solution precipitated 2.57 g. (79%) of the theoretical quantity of barium sulfate.

Addition of bromine with shaking to a suspension of 1,1-diphenylethene in water gave a yellow oil which gave colorless crystals on washing with acetone. Crystallization from acetone–water gave needles, m.p. 83.5–84°. A sample of 1,1-diphenyl-2,2-dibromoethene, m.p. 83–84°, was also obtained by reaction of bromine water with 1,1-diphenyl-2-bromoethene.

Reaction of 2,2,4,4-Tetraphenyl-4-hydroxybutanesulfonic Acid Sultone (III) with Sodium Hydroxide.—A 1.0-g. sample of III was refluxed for 3 hr. in 15 ml. of 0.33 *N* sodium hydroxide. Neutralization with hydrochloric acid gave 0.9 g. (90%) of colorless salt (VII). A quantitative yield of **S-(*p*-chlorobenzyl)-thiuronium 2,2,4,4-tetraphenyl-3-butene-1-sulfonate** was prepared from 0.4 g. of this salt. After crystallization from 95% alcohol it melted at 176–177° (dried under vacuum at 78°).

Anal. Calcd. for $C_{36}H_{33}O_3N_2S_2Cl\cdot C_2H_5OH$: C, 66.40; H, 5.72. Found: C, 66.58, 66.41; H, 5.83, 5.73.

Addition of bromine to a solution of 0.4 g. of IV in 50% aqueous ethanol gave 0.4 g. (90%) of a white solid. Recrystallization from acetone gave colorless crystals of **2,2,4,4-tetraphenyl-3-bromo-4-hydroxybutanesulfonic acid sultone (VIII)**.

Anal. Calcd. for $C_{28}H_{33}O_3SBr$: C, 64.74; H, 4.46. Found: C, 64.95; H, 4.74.

3-Phenylbenzothiophene 1,1-Dioxide.—Dry sodium 2,2-diphenylethenesulfonate (4.9 g., 0.0174 mole) was mixed with 4.0 g. (0.0192 mole) of phosphorus pentachloride. After heating for 4 hr. on the steam-bath the mixture was extracted with chloroform. The chloroform solution was washed several times with water and aqueous sodium bicarbonate and dried over anhydrous sodium sulfate. Concentration to a volume of 10 ml. and addition of 20 ml. of hexane induced the crystallization of 2.3 g. (47%) of the sulfonyl chloride, m.p. 78–80°. A second crop of 1.9 g. (39%) was obtained on further concentration.

The crude sulfonyl chloride (9.7 g., 0.035 mole) was dissolved in 75 ml. of dry nitrobenzene and treated with 9.0 g. (0.068 mole) of aluminum chloride in 25 ml. of nitrobenzene. After 24 hr. at room temperature hydrochloric acid was added and the nitrobenzene layer was separated and washed. Removal of the nitrobenzene by steam distillation left 8.1 g. of dark brown crystals. Crystallization from 125 ml. of ethanol (after decolorizing with activated charcoal) gave 6.3 g. (74%) of light tan crystals, m.p. 155–158°. Colorless crystals of **3-phenylbenzothiophene 1,1-dioxide**, m.p. 158–160°, were obtained by additional crystallization from 95% alcohol.

Anal. Calcd. for $C_{14}H_{10}O_2S$: C, 69.39; H, 4.16. Found: C, 69.25; H, 4.36.

Evanston, Ill.

[Contribution from the Chemistry Department of Northwestern University]

Sulfonation of Olefins. X. The Preparation of Tertiary 5- and 6-Membered Ring Sultones

By F. G. Bordwell, Richard D. Chapman and C. Edward Osborne

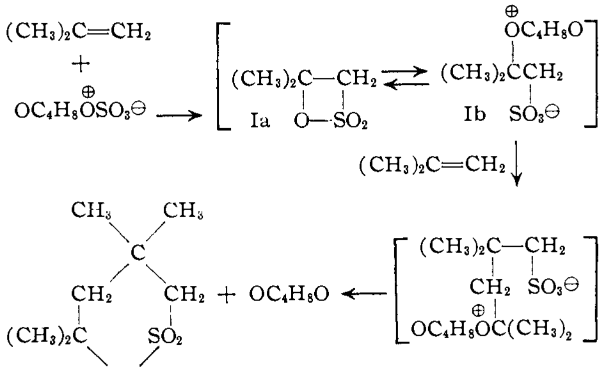
Received October 8, 1958

The preparation of sultones by dimerization–sulfonation, by the reaction of unsaturated sulfonates with bromine or chlorine and by the sulfonation of γ-branched olefins or 1,3-dienes is described. The sulfonation of γ-branched olefins provides a method of synthesis for a variety of hitherto inaccessible 5-membered ring tertiary sultones. Structures of these are assigned on the basis of their mode of formation, their hydrolysis rates and the products formed on hydrolysis.

In recent years improved methods for the preparation of primary and secondary sultones have been reported from several laboratories,[1-4] and a review of the preparation and properties of sultones has been compiled.[5] Dehydration of hydroxyalkanesulfonic acids in xylene–alcohol medium has been shown to be a versatile method for preparing a variety of primary and secondary 5-membered and 6-membered ring sultones.[4] One tertiary 5-membered ring sultone, 3-methyl-3-hydroxy-1-butanesulfonic acid sultone, has been prepared by a dehydrobromination technique.[1]

In the course of an investigation of the sulfonation of olefins with dioxane–sulfur trioxide[6] we have found that sultones may be formed: (1) by a dimerization–sulfonation reaction with certain olefins, (2) by treatment of γ,δ- and certain β,γ-unsaturated sulfonates with bromine or chlorine water, (3) by sulfonation of γ-branched olefins and (4) by the sulfonation of conjugated dienes.

Sultones by Dimerization–Sulfonation.—In earlier papers the formation of small amounts of sultones by a reaction involving two moles of styrene[7] or 1,1-diphenylethene[6] and one mole of sulfur trioxide has been observed. The structure of the sultone from styrene has been proved.[7] Since comparable β-sultone and/or dipolar ion intermediates are believed to be formed in the sulfonation of all types of olefins,[6,8] it was reasoned that the



II, m.p. 99–100°

---

[1] T. Nilsson, Ph.D. Dissertation, University of Lund, Sweden, 1946.

[2] (a) J. H. Helberger, *C. A.*, **41**, 4101 (1947); (b) J. H. Helberger, G. Manecke and H. M. Fischer, *Ann.*, **562**, 23 (1949).

[3] (a) C. W. Smith, D. G. Norton and S. A. Ballard, This Journal, **75**, 748 (1953); (b) W. E. Truce and F. D. Hoerger, *ibid.*, **76**, 5357 (1954).

[4] J. Willems, *Bull. soc. chim. Belg.*, **64**, 747 (1955).

[5] A. Mustafa, *Chem. Revs.*, **54**, 195 (1954).

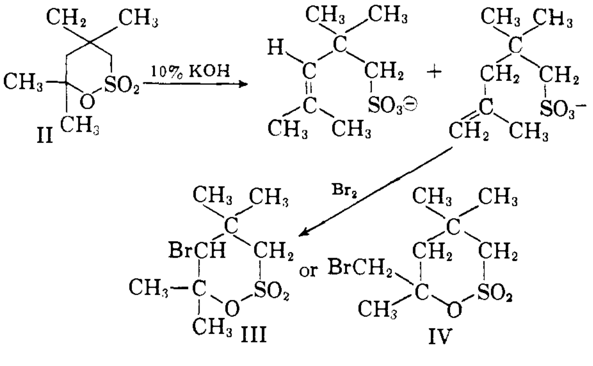
[6] See F. G. Bordwell and M. L. Peterson, This Journal, **81**, 2000 (1959), for paper IX in this series.

[7] See F. G. Bordwell, F. B. Colton and M. Knell, *ibid.*, **76**, 3950 (1954), and earlier papers.

[8] F. G. Bordwell and C. E. Osborne, *ibid.*, **81**, 1995 (1957).

conditions might be adjusted so as to extend the dimerization–sulfonation reaction to other olefins. By carrying out the sulfonation of isobutylene[9] at −70° in the presence of a large excess of olefin this expectation has been realized, sultone II being formed in 31% yield (based on sulfur trioxide). The reaction is formulated in a manner similar to that for the formation of a sultone from styrene[7] and 1,1-diphenylethene.[6] The structure of II rests mainly on this basis. However, the correctness of the assignment of a tertiary sultone structure for II seems assured by the fact that its hydrolysis rate is about 5000 times that of the parent 6-membered ring primary sultone and 500 times that of the 6-membered ring secondary sultone, as reported by Nilsson.[1,10] Sultone II is not formed by the sulfonation of "diisobutylene," since a large quantity of isobutylene and no "diisobutylene" was recovered from the sulfonation, and since the sulfonation of the individual "diisobutylenes" has been found to give unsaturated sulfonic acids and no sultone.[8]

The tertiary structure for sultone II was also supported by the unsaturation value of 59% for the sulfonic acids obtained on hydrolysis, which was raised to 70% by hydrolysis in 10% potassium hydroxide (primary and secondary sultones give low unsaturation values[1]). Bromide–bromate titrations were used for the determination of unsaturation, and a 48% yield of crude bromosultone (68% based on the amount of unsaturation) was formed during the reaction with bromine. A mixture of unsaturated sulfonic acids appears to be formed on hydrolysis, since formaldehyde and acetone were formed, each in about 20% yield, on ozonolysis and oxidation, respectively, of the sodium salts. Also, a mixture of bromosultones formed, judging from the low melting point of the initial product (70–90°), and the relatively high melting point of the purified product (130.5–131°). No choice between structures III and IV for the bromosultone isolated can be made on the basis of the present evidence.



The unsaturated sulfonic acids obtained from the hydrolysis of the styrene dimer and 1,1-diphenylethene dimer sultones[6,7] form good yields of single bromosultones with bromine water, as does sodium 2-methyl-3-phenyl-2-propene-1-sulfonate.[11] The formation of halosultones by the reaction of unsaturated sulfonates and bromine or chlorine water has been observed several times previously[2,6,7,11–14] although the earlier workers did not always realize what reaction they were observing. It seems likely that the reaction will be successful whenever addition of Br^+ or Cl^+ to the double bond of the unsaturated sulfonate places a positive charge in position to close a 5- or 6-membered ring. It should be general for γ,δ-unsaturated sulfonates, but is successful for β,γ-unsaturated sulfonates only when Br^+ is directed to the β-position, as in sodium 2-methyl-3-phenyl-2-propene-1-sulfonate.[11] The isomeric β,γ-unsaturated sulfonate, sodium 2-benzyl-2-propene-1-sulfonate fails to give a bromosultone,[11] as do also the sodium 2-propene-1-sulfonate and sodium 2-methyl-2-propene-1-sulfonate. In this respect it is interesting to note that bromo-β-lactone formation occurs with dimethylmaleic acid.[15]

It was hoped that the sultone from dimerization–sulfonation of isobutylene might correspond in structure to the "octane sultone" (m.p. 129°) isolated by Baldeschwieler and Cassar.[14] It now seems clear that the products from hydrolysis of their sultone, which they formulated as barium ether sulfonates,[14] were actually isomeric unsaturated barium sulfonates. Their analytical results can be accommodated by assuming that the salts were hydrated, as is often the case,[8] and the formation of halosultones strongly suggests unsaturated sulfonates. Judging from the almost quantitative yield of bromosultone formed from the potassium hydroxide hydrolysate, their "octane sultone" must have been hydrolyzed quantitatively under these conditions to an unsaturated sulfonate ("type A barium salt"). This indicates a tertiary structure, since primary and secondary sultones give chiefly hydroxy sulfonates on hydrolysis. Furthermore, the sultone must have more branching near the C–O link than does the tertiary sultone II (which gives only about 70% of unsaturated sulfonates on alkaline hydrolysis), or VII (see below), which gives only 15% of unsaturated sulfonates. Hydrolysis in neutral solution ($BaCO_3$ or $CaCO_3$) appears to have given two unsaturated sulfonates ("type B and type C"),[14] which are different from the type A barium salt formed with barium hydroxide. It is possible, however, that type C may have been a hydroxysulfonate. It seems likely that rearrangement of the double bond occurs under the neutral conditions (compare the hydrolysis of sultone XII below). This suggests a structure $-CH(CH_3)C(CH_3)_2OSO_2-$, since $-C(CH_3)_2C(CH_3)_2OSO_2-$ does not lead to rearrangement on hydrolysis (compare IX below). The formation of "octyl bromides" and "octenes" from the reaction of type C salt with bromine and dilute acid, respectively, suggests a $C{=}C{-}SO_3{-}$ structure.[6]

---

[9] See C. M. Suter and J. D. Malkemus, THIS JOURNAL, **63**, 978 (1941), for an earlier report on the sulfonation of isobutylene.

[10] The hydrolysis rates of sultones are discussed in detail in the next paper, F. G. Bordwell, R. D. Chapman and C. E. Osborne, *ibid.*, **81**, in press (1959).

[11] F. G. Bordwell, C. M. Suter and A. J. Webber, *ibid.*, **67**, 827 (1944).

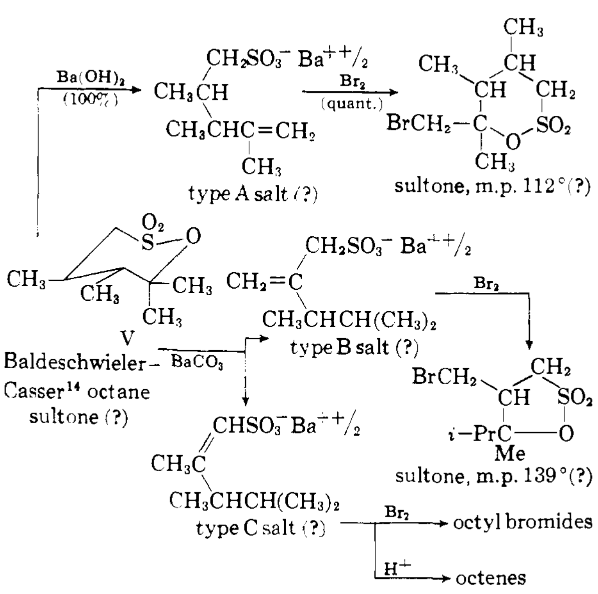
[12] A. W. Harvey and A. Lapworth, *J. Chem. Soc.*, **83**, 1102 (1903).

[13] E. P. Kohler, *Am. Chem. J.*, **31**, 252 (1904).

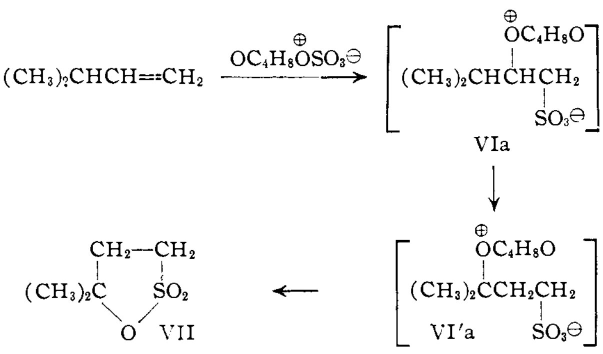
[14] E. L. Baldeschwieler and H. A. Cassar, THIS JOURNAL, **51**, 2969 (1929).

[15] D. S. Tarbell and P. D. Bartlett, *ibid.*, **59**, 407 (1939).

Too many assumptions are required to assign structures to the Baldeschwieler–Cassar sultone and its hydrolysis products with any assurance. Structure V, which could arise from the "dimerization"-sulfonation of propene and 2-methyl-2-butene, represents a reasonable guess. Under mildly acidic conditions the double bonds in branched unsaturated sulfonates appear to assume positions dictated primarily by steric factors.[8] The assignments indicated in the diagram for the double bonds in the hydrolysis products would be speculative, even if the sultone was known to have structure V.[16]



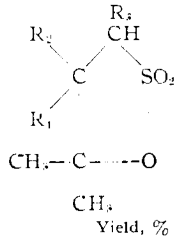
Tertiary γ-Sultones from γ-Branched Olefins.—The formation of a variety of products from the reaction of the dioxane-sulfur trioxide complex with olefins have been rationalized successfully in terms of dioxane-solvated carbonium ion sulfonate intermediates (such as Ia) and/or β-sultone intermediates (such as Ib). Applying this representation to olefins with a γ-branch, such as 3-methyl-1-butene, it might be anticipated that a hydride or methide shift would occur, since this would convert the secondary carbonium ion VIa to a tertiary carbonium ion VI'a. This indeed appears to be the main course of reaction, as much as 53% yield of VII being obtained in the reaction if conditions are controlled so as to minimize hydrolysis of VII during processing. 3-Methyl-3-hydroxy-1-butanesulfonic acid sultone (VII) was prepared by Nilsson[1] by dehydrobromination of 3-methyl-3-bromo-1-sulfonic acid. Our product agreed in melting point and hydrolysis rate with that of Nilsson, and its structure assignment appears to be secure on this basis.



The method appears to be applicable to the preparation of many tertiary 5-membered ring sultones. The six sultones listed in Table I have been prepared in this way. Except for the preparation of VII, all of these reactions involve methyl group shifts.

TABLE I

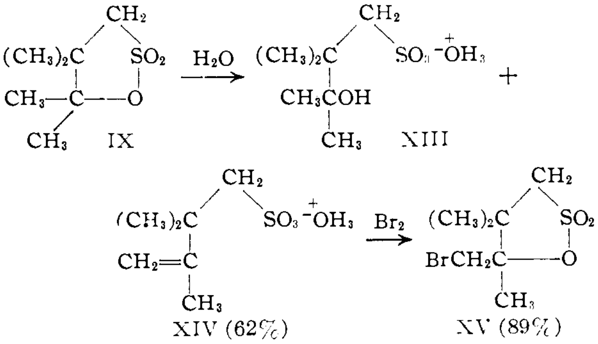
Sultones Prepared from γ-Branched Olefins and Dioxane–Sulfur Trioxide



	R_1	R_2	R_3	Olefin	Yield, %
VII	H	H	H	3-Methyl-1-butene	53
VIII	CH_3	H	H	3,3-Dimethyl-1-butene	71
IX	CH_3	CH_3	H	2,3,3-Trimethyl-1-butene	76
X	H	H	CH_3	4-Methyl-2-pentene	82[a]
XI	H	CH_3	CH_3	4,4-Dimethyl-2-pentene	51
XII	CH_3	C_6H_6	H	3,3-Dimethyl-2-phenyl-1-butene	73

[a] This sultone is unstable and its identification uncertain.

The structure of IX was established by identifying the unsaturated sulfonic acid 2,2,3-trimethyl-3-butene-1-sulfonic acid (XIV), which was formed in 62% yield on its hydrolysis (68% yield on barium hydroxide hydrolysis). The S-*p*-chlorobenzylthiuronium salt of XIV was isolated. The other product formed in the hydrolysis is no doubt 2,2,3-trimethyl-3-hydroxy-1-butanesulfonic acid (XIII), but this was not proved. The S-*p*-chlorobenzylthiuronium salt of XIV exhibited a strong band in the 11.2 μ region, indicating the presence of a $CH_2{=}CR_2$ type double bond. This was confirmed by the formation of 89% of the theoretical quantity of formaldehyde on ozonolysis. The double bond must be γ,δ to the sulfonate group, since a β,γ-unsaturated sulfonate would not have undergone the reaction with bromine to give the bromosultone XV (see discussion above). These data, together with the fact that the sul-



---

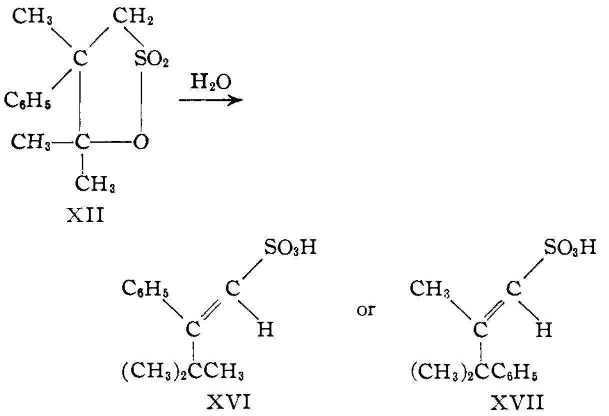
(16) H. O. Mottern of the Standard Oil Development Co., Linden, N. J., has isolated two sultones, m.p. 92° and 109°, as by-products from the sulfation of C_4-olefins (private communication). A sample of Mottern's 108° sultone gave a first-order rate constant in 2.86% dioxane of 4×10^{-4} sec.$^{-1}$ at 50° (determined by Mr. R. Wayne Ohline).

fonation is analogous in type to that leading to VII, leave little doubt as to the correctness of the structure assignment for IX.

The remaining structure assignments were made on the assumption that the sulfonations took courses comparable to those established for the formation of VII and IX. Hydrolysis of VII gave about 15% of unsaturated sulfonic acid, and about 38% of unsaturated sulfonic acid was formed by hydrolysis of VIII. Neither of these unsaturated sulfonates gave bromosultones with bromine water indicating that the more highly substituted unsaturated sulfonic acids (β,γ rather than γ,δ) had been formed. This contrasts with the formation of the γ,δ-unsaturated sulfonate from IX (see above), but this is the only unsaturated product possible from IX, unless a methyl shift occurs during hydrolysis. Such a shift could give rise to a $CH_2{=}CR_2$ type olefin sulfonate, 2-*t*-butyl-2-propene-1-sulfonic acid, but this structure has been ruled out for XIV.[8]

Most of these tertiary sultones are stable at ordinary temperatures. Sultones IX and XII have been kept for several years with no apparent decomposition. However, sultone VII decomposes in a few days time unless stored at −10°. Sultone X decomposes rapidly even at low temperatures. The compounds containing a β-hydrogen therefore appear to be more labile than those with two β-substituents. Sultone X has a β-hydrogen and is probably further labilized by the fact that it has alkyl substitution on both the carbons attached to hetero atoms.

The unsaturated sulfonic acid (isolated as its S-*p*-chlorobenzylthiuronium salt) from the hydrolysis of sultone XII differed strikingly from that (XIV) obtained from sultone IX, since it exhibits no 11.2 mμ band and fails to form a bromosultone when treated with bromine water. Sultone XII differs from IX in that a β-phenyl group has replaced a β-methyl. The only unsaturated sulfonic acids not having terminal methylene groups that conceivably could be formed by hydrolysis of XII are XVI and XVII, which would result from methyl migration or phenyl migration, respectively. Since phenyl migration should occur more readily than methyl migration, structure XVII is favored. Structure XVI was ruled out by the absence of strong absorption in the 245 mμ ultraviolet region, which is characteristic of styrene ($\lambda_{max.}$, 244, log ϵ 4.1), leaving XVII as the only reasonable possibility.



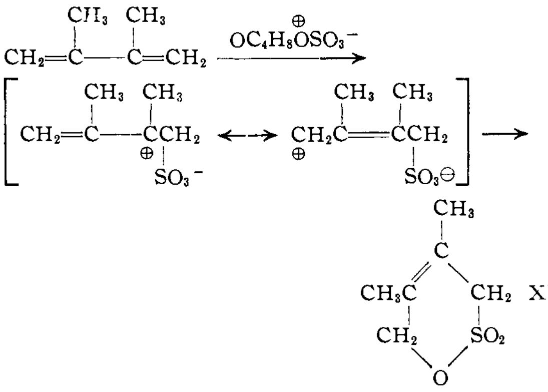
XII

XVI

XVII

Sulfonate XVII is unique among α,β-unsaturated sulfonates in that it absorbs bromine under the conditions of coulometric titration.[17] It seems likely that phenyl participation[18] accelerates the reaction of bromine with XVII sufficiently to allow application of the coulometric method. However, phenyl participation fails to accelerate the hydrolysis rate of sultone XII.[10]

Sultones from 1,3-Dienes.—It might be anticipated that the carbonium–sulfonate dipolar ion intermediate formed by sulfonation of a 1,3-diene could cyclize to a sultone. We have tested this so far only with 2,3-dimethyl-1,3-butadiene. The isolation of sultone XVIII suggests that this offers a possible general approach to allyl-type sultones. The assigned structure is supported by the observation that the hydrolysis rate of XVIII is about 1000 times that of saturated 6-membered ring primary sultones.[10] The failure of the sulfonates formed on hydrolysis to exhibit a conjugated diene type ultraviolet absorption suggests that the hydrolysis gives almost entirely a hydroxy alkanesulfonic acid, which is consistent with Nilsson's observation[1] that primary sultones give hydroxyalkanesulfonic acids and only very small amounts of unsaturated sulfonic acids on hydrolysis.



XVIII

Experimental[19]

Sulfonation of Isobutylene at −70°.—Dioxane–sulfur trioxide reagent prepared from 13.7 g. (0.17 mole) of sulfur trioxide and 16 ml. of dioxane in 200 ml. of methylene chloride was cooled to −70° in a Dry Ice-bath, and a solution of 99.5 g. (1.78 moles) of isobutylene in 100 ml. of methylene chloride, which had been cooled to −60°, was added in one portion. The solution was kept below −60° for 24 hr., and warmed to −10° over a period of two days. The solution was then hydrolyzed by addition of 100 ml. of water and the layers were separated. After washing, the organic layer was evaporated to dryness at room temperature under reduced pressure, leaving 10.3 g. (31%) of colorless **2,2,4-trimethyl-4-hydroxypentanesulfonic acid sultone** (II), m.p. 97–99°. Recrystallization from alcohol gave material melting at 99–100°.

Anal. Calcd. for $C_8H_{16}O_3S$: C, 50.00; H, 8.39. Found: C, 50.32; H, 8.36.

The aqueous layer was boiled with barium carbonate and evaporated to dryness to give 25.3 g. of barium sulfonates

---

[17] J. W. Miller and D. D. DeFord, *Anal. Chem.*, **29**, 475 (1957). We wish to thank Dr. John W. Miller for this determination. See ref. 8 for a discussion of the application of this method to determining the location of double bonds in unsaturated sulfonates.

[18] S. Winstein, *et al.*, THIS JOURNAL, **74**, 1113, 1140 (1952); **75**, 147 (1953).

[19] Microanalyses were by Miss Hilda Beck.

TABLE II

PHYSICAL PROPERTIES AND ANALYSES OF γ-SULTONES

Sultone of: -sulfonic acid	M.p., °C.	Molecular formula	Calculated C	Calculated H	Found C	Found H
2,3-Dimethyl-3-hydroxy-1-butane- (VIII)	61–63	$C_6H_{12}O_3S$	43.88	7.37	44.03	8.00
2,2,3-Trimethyl-3-hydroxy-1-butane- (IX)	145–146^a	$C_7H_{14}O_3S$	47.07	7.91	47.16	7.81
3,4-Dimethyl-4-hydroxy-2-pentane- (XI)	76–77^b	$C_7H_{14}O_3S$	47.07	7.91	46.80	7.78
2,3-Dimethyl-2-phenyl-3-hydroxy-1-butane- (XII)	132–133	$C_{12}H_{16}O_3S$	59.98	6.71	59.89	6.60

^{a} Preparation described in ref. 8. ^{b} A form melting at 42–43° was also obtained.

[55% of the sulfur trioxide as determined by barium analysis (29.09% barium)]. Digestion of the barium carbonate residue with 10% hydrochloric acid left 2.30 g. of barium sulfate (5.8% based on sulfur trioxide). A total of 90.4% of the sulfur trioxide was accounted for in this experiment.

In another experiment distillation of the organic layer was found to give practically no material boiling above 40° other than sultone decomposition products. No "diisobutylene" was recovered.

Ozonolysis and Oxidation of Hydrolysates of II.—Ozonolysis in glacial acetic acid of 0.2-g. samples of barium sulfonates, obtained either by hydrolysis and neutralization or hydrolysis in the presence of barium hydroxide, gave about 20% of formaldehyde as its dimethone derivative. Oxidation of 0.2-g. samples of these barium salts also gave about 20% of acetone, as determined under the conditions previously described.[20]

Formation of Bromosultone IV.—A suspension of 0.25 g. of II in 2 ml. of 10% potassium hydroxide was heated for 1.5 hr. on the steam-bath. Bromine water was added until the color persisted, and the solid was collected on a filter and dried; weight 0.17 g. (48%), m.p. 76–90°. Several crystallizations from alcohol were required to obtain material of constant m.p., 130.5–131°.

Anal. Calcd. for $C_8H_{15}O_3SBr$: C, 35.42; H, 5.58. Found: C, 35.18; H, 5.65.

Hydrolysis in sodium carbonate followed by treatment with bromine water gave a lower yield of the same bromosultone.

Sources of Olefins.—3-Methyl-1-butene and 4-methyl-2-pentene were purchased from the Phillips Petroleum Co.

3,3-Dimethyl-1-butene and 4,4-dimethyl-2-pentene were synthesized by pyrolysis of the S-methyl xanthates using the general method of Schurman and Boord.[21]

The preparation of 2,3,3-trimethyl-1-butene has been described previously.[8]

3,3-Dimethyl-2-phenyl-2-butanol, b.p. 116–119° (15 mm.), $n^{25}D$ 1.5058 (reported[22] b.p. 116–117° (15 mm.), $n^{25}D$ 1.5135), was prepared by the reaction of phenylmagnesium bromide (1 mole) and pinacolone (1 mole) followed by hydrolysis in ice. The layers were separated, the ether layer washed three times with potassium carbonate, dried over anhydrous magnesium sulfate and potassium carbonate and the product distilled. Lower yields were obtained when ammonium chloride was used in the hydrolysis step. A mixture of 53.6 g. (0.30 mole) of 3,3-dimethyl-2-phenyl-2-butanol, 47.1 g. (0.60 mole) of acetyl chloride and 61.2 g. (0.60 mole) of acetic anhydride was refluxed for 7 hr. After standing for 8 days, the mixture was cautiously hydrolyzed with 100 g. of ice and 500 ml. of water and made alkaline with sodium carbonate. The aqueous layer was extracted three times with pentane. The combined organic layers were dried over anhydrous sodium sulfate, the solvent removed and the fractions boiling at 79–81° (13 mm.), $n^{25}D$ 1.5015, and 81–82° (14 mm.), $n^{25}D$ 1.5017, were taken, the total yield being 32 g. (66%). Reported value for 3,3-dimethyl-2-phenyl-1-butene are: b.p. 80° (15 mm.), $n^{15}D$ 1.50228,[23] and b.p. 88–90° (15 mm.), $n^{25}D$ 1.50133.[24]

Sulfonation of γ-Branched Olefins.—The procedure used was essentially that described in an earlier paper.[8] However, care must be taken in processing the sultones to minimize hydrolysis. This is particularly true for sultones such as VII and X. The procedure used for VII will be described as illustrative.

The sulfonation was carried out by adding 19.5 g. (0.278 mole) of 3-methyl-1-butene to a reagent prepared from 22.2 g. (0.278 mole) of sulfur trioxide, 150 ml. of methylene chloride and 26 g. (0.296 mole) of dioxane. The mixture was hydrolyzed by shaking with 75 ml. of ice-water and the layers separated as soon as possible (the half-life for this sultone in aqueous solution is only 3.7 min.[19] at 0°). Anhydrous calcium sulfate was added immediately to the organic layer. Analysis of the aqueous layer showed the presence of 3.2% of the sulfur trioxide as sulfate and 65% as sulfonic acids.

The dried organic layer was evaporated almost to dryness under vacuum with very gentle heat. The oily solid was dissolved in ether, pentane was added to saturation and the solution was cooled in an ice–salt-bath. The 7.0 g. of nearly colorless crystals melted at 70–71°. After removal of about 1 ml. of dark oil the mother liquor was cooled to −78° where 4.5 g. of additional material, m.p. 70–71°, separated. The total yield was 11.5 g. (28%)[25]; Nilsson[1] reports m.p. 71.5–72°.

Properties of Sultones VIII–XII.—The physical properties and analyses of the sultones are summarized in Table II.

Hydrolysis of 2,2,3-Trimethyl-3-hydroxy-1-butanesulfonic Acid Sultone (IX).—Sultone IX (3.3 g., 0.0185 mole) was suspended in 200 ml. of water and the mixture allowed to stand at room temperature for 12 hr. Bromide–bromate titration[8] of aliquots of the resulting solution gave unsaturation values of 62.8 and 61.8% unsaturation. From one of these titrations 67% of **2,3-dimethyl-3-bromomethyl-3-hydroxy-1-butanesulfonic acid sultone**, m.p. 131–132.5°, was isolated. One recrystallization from ether–ethanol raised the melting point to 135–135.5°.

Anal. Calcd. for $C_7H_{13}O_3SBr$: C, 32.69; H, 5.09. Found: C, 33.01; H, 5.16.

Titration of two aliquots of the hydrolysis mixture for acidity showed 0.01848 equivalent of acid to be present (100%).

Addition of saturated S-*p*-chlorobenzylthiuronium chloride solution to an aliquot precipitated 51% of derivative, m.p. 155–160°. Recrystalllization from water (86% recovery) gave material, m.p. 165–166.5°, and an additional recrystallization gave **S-*p*-chlorobenzylthiuronium 2,2,3-trimethyl-3-butene-1-sulfonate**, m.p. 166–167°. (*Anal.* Calcd. for $C_{15}H_{23}O_3S_2N_2Cl$: C, 47.54; H, 6.12. Found: C, 47.66; H, 6.11.) The infrared spectrum of this salt showed a strong band at 11.21 μ, which is indicative of the $CH_2{=}CR_2$ double bond. The isomeric salt, S-*p*-chlorobenzylthiuronium 2,2,3-trimethyl-1-butene-1-sulfonate,[8] m.p. 168–169°, does not exhibit this band. A mixed m.p. of the two salts was 160–164°.

Hydrolysis of IX (2 g., 0.0112 mole) with 100 ml. of 10% hydroxide was effected by warming on the steam-bath for 3 hr. The solution was acidified with dil. sulfuric acid and neutralized with barium carbonate. The barium salts isolated by evaporation of the filtrate after removal of the barium sulfate and barium carbonate gave an unsaturation value of 68%. A 0.35-g. sample of barium salt (containing 6.043×10^{-4} mole of unsaturated sulfonate) was dissolved in 30 ml. of glacial acetic acid and 3–7% ozone was passed into the solution until the gases liberated iodine from an

---

(20) F. G. Bordwell and G. W. Crosby, THIS JOURNAL, **78**, 5367 (1956).

(21) I. Schurman and C. E. Boord, *ibid.*, **55**, 4930 (1933).

(22) Mme. Ramart-Lucas, *Ann. chim.*, [8] **30**, 350 (1913).

(23) G. A. Tsatsas, *ibid.*, [12] **1**, 342 (1946).

(24) Mme. Remart-Lucas, *ibid.*, [8] **30**, 382 (1913).

(25) Recently R. Wayne Ohline has increased the yield to 53% of crude sultone by working in more concentrated solution [100 ml. of methylene chloride, 40 g. (0.5 mole) of sulfur trioxide, 50 g. (0.55 mole) of dioxane and 35 g. (0.5 mole) of 3-methyl-1-butene), and by taking extra precautions to minimize hydrolysis and decomposition during processing.

acidified potassium iodide solution. The mixture was poured into 75 ml. of water, heated 15–20 min. on a steam-bath and neutralized with 15% sodium hydroxide. Addition of 0.5 g. of methone in 10 ml. of 95% ethanol precipitated 0.1576 g. (5.390×10^{-4} mole, 89%) of formaldehyde methone derivative m.p. 187.5–188.5°.

A 0.39-g. sample of S-*p*-chlorobenzylthiuronium 2,2,3-trimethyl-3-butene-1-sulfonate was dissolved in methanol and passed over Dow-X-50 cation exchange resin to liberate the free sulfonic acid. The column was eluted with methanol. Bromide–bromate titration gave an unsaturation value of 103%.

4-Methyl-4-hydroxy-2-pentanesulfonic Acid Sultone (X).—Evaporation of the solvent from the organic layer (separated from the aqueous layer after hydrolysis of the sulfonation of 4-methyl-2-pentene) with gentle heat gave only decomposition products. Evaporation without heat gave a residual amber oil. This was dissolved in ether and saturated at 0° with pentane. Cooling to −78° produced colorless crystals melting at about −48 to −44°. Carbon and hydrogen analyses on two different samples gave C, 46.76 and 46.83; H, 8.24 and 7.72. The theoretical values are: C, 43.89; H, 7.37. Neutral equivalents on different samples ranged from 270–311 (calcd. 164). The molecular weight, determined cryoscopically in acetic acid, was 141. The sultone decomposed at room temperature within a few hours.

3,4-Dimethyl-4-hydroxy-2-pentanesulfonic Acid Sultone (XI).—The two crops of crystals of crude sultone as precipitated from ether solution with pentane melted at 50–53° and 50–58°. Recrystallization of the first crop gave material melting at 42–43°. After standing for five months the solid melted at 74–76°. The 42–43° melting material on recrystallization from ether–pentane melted at 43–43.5°, but a second crystallization raised the m.p. to 70–73°, and a final crystallization gave material, m.p. 76–77°. Recrystallization of the initial material, m.p. 50–58°, gave the higher melting form. The infrared spectra of the 42–43° and 76–77° materials were identical except for two additional weak absorption bands at 10.95 and 12.5 μ present in the lower melting form. These appear to be dimorphic forms of the sultone, rather than *cis–trans* isomers.

Hydrolysis of 2,3-Dimethyl-2-phenyl-3-hydroxy-1-butanesulfonic Acid Sultone (XII).—Four grams (0.0167 mole) of XII was hydrolyzed in 400 ml. of water at steam-bath temperature, and the solution diluted to 500 ml. Titration of a 20-ml. aliquot with standard base showed the presence of a theoretical quantity of sulfonic acid. Bromide–bromate titration of a 50-ml. aliquot gave an unsaturation value of 147% (a small amount of solid precipitated).

Repetition of this experiment using 10% potassium hydroxide gave a solution an aliquot of which showed 190% unsaturation on bromide–bromate titration (high unsaturation values are typical of unsaturated sulfonic acids with a branch at the double bond; see ref. 8). Neutralization of the major portion of this solution with hydrochloric acid and evaporation gave 3.0 g. of potassium salts (84%). Coulometric titration[17] of a sample gave 71% unsaturation. S-*p*-Chlorobenzylthiuronium 2,3-dimethyl-3-phenyl-1-butene-1-sulfonate, m.p. 171–172°, was obtained in 62% yield (after three crystallizations, assuming 71% initial unsaturation) from the potassium salts.

Anal. Calcd. for $C_{20}H_{25}O_3N_2S_2Cl$: C, 54.47; H, 5.72. Found: C, 54.25; H, 5.51.

An identical derivative was obtained from the potassium salt isolated from the "neutral" hydrolysis.

The infrared spectrum of the potassium salt from the basic hydrolysis showed no absorption in the 11.2 μ region. The ultraviolet absorption spectrum of an aqueous solution showed a maximum at 258 mμ (ϵ_{max} 210), typical of an alkylbenzene, and no high intensity absorption at 244 mμ, characteristic of styrenes.

2,3-Dimethyl-4-hydroxy-2-butene-1-sulfonic Acid Sultone (XVIII).—The sulfonation was carried out using 12.0 g. (0.146 mole) of 2,3-dimethyl-1,3-butadiene, 11.4 g. (0.142 mole) of sulfur trioxide, 13 ml. of dioxane and 200 ml. of ethylene chloride. After hydrolysis, the organic layer was concentrated under vacuum at room temperature to give a sizable quantity of oil. Distillation in a Hickman still at 100° and 0.3 mm. gave 1.5 g. (6.5%) of XVIII, m.p. 40–41°. Crystallization from ether failed to raise the melting point.

Anal. Calcd. for $C_6H_{10}O_3S$: C, 44.44; H, 6.22. Found: C, 44.95; H, 6.37.

The aqueous layer contained only 30% of the sulfur trioxide used (3% as sulfate and 27% as sulfonic acid), suggesting that the yield of sultone was much higher than was isolated.

Repetition of this experiment using pentane to precipitate the sultone from the organic layer gave a 16% yield of sultone.

These experiments were performed at an early stage of the work and the precautions later adapted for the hydrolysis stage were not employed. It seems likely that the yield could be improved substantially over that realized.

EVANSTON, ILL.

[CONTRIBUTION FROM THE INSTITUTE OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OSAKA UNIVERSITY]

The Curtius Rearrangement. III. The Decomposition of Substituted Benzazides in Acidic Solvents, the Acid Catalysis

BY YASUHIDE YUKAWA AND YUHO TSUNO

RECEIVED MAY 26, 1958

Kinetic study of the Curtius rearrangement of various substituted benzazides was carried out in acidic solvents such as acetic acid, aqueous acetic acid and acetic acid containing sulfuric acid. The rate for a given substituent was increased by the changes of solvents in the order: toluene, acetic anhydride, AcOH, aq. AcOH and AcOH containing H_2SO_4. In acetic acid containing sulfuric acid, a linear Hammett correlation was observed. This result on the substituent effect was similar to that of the Schmidt reaction and was different from that of the Curtius rearrangement in toluene. However, in acetic acid without H_2SO_4, the linear Hammett plot was not given; the rates of the derivatives containing *para* electron releasing groups were nearly equal to that of parent compound. The analogous shape of Hammett plot was obtained in aqueous acetic acid and acetic acid containing lithium chloride. The energy of activation varied considerably by the change of substituent. In acetic acid without sulfuric acid, the change of log *PZ* was parallel with that of activation energy, whereas the log *PZ* was constant in the presence of sulfuric acid.

A previous paper[1] reported the substituent effect of the Curtius rearrangement of the various substituted benzazides in toluene; in the *meta*-substituted benzazides, the polar nature of the substituents controlled the rate, whereas, in the *para*-substituted one both electron releasing and attracting substituents in any case retarded the rate as compared with the unsubstituted. These results are somewhat unusual and differ from the Lossen,[2]

---

[1] Y. Yukawa and Y. Tsuno, THIS JOURNAL, **79**, 5530 (1957).

[2] T. F. Bright and C. R. Hauser, *ibid.*, **61**, 618 (1939); W. B. Renfrow, Jr., and C. R. Hauser, *ibid.*, **59**, 2308 (1939).