947; Allied Chemical and Dye Corp. Fellow, 1947–1948. Abstracted from the Ph.D. dissertation of G. W. Crosby, Northwestern University, June, 1949.

(2) See Paper VI in this series, F. G. Bordwell and M. L. Peterson, THIS JOURNAL, **76**, 3957 (1954), for leading references.

(3) This point will be discussed in a later paper in this series.

(4) F. G. Bordwell, M. L. Peterson and C. S. Rondestvedt, THIS JOURNAL, **76**, 3945 (1954).

(5) L. F. Goodwin, *ibid.*, **42**, 39 (1920).



the olefin. The lower yields of acetone and of other derivatives from the disulfonate pointed to a lower purity for this material.

The formation of acetone indicated that the other products from these oxidations were benzophenone mono- and disulfonic acids VI and VII. Carbon and hydrogen analyses of the S-benzylthiuronium salts and of the sulfonamides of VI and VII supported this view.

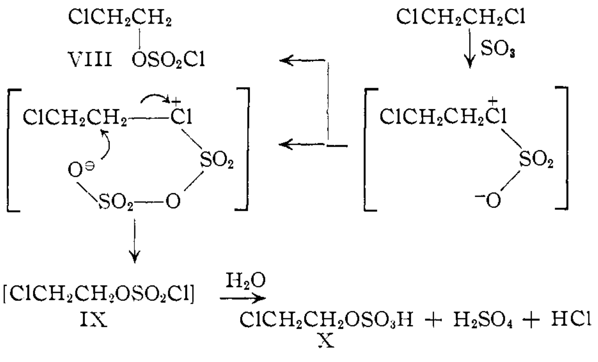
It seemed reasonable to suppose that the $(CH_3)_2C{=}C{<}$ group in I had promoted a *para* orientation of the sulfonic acid group(s) during sulfonation, since even negatively substituted vinyl groups are *o*–*p*-directing.[6] The possibility of a *meta* orientation of the groups in the disulfonic acid IV was further obviated by demonstrating the dissimilarity of the S-benzylthiuronium salt of its oxidation product with that of *m*-(*m*-sulfobenzoyl)-benzenesulfonic acid (*m,m'*-benzophenonedisulfonic acid).

The sulfonation of diphenylmethane with chlorosulfonic acid has been shown to give an 82% yield of *p*-benzylbenzenesulfonic acid, isolated as the barium salt.[7] A comparable sulfonation was effected in the present work using dioxane–sulfur trioxide. Since no derivative to allow comparison had been reported by the previous workers,[7] the sodium salt of our product was fused with sodium hydroxide to give *p*-benzylphenol in order to make certain of the position of the sulfo group. Preparation of the sulfonamide *via* the barium salt proved unsatisfactory, but an over-all yield of 75% of *p*-benzylbenzenesulfonamide was obtained starting with the sodium salt. Oxidation of *p*-benzylbenzenesulfonamide with chromic anhydride in acetic acid gave a 50% yield of *p*-benzoylbenzenesulfonamide, m.p. 172–173°, which proved to be identical with the sulfonamide prepared from VI, the oxidation product of the monosulfonic acid III.

Lapworth obtained *p*-(*p*-chlorosulfonylbenzyl)-benzenesulfonyl chloride from the disulfonic acid formed by sulfonation of diphenylmethane.[8] He did not prove the structure, but, since monosulfonation has been shown to give the *para* isomer, there is no reason to doubt this assignment. A diphenylmethanedisulfonyl chloride agreeing in melting point with that reported by Lapworth[8] was obtained by sulfonation of diphenylmethane with excess chlorosulfonic acid. The disulfonamide was prepared from this, and was oxidized to *p*-(*p*-sulfonamidobenzoyl)-benzenesulfonamide, which proved to be identical with the disulfonamide prepared from VII. The ready oxidation of the diphenylmethanedisulfonamide to the benzophenonedisulfonamide contrasts with Lapworth's report[8] that "all attempts to oxidize the sulphonamide were fruitless."

The crystalline sultone V obtained from the ethylene chloride layer, after hydrolysis of the sulfonation mixture, was found to have a molecular formula $C_{16}H_{16}SO_3$. Its identity was not established, but in view of later work[9] it seems likely that it is 2-methyl-3,3-diphenylpropane-1,3-sultone, which could be formed from small amounts of 3,3-diphenyl-2-methyl-1-propene present in the sample of I used for the sulfonation.

The slowness of sulfonation of I caused concern over the formation of by-products from reaction of the sulfonating agent with the ethylene chloride, which was used as the solvent, or with dioxane. These possibilities were investigated. Ethylene chloride was found to react very slowly with sulfur trioxide, only about 3% reaction occurring at room temperature in four days. From reactions allowed to stand for longer periods of time, 2-chloroethyl chlorosulfonate (VIII)[10] and 2-chloroethyl hydrogen sulfate (X) were identified as products (after hydrolysis).



2-Chloroethyl chlorosulfonate was found to hydrolyze much too slowly under the conditions used to account for the formation of 2-chloroethyl hydrogen sulfate, and the presence of a more reactive intermediate, such as IX, is indicated. Hydrolysis of an intermediate of similar type has been shown to be very rapid.[11]

One possible formulation of the reactions occurring between sulfur trioxide and ethylene chloride

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(6) F. G. Bordwell and K. Rohde, THIS JOURNAL, **70**, 1191 (1948).

(7) E. Wedekind and D. Schenk, *Ber.*, **44**, 200 (1911).

(8) A. Lapworth, *J. Chem. Soc.*, **73**, 402 (1898).

(9) C. E. Osborne, unpublished data from this Laboratory.

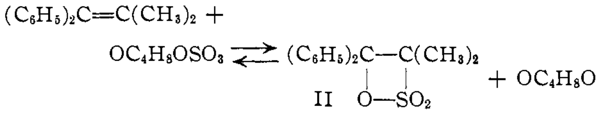
(10) R. M. Isham and O. Spring, U. S. Patent 1,918,967 [*C. A.*, **27**, 4815 (1933)], have reported the preparation of 2-chloroethyl chlorosulfonate in a similar manner.

(11) F. G. Bordwell and M. L. Peterson, THIS JOURNAL, **76**, 3952 (1954).

is shown below. S$_{\text{N}}$i type reactions, such as those shown, appear to be reasonable under these conditions. The formation of ethyl chlorosulfonate from ethyl chloride and sulfur trioxide[12] can be represented similarly.

The reaction of sulfur trioxide with dioxane was much more rapid than that with ethylene chloride. At 0° in 0.4 *M* solution, about 9% of sulfonation of dioxane occurred in 0.5 hour, 13% in 20 hours. Formation of by-products from this reaction during the sulfonation of I therefore was inevitable.

The slow nuclear sulfonation of I is in marked contrast to the very rapid side-chain sulfonation of other styrenes, such as styrene itself,[4] 2-methyl-1-phenylethene[13] and 1-phenylpropene.[13] It seems highly probable from the other sulfonation studies[2,4,13] that an intermediate II, or the like, will be formed rapidly. Since I is recovered, along with sulfuric acid, from reaction mixtures allowed to stand for short periods of time, the concentration of II or the like in the reaction mixture must be low. This is probably due to a rapid reversal of the side-chain sulfonation by which II is formed. This is not surprising in view of the instability of β-sultones,[4] the particular lability predicted for a tertiary benzhydryl-type sulfonate, and the fact that the sulfur atom in II is also linked to a tertiary carbon. Evidently possible irreversible transformations that might be visualized for II, such as migration of methyl and loss of a proton to give an unsaturated sulfonic acid $(C_6H_5)_2C(CH_3)C(SO_3H){=}CH_2$, are too slow to be of any importance, despite the long reaction time required to effect sulfonation of the benzene ring.



$$(C_6H_5)_2C{=}C(CH_3)_2 + OC_4H_8OSO_3 \rightleftharpoons \underset{\text{II}\quad O{-}SO_2}{(C_6H_5)_2C{-}C(CH_3)_2} + OC_4H_8O$$

Experimental[14]

Sulfonation of 1,1-Diphenyl-2-methyl-1-propene (I).—The olefin was prepared by dehydration of 1,1-diphenyl-2-methyl-1-propanol[15] by distillation from alumina or from sulfuric acid using a modified claisen flask. The product, b.p. 150–155° (14 mm.), n^{16}_{D} 1.5910, differs somewhat in refractive index from that reported by Sabatier and Murat,[15] n^{16}_{D} 1.596; the suspected impurity in our product is 3,3-diphenyl-2-methyl-1-propene.

A solution of 9.7 g. (0.047 mole) of the olefin in 9 ml. of ethylene chloride was added to the sulfonating agent prepared[4] from 3.8 g. (0.047 mole) of sulfur trioxide, 4.5 ml. (0.051 mole) of dioxane, and 11 ml. of ethylene chloride, which was kept at −5°. The reaction mixture was allowed to warm to room temperature, and was kept overnight. It was then washed several times with water, the aqueous layer neutralized with barium carbonate, and the precipitate collected on a filter.

The precipitate obtained was extracted continuously for 40 hr. with 600 ml. of water. Upon cooling, 7.7 g. (46% yield) of **barium *p*-(2-methyl-1-phenyl-1-propenyl)-benzenesulfonate** (barium salt of III) crystallized from the extract.

Anal. Calcd. for $C_{32}H_{30}O_6S_2Ba$: Ba, 19.3. Found: Ba, 19.2.

A 90% yield of the **S-benzylthiuronium salt of III**, m.p. 154–155°, was obtained from 0.51 g. of the barium salt. Two crystallizations from dilute alcohol gave material melting at 156–157°.

Anal. Calcd. for $C_{24}H_{26}N_2O_3S_2$: C, 63.41; H, 5.76. Found: C, 63.61; H, 5.92.

Evaporation of the filtrate from the barium carbonate neutralization gave 3.6 g. (31%) of impure **barium *p*-[2-methyl-1-(*p*-sulfophenyl)-1-propenyl]-benzenesulfonate** (barium salt of IV).

Anal. Calcd. for $C_{16}H_{14}O_6S_2Ba$: Ba, 27.3. Found: Ba, 27.8.

Evaporation of the filtrate from the extract gave 1.4 g. of barium sulfonates, which contained 25.3% of barium. From the barium analysis it is estimated that this contains about 25% monosulfonate and 75% disulfonate (increasing the yields of these products by 3 and 9%, respectively).

The barium carbonate residue yielded 7% of barium sulfate on acid treatment and ignition.

The ethylene chloride layer contained about 0.6 g. of a sultone, believed to be **2-methyl-3,3-diphenylpropane-1,3-sultone** (V). After crystallization from alcohol it melted at 134–135°.

Anal. Calcd. for $C_{16}H_{16}O_3S$: C, 66.63; H, 5.59; sapn. equiv., 288; mol. wt., 288. Found: C, 66.65; H, 5.70; sapn. equiv., 287; mol. wt.,[16] 284.

Oxidation Products from the Barium Salt of III.—A mixture of 0.70 g. (0.00185 eq.) of the barium salt of III and 100 ml. of water was placed in a three-neck flask fitted with a dropping funnel, stirrer and downward condenser. The condenser tip was kept beneath the surface of about 25 ml. of water in a small flask. The mixture was heated to boiling and stirred while a solution containing 1.4 g. (0.0089 mole) of potassium permanganate in 40 ml. of water was added over a 0.5-hour period. Heating was continued until two distillate fractions of 75 and 25 ml. were collected. Analysis of the distillates for acetone according to the Messinger method[5] showed a total of 68% of the theoretical as being present. The analysis was adapted to the present conditions by checking known samples, and by making preliminary runs to estimate the amount of acetone to be expected.

In a separate run under these conditions the distillate was collected in a 0.1% 2,4-dinitrophenylhydrazine solution, whereby acetone 2,4-dinitrophenylhydrazone, m.p. 125–126°, was obtained.

A solution of 3.6 g. (0.010 eq.) of the barium salt of III in 500 ml. of boiling water was treated with potassium permanganate [6.4 g. (0.040 mole) required] until the solution remained colored for about ten minutes. The mixture was then boiled until decolorized, and filtered using a filter-aid. One-tenth of the filtrate was treated with 1.5 ml. of 0.7 *N* S-benzylthiuronium chloride solution, and the resulting solution concentrated. The crystalline derivative weighed 0.22 g. (51% yield); it melted at 185–187°. Crystallization from water containing a drop of hydrochloric acid gave **S-benzylthiuronium *p*-benzoylbenzenesulfonate**, m.p. 187–188°.

Anal. Calcd. for $C_{21}H_{20}N_2O_4S_2$: C, 58.86; H, 4.70. Found: C, 58.74; H, 4.67.

Nine-tenths of the filtrate from the oxidation described above was evaporated to dryness, and the salt dried under vacuum at 100° over phosphorus pentoxide for 4 hr. The solid was mixed with an equal weight (3.4 g.) of phosphorus pentachloride, and the mixture was heated at 120° for 18 hours. A benzene solution of the product was washed twice with water and then shaken with 30 ml. of concd. aqueous ammonia. After standing overnight, 0.9 g. of product, m.p. 163–167°, was collected by filtration. An additional 0.4 g. was obtained by extracting the benzene layer with sodium hydroxide followed by neutralization of the extract (total yield, 55%). After two crystallizations from alcohol a sample of *p*-benzoylbenzenesulfonamide, m.p. 172–173°, was obtained.

Anal. Calcd. for $C_{13}H_{11}NO_3S$: C, 59.74; H, 4.23. Found: C, 60.01; H, 4.13.

The 2,4-dinitrophenylhydrazone of *p*-benzoylbenzenesulfonamide melted at 234–235°, after crystallization from alcohol.

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[12] Th. Purgold, *Compt. rend.*, **67**, 451 (1868).

[13] C. M. Suter and W. E. Truce, THIS JOURNAL, **66**, 1105 (1944).

[14] Microanalyses were by Misses P. Craig and J. Gibbs. Melting points are uncorrected.

[15] P. Sabatier and M. Murat, *Compt. rend.*, **156**, 1430 (1913).

[16] Determined by the boiling point elevation method in a modified Menzies-Wright apparatus; W. E. Hanson and J. R. Bowman, *Ind. Eng. Chem., Anal. Ed.*, **11**, 440 (1939).

Anal. Calcd. for $C_{19}H_{15}O_6N_5S$: C, 51.70; H, 3.43. Found: C, 51.53; H, 3.70.

Monosulfonation of Diphenylmethane.—Sulfur trioxide (17.4 g., 0.218 mole) was distilled into 80 ml. of ethylene chloride, and 19.5 ml. of dioxane was added in 0.5 hour at 0°. Diphenylmethane (36.5 g., 0.218 mole) was then added and the mixture allowed to stand at room temperature. After standing overnight, the mixture was washed with water, and the aqueous solution was neutralized with barium carbonate while on the steam-bath. The soluble salts were brought into solution by continuous extraction with water. The product obtained on cooling was crystallized twice from water to yield 22.2 g. (32%) of **barium *p*-benzylbenzenesulfonate.**

Anal. Calcd. for $C_{26}H_{22}O_6S_2Ba$: Ba, 21.7. Found: Ba, 21.7.

A low yield of *p*-benzylphenol, m.p. 80.5–81.5°, was obtained by fusion of a small sample of this barium salt with potassium hydroxide at 250–310°.

A 1.0-g. sample of the barium salt was treated with an equivalent quantity of aqueous sodium sulfate and the barium sulfate formed was removed by filtration. An almost quantitative yield of **S-benzylthiuronium *p*-benzylbenzenesulfonate**, m.p. 153–154°, was obtained from the filtrate. After two crystallizations from water a 70% yield of derivative, m.p. 155°, was obtained.

Anal. Calcd. for $C_{21}H_{22}N_2O_3S_2$: C, 60.84; H, 5.35. Found: C, 60.87; H, 5.50.

The sulfonamide prepared from the barium salt resisted repeated attempts at purification. The dried sodium salt (8.7 g.) was mixed with 4.5 g. of phosphorus pentachloride, and the mixture was heated under reflux for 3 hr. at a bath temperature of 140°. After cooling and adding benzene the mixture was filtered, and the filtrate was washed three times with cold water. The solution was dried over Drierite, the solvent was evaporated, and the residue was distilled at 0.2 mm. using a Hickman still. An 86% yield of sulfonyl chloride was obtained. A benzene solution containing 5.6 g. (0.021 mole) of the sulfonyl chloride was shaken with 50 ml. of concd. aqueous ammonia. The crude sulfonamide obtained from the benzene layer was dissolved in aqueous sodium hydroxide. The material precipitated by addition of dil. hydrochloric acid melted at 125–126° before and after crystallization from alcohol. The yield of ***p*-benzylbenzenesulfonamide** based on the sulfonyl chloride was 87%.

Anal. Calcd. for $C_{13}H_{13}NO_2S$: C, 63.13; H, 5.30. Found: C, 62.90; H, 5.41.

p-Benzylbenzenesulfonamide gave *p*-benzoylbenzenesulfonamide in good yield when oxidized with chromic anhydride in acetic acid for 2 hours at steam-bath temperature.

Oxidation Products from the Barium Salt of IV.—Oxidation of the disulfonate, as described above, gave 44% of acetone, which was determined as before.

A 21% yield of **S-benzylthiuronium *p*-sulfobenzoylbenzenesulfonate**, m.p. 238–240°, was obtained in the manner described for the monosulfonate. After crystallization from water and from alcohol–hexane the melting point was 249–250°.

Anal. Calcd. for $C_{29}H_{30}N_4O_7S_4$: C, 51.61; H, 4.48. Found: C, 51.79; H, 4.50.

A sample of **S-benzylthiuronium *m*-sulfobenzoylbenzenesulfonate**, prepared from the barium salt for comparison, melted at 230–231°.

Anal. Calcd. for $C_{29}H_{30}O_7N_4S_4$: C, 51.61; H, 4.48. Found: C, 51.70; H, 4.77.

A 15% yield of ***p*-sulfonamidobenzoylbenzenesulfonamide**, m.p. 238–242°, was obtained from the barium salt of IV in a manner similar to that described for III. Crystallization from alcohol and from water gave material melting at 247–248°.

Anal. Calcd. for $C_{13}H_{12}O_5N_2S_2$: C, 45.86; H, 3.55. Found: C, 45.73; H, 3.61.

Disulfonation of Diphenylmethane.—Diphenylmethane (6.0 g., 0.036 mole) was added dropwise to 19 g. (0.16 mole) of chlorosulfonic acid. After standing 1 hr. the reaction mixture, in which crystals had formed, was poured into ice-water. The product was dissolved in benzene, and the benzene solution was washed with water until neutral. After drying over anhydrous calcium sulfate the benzene was evaporated to yield 5.8 g. (45%) of a crystalline residue, m.p. 114–118°. After two crystallizations from benzene-heptane 2.7 g. (21%) of product melting at 122–123° was obtained. **S-Benzylthiuronium *p*-(*p*-sulfobenzyl)-benzenesulfonate**, m.p. 191–192°, was obtained by hydrolysis of the disulfonyl chloride and addition of S-benzylthiuronium chloride solution to the hydrolysate.

Anal. Calcd. for $C_{29}H_{32}O_6N_4S_4$: C, 52.71; H, 4.88. Found: C, 52.53; H, 4.67.

A 51% yield of ***p*-(*p*-sulfonamidobenzyl)-benzenesulfonamide**, m.p. 178–180°, was obtained from the disulfonyl chloride by a procedure similar to that described previously. Crystallization from water gave material melting at 182–183°.

Anal. Calcd. for $C_{13}H_{14}O_4N_2S_2$: C, 47.82; H, 4.32. Found: C, 47.65; H, 4.26.

A solution of 0.10 g. (0.00029 mole) of the disulfonamide in 2 ml. of glacial acetic acid was added to a solution of 0.10 g. of chromic anhydride in a few drops of water and 1 cc. of glacial acetic acid. After heating on the steam-bath for 3 hr., the solution was diluted with several volumes of water. Crystallization occurred on cooling. After recrystallization from water the product weighed 0.05 g. (50% yield). It melted at 247–248°, and did not depress the melting point of the sample of *p*-(*p*-sulfonamidobenzoyl)-benzenesulfonamide prepared starting from the barium salt of IV. Lapworth[8] reports failure of this oxidation, but does not give experimental details.

Reaction of Ethylene Chloride and Sulfur Trioxide.—Sulfur trioxide (38.8 g., 0.485 mole) was distilled into 300 ml. of ethylene chloride and the resulting solution was allowed to stand at room temperature for 26 days. The reaction was finally added to water, and the ethylene chloride layer washed four times with water. The aqueous solution was found to contain 0.24 eq. of chloride ion per mole of SO_3 charge.

The aqueous solution was neutralized with barium carbonate and the resulting mixture filtered. A one-tenth portion of the filtrate was evaporated to about 5 ml., and treated with 0.25 *N* S-*p*-chlorobenzylthiuronium chloride solution. After crystallization from ethylene chloride, a 5% yield (based on SO_3) of **S-*p*-chlorobenzylthiuronium 2-chloroethyl sulfate**, m.p. 118–119°, was obtained. This salt was prepared also by heating together equal weights of sulfamic acid and ethylene chlorohydrin on the steam-bath overnight and then adding S-*p*-chlorobenzylthiuronium chloride solution. Attempts to crystallize the salt gave S-*p*-chlorobenzylthiuronium sulfate unless dry solvents were used.

Anal. Calcd. for $C_{10}H_{14}O_4N_2Cl_2S_2$: C, 33.33; H, 3.91. Found: C, 32.98; H, 4.04.

The ethylene chloride layer was dried, the solvent was removed under reduced pressure and the residue was vacuum distilled through a 3-inch Vigreux column. A 13.5-g. fraction (15% yield) of **2-chloroethyl chlorosulfonate**, b.p. 46–48° (0.5 mm.), was collected.

Anal. Calcd. for $C_2H_4O_3Cl_2S$: C, 13.42; H, 2.25; Cl, 39.6; mol. wt., 179. Found: C, 13.44; H, 2.20; Cl, 40.3; mol. wt.,[16] 177, 190.

In separate experiments 2-chloroethyl chlorosulfonate was found to hydrolyze only slowly in aqueous dioxane solution, which eliminates it as a possible progenitor of X.

A 0.2952-g. (0.001650 mole) sample of the chlorosulfonate was dissolved in 20 ml. of 2% aqueous sodium hydroxide by refluxing, acidified with hydrochloric acid, and the sulfate precipitated with barium chloride (0.00151 mole, 92% of $BaSO_4$). The filtrate was freed of barium ion, neutralized with sodium bicarbonate and treated overnight with 50 ml. of 0.0536 *N* potassium iodate solution. Arsenite in excess (25 ml. of 0.0965 *N*) and a few potassium iodide crystals were added, and the solution was titrated with 0.0515 *N* iodine solution after 15 min. (36.3 ml. required). This corresponds to utilization of periodate to an extent of 30% beyond theory. Addition of 1 g. of 5,5-dimethyl-1,3-cyclohexanedione gave 0.6 g. (0.002 mole, 60%) of the derivative of formaldehyde. The m.p. and mixed m.p. with a known sample was 186–188°.

Reaction of Sulfur Trioxide with Dioxane.—A solution of 13 ml. (0.15 mole) of purified dioxane[17] in 150 ml. of ethylene chloride was added to an ice-cold solution of 11.2 g. (0.14

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[17] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1941, p. 369.

mole) of sulfur trioxide in 175 ml. of ethylene chloride. Aliquots withdrawn at various intervals were hydrolyzed, and the aqueous layer and washings from the ethylene chloride layer were digested with excess barium carbonate. After removal of the barium sulfate and barium carbonate, the filtrate was analyzed for barium ion as barium sulfate.

The solution was kept at 0° for 19.5 hours. After 0.5, 1.5 and 19.5 hours the percentages of sulfur trioxide reacting to form soluble barium salts were 9.3, 9.5 and 12.7, respectively. The solution was then allowed to warm to 25°. After a total of 25.5 hr. the percentage of sulfur trioxide-forming soluble barium salts was still 12.7; after a total of 116.5 hr. the amount had risen to 13.8%. Chloride ion from ethylene chloride reaction amounted to less than 2% of the soluble barium salts produced.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN]

The Solvolysis of 6-Ketocyclodecyl *p*-Toluenesulfonate and *p*-Bromobenzenesulfonate

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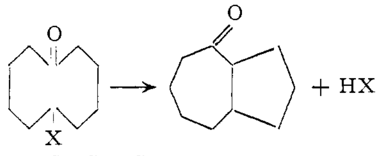
The solvolysis of 6-ketocyclodecyl *p*-toluenesulfonate (Ia) in ethanol results in the formation of a mixture of *cis*- and *trans*-[5.3.0]bicyclodecan-2-one (II). The composition of this mixture (60–80% *trans* isomer) is indistinguishable from that resulting from treatment of the *p*-toluenesulfonate with base. Ethanolysis of Ia is autocatalytic—the solvolysis is acid catalyzed. The dependence of the rate on various concentrations indicates that solvolysis involves an acid-catalyzed (second-order) reversible enolization followed by conversion of the enol III to product II. The enol III is solvolyzed much faster than cyclodecyl *p*-toluenesulfonate. The high reactivity of the enol and its conversion to the bicyclic ketone II are evidently manifestations of a transannular interaction between the carbon–carbon double bond and C_1.

In the course of an investigation of cyclodecyl and cyclodecenyl arylsulfonates in which transannular interactions might be expected, we have studied the ethanolysis of 6-ketocyclodecyl *p*-toluenesulfonate (Ia) and *p*-bromobenzenesulfonate (Ib). This reaction shows two unusual features. (i) Instead of the expected product from an E_1 or S_N1 reaction, [5.3.0]bicyclodecan-2-one (II) appears to be the exclusive product—an 88% yield of pure II was isolated. (ii) Contrary to the usual behavior of alkyl arylsulfonates in hydroxylic solvents, the ethanolysis of I is catalyzed by acid and thus is autocatalytic. The uncatalyzed solvolysis is so slow compared to the acid-catalyzed reaction that essentially all of the product is formed by the acid-catalyzed process.



Ia, X = $—OSO_2C_6H_4CH_3$-*p* II
Ib, X = $—OSO_2C_6H_4Br$-*p*

The [5.3.0]bicyclodecan-2-one (II) resulting from the ethanolysis of I, *i.e.*, the product of the acid-catalyzed process, was compared with that which results from the treatment of Ia with *t*-butoxide in *t*-butyl alcohol.[2] The products obtained by the two methods had indistinguishable infrared spectra and gave similar mixtures of 2,4-dinitrophenylhydrazones and oximes. Thus it appears that the *cis–trans* compositions of the two products are very similar. Evidently the thermodynamically controlled product is obtained in each case. Isomeric 2,4-dinitrophenylhydrazones were formed in a ratio of 3–4:1. From this observation, together with the fact that the previously known[3] *trans*-[5.3.0]bicyclodecan-2-one oxime was formed in larger amounts than the *cis* isomer, we infer that the ketone mixture, II, consists of 60–80% of the *trans* isomer.

The rates of ethanolysis of 6-ketocyclodecyl *p*-toluenesulfonate (Ia) and *p*-bromobenzenesulfonate (Ib) were measured at 20 and 30°. The progress of the reaction was followed by titration of the acid produced by the solvolysis. Plots of acid concentration *vs.* time for the ethanolysis of Ia and Ib are shown in Fig. 1. These data clearly show that the reaction is autocatalytic and suggest that the process is nearly first order in keto-*p*-toluenesulfonate and in one of the solvolysis products. If the process were cleanly first order in both reactant and product, the sigmoidal curves in Fig. 1 would be symmetrical with the steepest slope (greatest rate) at 50% completion.

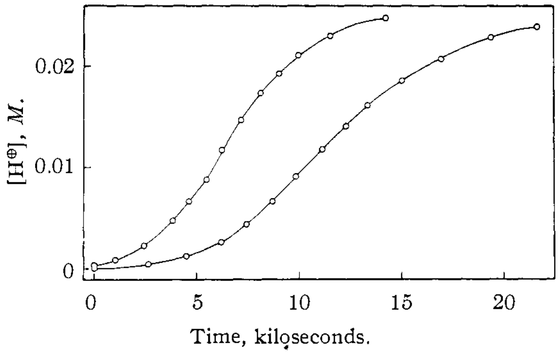


Fig. 1.—The solvolyses of 6-ketocyclodecyl esters in absolute ethanol at 30.05°: upper curve, *p*-bromobenzenesulfonate (expt. 2a); lower curve, *p*-toluenesulfonate (expt. 1a).

It was demonstrated readily that the autocatalytic behavior is due to catalysis by the acid formed in the solvolysis. The rate during the induction period is so slow that it is clear that essentially all of the material reacts by the acid-catalyzed process. It was not possible to determine the rate of the uncatalyzed reaction by solvolyzing the keto-*p*-toluenesulfonate in the presence of base because under these conditions I is rapidly converted to II

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[2] A. C. Cope and G. Holzman, THIS JOURNAL, **72**, 3062 (1950).

[3] W. Hückel and L. Schnitzspahn, *Ann.*, **505**, 274 (1933).