The oxidants of the indigo sulfonates changed color from blue through green to yellow as the *p*H was gradually changed from *p*H 12 to 15. Going from *p*H 10 to 12, the absorption band in the yellow was replaced by a band in the red extending into the infrared and from *p*H 12 to 14, as the color changed from green to yellow, the absorption band in the red was replaced by one in the violet.

Three colored species of the indigo group are involved, the acid or un-ionized group, the first salt or monobasic ion, and the second salt or dibasic ion.

The form of Beer's Law equation used was $-\log P_e/P_i = \epsilon Cl$ where P_e is the emergent power per unit cross section, P_i the incident power, ϵ the molar absorption coefficient, C the concn. in moles/liter and l the length in cm.

The wave length maxima (Table III) were determined for the potassium salts in aqueous solution and for 80% ethanol.

The absorption coefficients of indigo disulfonate were determined also for buffers of *p*H 7.0, 12.5 and 14.7. The wave length at the maxima (Fig. 1) were those used in estimating the amount of the various ionic species plotted (Fig. 2). The proportion of monobasic ion could not be accurately estimated directly because pK'_{O1} and pK'_{O2} were too close.

The reductants were pale yellow in solutions more acid than *p*H 4 and, as the *p*H was increased, they became lighter yellow, until about *p*H 9. Further increase caused no noticeable change until beyond *p*H 10.5, when the solutions became more yellow or orange (Fig. 3), indicating ionizations of about $pK'_{R_1} = 7.5$ and $pK'_{R_2} = 12$. If there were but one ionization in the reductant above *p*H 10, the absorption curves would become parallel to the *p*H axis at about *p*H 14. However, from the shape of the curves, a third is indicated. Because of the possible interference of this third ionization, pK'_{R_3} was estimated by a trial and error method. A trial pK'_{R_2} was chosen and the transmittance of a selected characteristic wave length for the dibasic ion at this *p*H was assumed to be 50%; the fraction of dibasic ion present at other *p*H were calculated by dividing the transmittance at a *p*H by twice the transmittance at the assumed pK'; the results were then plotted and compared to the theoretical ionization curve for the pK'; the pK' was varied until the best fit to a particular theoretical pK' curve was obtained. The final pK'_{R_3} so estimated are given in Table II.

The intermediates were bright red in color and had a narrow absorption band in the green which is easily recognized from about *p*H 11 to 15. The band shifts toward the red with increasing sulfonation (Table III). The pK' were estimated from the electrometric curves; that for the disulfonate from Fig. 4.

ST. LOUIS, MISSOURI

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

Sulfonation of Olefins. VIII.[1] Formation of Unsaturated Sulfonic Acids

BY F. G. BORDWELL AND C. EDWARD OSBORNE

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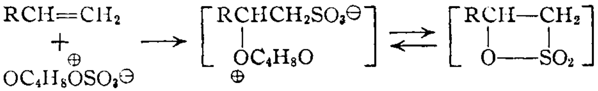
The sulfonation of olefins with β- and δ-branches was found to give predominantly unsaturated sulfonic acid. The position of the double bond (α,β or β,γ) in these unsaturated sulfonic acids appears to be determined primarily by steric factors. Evidence is presented to show that the unsaturated sulfonic acids are formed from carbonium-sulfonate or β-sultone intermediates rather than by a one-step concerted mechanism.

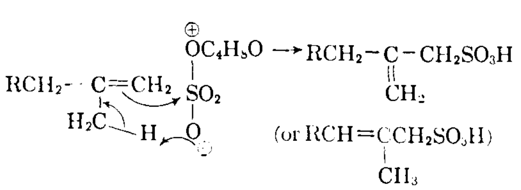
The reaction of unbranched olefins such as styrene,[2] 1-hexene[3] or cyclopentene[4] with an *equimolar* quantity of dioxane–sulfur trioxide is believed to form a dioxane-solvated carbonium ion (Ia) and/or a β-sultone (Ib). Hydrolysis of sulfonation mixtures containing these intermediates gives largely β-hydroxyalkanesulfonic acids, which can be accounted for as hydrolysis products of Ia or Ib.



Ia Ib

About 10–20% of unsaturated sulfonic acids are also formed in the above sulfonations, and for styrene[2a] or 1-hexene[3] the proportion of unsaturated sulfonic acid may be increased by heating the sulfonation mixture prior to hydrolysis. The proportion of unsaturated product is also increased for styrene by treatment of the sulfonation mixture with bases, such as pyridine, aniline, sodium methoxide or sodium hydroxide.[2b] These observations are explicable by postulating E1 and E2 type reactions of the solvent and/or added solvents or reagents with Ia or Ib.

Sulfonation of α-olefins with a β-branch such as isobutylene,[5] methallyl chloride,[6] α-methylstyrene,[7] 2-methyl-3-phenyl-1-propene[8] and methylenecyclohexane[9] gives predominantly unsaturated sulfonic acids. While it is clear from the work described above[2-4] that these unsaturated sulfonic acids may be formed from intermediates Ia or IIa, a concerted one-step mechanism *via* a quasi six-membered ring transition state, as suggested by Arnold for sulfonation and chlorination,[9] is an attractive alternative. As indicated in the equation



this mechanism would predict the formation of β,γ-rather than α,β-unsaturated sulfonic acids, which is in agreement with most of the recorded data.[5,6,8,9] On the other hand, one would expect α,β-unsaturated sulfonic acids to be formed from intermediates such as Ia or Ib since this would allow formation of the conjugated compound (E1

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[1] For Part VII, see F. G. Bordwell and G. W. Crosby, THIS JOURNAL, **78**, 5367 (1956).

[2] (a) F. G. Bordwell and C. S. Rondestvedt, Jr., *ibid.*, **70**, 2429 (1948); (b) F. G. Bordwell, M. L. Peterson and C. S. Rondestvedt, Jr., *ibid.*, **76**, 3945 (1954).

[3] F. G. Bordwell and M. L. Peterson, *ibid.*, **76**, 3952 (1954).

[4] F. G. Bordwell and M. L. Peterson, *ibid.*, **76**, 3957 (1954).

[5] C. M. Suter and J. D. Malkemus, *ibid.*, **63**, 978 (1941).

[6] C. M. Suter and F. G. Bordwell, *ibid.*, **65**, 507 (1943).

[7] C. M. Suter and W. E. Truce, *ibid.*, **66**, 1105 (1944).

[8] F. G. Bordwell, C. M. Suter and A. J. Webber, *ibid.*, **67**, 827 (1946).

[9] R. T. Arnold and J. F. Dowdall, *ibid.*, **70**, 2590 (1948).

mechanism) or release of the more acidic hydrogen (E2 mechanism). A number of other olefins have now been sulfonated to obtain more information on these points.

It was necessary first to devise a method of analysis of the sulfonation mixtures for α,β- and β,γ-unsaturated sulfonic acids. Relatively pure samples of α,β-unsaturated sulfonates give considerable quantities of sulfate ion on oxidation with potassium permanganate.[3] However, the oxidation to sulfate is not quantitative under the conditions we have used. Its use for analysis is further limited by the formation of as much as 10–20% of sulfate from some β,γ-unsaturated sulfonates. Preliminary experiments utilizing ozone, performic acid or periodic acid as oxidants were also unpromising.

In the present work titration with bromine has been used both to estimate the amount of unsaturated sulfonate present and to distinguish between double bonds in α,β and other positions to the sulfonate group. Titrations were run both coulometrically, by electrolytic bromine generation using ultraviolet light to detect the end point,[10] and by bromide–bromate titration. The results of these titrations with a number of α,β- and β,γ-unsaturated sulfonates of known structure are given in Table I.

TABLE I

COMPARISON OF COULOMETRIC AND BROMIDE-BROMATE TITRATIONS OF α,β- AND β,γ-UNSATURATED SULFONATES

Unsaturated sodium sulfonate	Type	Titration value, % Coulometric	Bromide–bromate
2-Methyl-2-propene-1-	β,γ	98	147
2-Phenylethene-1-	α,β	0	107
3-Phenyl-2-methyl-2-propene-1-	β,γ	104	*ca.* 100[a]
Ethene-	α,β	0	...
2-Methyl-1-propene-1,3-di-	α,β	0	...
2-Hexene-1- (impure)	β,γ	83	88

[a] Forms a stable bromosultone on titration.

In the coulometric titrations a sharp end-point is observed only if bromine reacts with the carbon–carbon double bond as rapidly as it is formed. The failure of the double bond in α,β-unsaturated sulfonates to be titrated is understandable since the sulfonate group, despite its negative charge, is electron withdrawing, and bromine reacts only slowly with α,β-unsaturated sulfonates. The titration provides a clean-cut way of distinguishing α,β-unsaturation in these sulfonates from other types.

In the bromide-bromate method standard bromate solution is added to an acid solution of the unsaturated sulfonate and sodium bromide until the yellow bromine color persists. The excess bromine present is then determined by adding potassium iodide and titrating the iodine released with standard thiosulfate. The bromine end-point is indefinite for α,β-unsaturated sulfonates because of the slowness of reaction and is indefinite for β,γ-unsaturated sulfonates, particularly for those with β- or γ-branches, because they react with more than one mole of bromine (the first mole reacting by substitution as well as by addition). For this reason a standardized procedure was used in which bromate was added until the bromine color persisted for five minutes. Under these conditions titration of α,β-double bonds and non-branched β,γ-double bonds approach 100%. β,γ-Unsaturated sulfonates branched at a doubly-bonded carbon appear to absorb an average of 150% of the theoretical quantity of bromine.

The olefins listed in Table II were sulfonated and the sulfonation mixtures hydrolyzed in the usual manner. The sulfur trioxide present as sulfate was determined by precipitation with barium carbonate. The quantity of barium sulfonates in the filtrate was determined by precipitating the barium with sodium sulfate. The water was then removed and the sodium sulfonates separated from sodium sulfate by alcohol extraction. The two types of bromine analyses were made using the sodium sulfonates from the alcoholic extracts. The results of these various analyses are given in Table II.

TABLE II

DETERMINATION OF α,β- AND β,γ-UNSATURATED SULFONIC ACIDS FORMED DURING OLEFIN SULFONATIONS

Olefin	Sulfate, %	Sulfonic acids, %	Titration, % Bromate–bromide	Coulometric	Double bond position
2-Methyl-1-butene	18	82	115	74	β,γ[a]
2-Methyl-2-butene	12	91	124	110	β,γ[b]
1-Hexene[4]	18	71	15–20	..	β,γ
4-Methyl-1-pentene	1	77	53	0	α,β
4,4-Dimethyl-1-pentene	6	69	96	0	α,β
2,3,3-Trimethyl-1-butene	7	17[c]	163[d]	0	α,β[e]
2,4,4-Trimethyl-1-pentene	6	75	147	0	α,β[e]
2,4,4-Trimethyl-2-pentene	33	42	175	0	α,β[e]

[a] The 11.2 μ band ($RR'C{=}CH_2$) is of medium strength. [b] Strong band at 11.2 μ. [c] A sultone is formed in 75% yield. [d] Titration of the pure unsaturated sulfonate. [e] No band at 11.2 μ.

The absence of bands in the 11.2 μ region for the sulfonates from 2,3,3-trimethyl-1-butene, 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene indicates the absence of terminal methylene groups (β,γ-unsaturation) and supports the α,β-structure assignment made on the basis of the failure of the coulometric titrations. The absence of terminal methylene is in itself sufficient to establish the structures of the unsaturated sulfonic acids from 2,3,3-trimethyl-1-butene and 2,4,4-trimethyl-2-pentene, since all reasonable structures, other than α,β, would have terminal methylene groups.

S-(*p*-Chlorobenzyl thiuronium 2,2,4-trimethyl-1-pentene-1-sulfonate was isolated from the sulfonates from the sulfonation of 2,4,4-trimethyl-1-pentene and was purified by crystallization. By passing a solution of this salt over an ion exchange resin a solution of purified 2.4,4-trimethyl-1-pentene-1-sulfonic acid was obtained. Bromide–bromate titration of this solution gave practically the same unsaturation value (148% *vs.* 147%) as obtained for the sodium salt isolated from the

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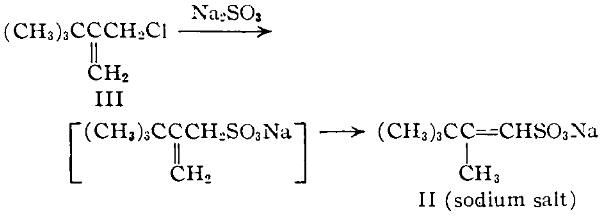
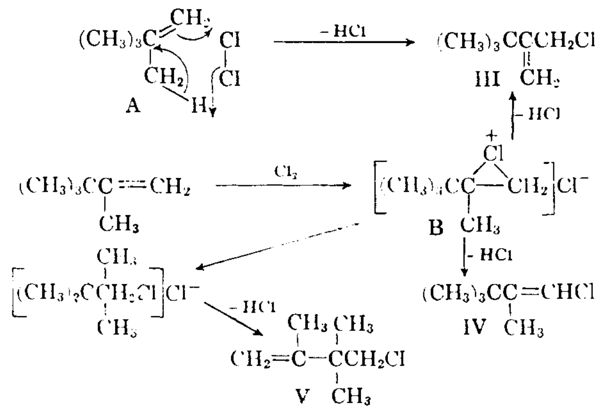
[10] J. W. Miller and D. D. DeFord, *Anal. Chem.*, **29**, 475 (1957). We wish to thank Dr. J. W. Miller for the coulometric titrations reported herein.

original hydrolysate, indicating that no hydroxy sulfonate was formed in the sulfonation and hydrolysis. The sodium salt exhibited a strong tendency toward hydration. This observation precludes the possibility of detecting the presence of hydroxy sulfonates by infrared analysis on the sodium sulfonates. In general the sulfonation of α-olefins with β-branches (or comparable types) appears to give only small amounts of hydroxy sulfonates or none at all.

Sulfonation of 2,3,3-trimethyl-1-butene gave about 10% of an unsaturated sulfonic acid, which from the above evidence must be 2,3,3-trimethyl-1-butene-1-sulfonic acid (II), and about 75% of a γ-sultone of rearranged carbon skeleton.[11] The sodium salt of II was also obtained by chlorination of 2,3,3-trimethyl-1-butene and reaction of the allylic chloride (III) so formed with aqueous sodium sulfite.



The failure of appreciable rearrangement to occur during the chlorination of α- or β-pinene has led Arnold to postulate that this reaction proceeds by way of a concerted mechanism involving a quasi six-membered ring transition state.[12] The products from the chlorination of 2,3,3-trimethyl-1-butene are of particular interest in this respect since skeletal rearrangement does occur during sulfonation of this olefin.[11] According to Arnold's mechanism (A) chlorination would be expected to give largely the allylic chloride, 2-chloromethyl-3,3-dimethyl-1-butene (III). This product could also arise from the chloronium-carbonium ion



intermediate B, but it would be anticipated that some rearranged chloride V also would be formed. Since V is a neopentyl chloride and the other possible product (IV) is a vinyl chloride, the only reactive chloride formed would be III.

Chlorination of 2,3,3-trimethyl-1-butene in methylene chloride at 0° in the presence of sodium carbonate gave 35% of a monochloride fraction. This chloride released 80.0% of chloride ion when treated with alcoholic sodium hydroxide for two hours at the reflux point. Under comparable conditions methallyl chloride released 79.1% of chloride ion. Evidently III is the only monochloride formed in the chlorination of 2,3,3-trimethyl-1-butene. This supports Arnold's representation[12] of the chlorination reaction.

The formation of II from III must proceed by way of sodium 2-*t*-butyl-2-propene-1-sulfonate, as shown. The shift of the double bond from a β,γ- to α,β-position under such mild conditions is analogous to the shift occurring in the formation of sodium 2-methyl-1-propene-1,3-disulfonate from 2 chloromethyl-3-chloro-1-propene and sodium sulfite.[6] The facile rearrangement of the double bond in these instances under mildly acidic conditions strongly suggests that rearrangement of double bonds may occur under the much stronger acidic conditions existing during sulfonation. It seems very likely, then, that the double bond positions indicated in Table II are those assumed under equilibrium conditions.

From Table II it appears that, whereas simply-branched olefins give mainly β,γ-unsaturated sulfonic acids on sulfonation,[5-9] more highly branched olefins give mainly the α,β-isomers. Since the major basis for the assumption of a concerted mechanism[9] was the predominant formation of β,γ-unsaturation, there is no longer much reason for favoring this mechanism, inasmuch as formation of the β,γ-isomers is now seen to be the result of a favorable equilibrium rather than the result of a kinetically controlled reaction. The best test of the concerted mechanism comes in the sulfonation of olefins like 2,3,3-trimethyl-1-butene where a concerted process should give unrearranged sulfonates whereas intermediates such as Ia could lead to rearranged products. In this particular instance rearrangement to form a sultone[11] occurs to the extent of about 76% and about 24% of the product is water soluble. From the 24% of water-soluble material about 7% of the original sulfur trioxide was recovered as sulfate and 17% as sulfonates. Of the sulfonates about 9% was II and 8% was hydroxy sulfonate (probably from hydrolysis of the sultone). This means that no more than 10% of the reaction can be occurring by a concerted path, and even this much is doubtful since II can also arise from Ia or Ib.

The equilibrium double bond position in these unsaturated sulfonic acids will probably be determined primarily by three factors: (1) conjugation of C=C and SO_3^- (favoring α,β),[13] (2) conjugation of C=C with alkyl (hyperconjugation, favoring the most highly substituted C=C) and (3) steric factors.[14]

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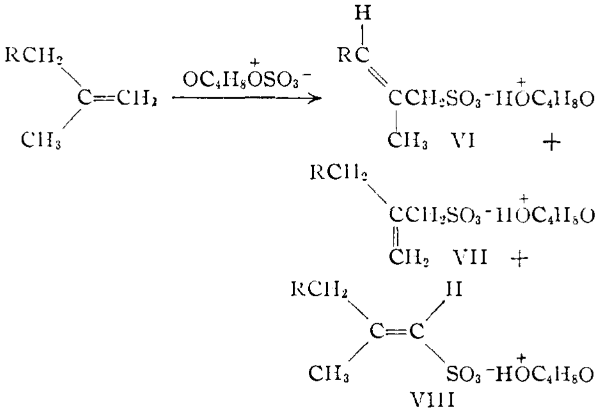
[11] F. G. Bordwell, R. D. Chapman and C. E. Osborne, THIS JOURNAL, **81**, 2002 (1959).

[12] R. T. Arnold and W. W. Lee, *ibid.*, **75**, 5396 (1953).

[13] H. Zollinger, *Nature*, **172**, 256 (1953) has demonstrated the conjugative ability of SO_3^-.

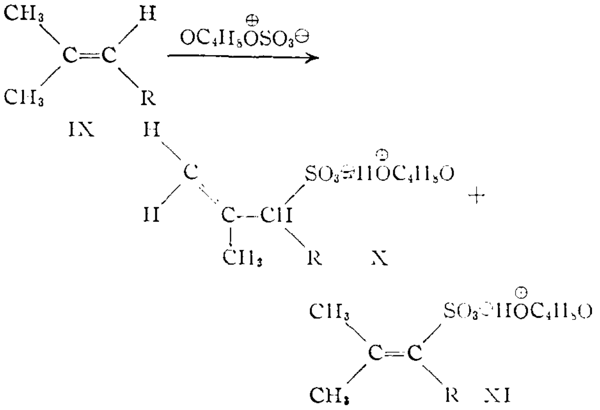
[14] (a) K. L. Rinehart, Jr., and L. J. Dolby, *J. Org. Chem.*, **22**, 13 (1957), have recently given a detailed analysis of the position of equilibrium in α,β- and β,γ-unsaturated carboxylic acids, with particular emphasis on steric effects; (b) H. C. Brown and I. Moritani, *ibid.*, **77**, 3607 (1955), and H. C. Brown and M. Nakagawa, *ibid.*, **77**, 3610, 3614 (1955), have shown that the structure of the olefin formed from

The $-SO_3^-$ group, like the $-CO_2^-$ group,[14a] probably has a much larger steric effect than is indicated by Fisher–Herschfelder type models, since a full negative charge is distributed among the oxygen atoms[15] and the group is no doubt surrounded by a tightly held solvent shell. The $-SO_3^-$ group appears to be similar to the *t*-Bu group[14] in avoiding situations where it would be *cis* to an alkyl group. At least, the predominant formation of β,γ-unsaturated sulfonic acids VI and VII rather than VIII from $RCH_2C(CH_3){=}CH_2$ type olefins [R = H,[5] Cl,[6] C_6H_5[8] or CH_3 (see Table II)] is explicable if it is assumed that the $-SO_3^-$ group is large and gives rise to sizeable steric effects when it must be placed in a *cis* position to a methyl group, as in VIII. When R = H,[5] VIII is the more highly substituted isomer and is also favored by conjugation of C=C and SO_3^-, but these factors are apparently overridden by the large steric repulsion between CH_3 and $-SO_3^-$. When R = CH_3 (see Table II), Cl[6] or C_6H_5[8] the formation of VI and VII as major products is again probably decided by the steric factor, although VI is trisubstituted in these instances, which provides some additional stabilization (this is counteracted to some extent by the steric repulsions between R and CH_3).

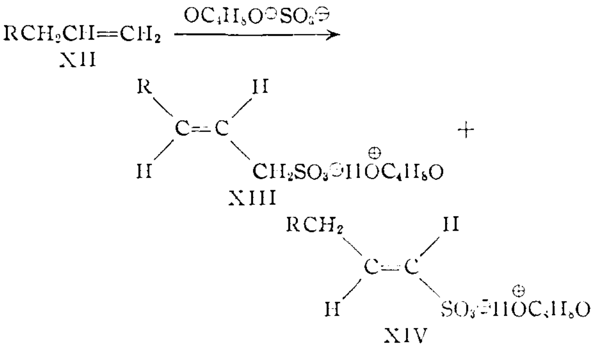


When R becomes large (2,4,4-trimethyl-1-pentene, R = *t*-Bu), VIII is favored over VI, presumably because the steric repulsions between R and CH_3 are greater in this compound than those between SO_3^- and CH_3 [*t*-Bu larger than SO_3^-]. The situation is similar to that in "diisobutylene" itself (H instead of SO_3^-) where VI is not favored.[14] Choice between VII and VIII is not so clear-cut when R = *t*-Bu. In VIII C=C is conjugated with SO_3^- and there is a higher degree of substitution, but SO_3^- must be *cis* to CH_3. Steric repulsions occur also in VII, however, between the two large groups $CH_2C(CH_3)_3$ and $CH_2SO_3^-$. The formation of VIII apparently results from a balance of these factors with the latter being dominant.

With olefins of type IX the situation is somewhat similar. When R is small (2-methyl-2-butene, R = CH_3) the β,γ-isomer X is favored, but when R is large (2,4,4-trimethyl-2-pentene, R = *t*-Bu) the α,β-isomer XI is the principal product. It would have been difficult to predict the latter result, since in XI both SO_3^- and *t*-Bu are *cis* to CH_3 groups. This unfavorable steric situation may be partially offset by the greater separation of SO_3^- and *t*-Bu groups allowed in XI (120° angle *vs.* 109°).



In the sulfonation of olefins of type XII the proportion of unsaturated sulfonic acids increases from about 15% when R = *n*-Pr, to about 50% when R = *i*-Pr, to about 90% when R = *t*-Bu-. The unsaturated product is predominantly XIII when R = *n*-Pr, but appears to be exclusively XIV when R = *i*-Pr or *t*-Bu. The increase in the proportion of unsaturated sulfonic acid with increased branching at a point seemingly so remote from the reaction site is striking. It is unlikely that this remote branching would have much effect in promoting the formation of unsaturated acids by hydrolysis from intermediates Ia or Ib. However, branching in R would lower the stability of Ia or Ib and would favor their decomposition to unsaturated sulfonic acids prior to hydrolysis. It is also possible that as R becomes larger formation of intermediates Ia and Ib become slower and unsaturated sulfonic acids are formed to a greater extent by a concerted mechanism. The latter consideration does not seem to be of paramount importance, since with 2,3,3-trimethyl-1-butene, where the stability of the Ia and Ib intermediates should be even lower, the primary product appears to be formed *via* such intermediates,[11] and the operation of the concerted mechanism is of minor importance, if it operates at all.



Preferential formation of XIV rather than XIII appears to correspond to the steric demands of R as it becomes bulkier.

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the solvolysis of branched halides and brosylates is often determined primarily by steric factors, particularly when one of the groups is *t*-butyl.

(15) There is evidence for a sizeable steric effect for the closely analogous–$SO_2C_6H_5$ group; see F. G. Bordwell and G. D. Cooper, *J. Org. Chem.*, **73**, 5184 (1951); **79**, 916 (1957).

Acknowledgment.—This work was supported in part by a grant from the American Petroleum Institute (Project 48B).

Experimental[16]

General Sulfonation Procedure.—A measured quantity of dry methylene chloride or ethylene chloride was placed in a 3-neck flask equipped with a mercury seal stirrer, stopper and calcium chloride drying tube, and the flask and its contents were weighed. Sulfur trioxide was distilled into the stirred solvent in the flask which was cooled in an ice-bath. Reweighing gave the weight of sulfur trioxide. About a 10% molar excess of purified dioxane[17] was added slowly with stirring and cooling, and then a solution of the alkene in methylene or ethylene chloride was added dropwise with stirring to the slurry. Stirring was continued for approximately one hour at 0°, and then water was added with vigorous stirring. The hydrolysis time was about 10 min.

The layers were separated, inverting with ether in instances where an emulsion formed. The organic layer was immediately dried and the solvent removed under vacuum. The water layer was treated with excess barium carbonate (caution) and the precipitate removed by filtration. The solid was treated with dil. hydrochloric acid, dried at 150° and weighed to give the amount of sulfur trioxide recovered as barium sulfate (% sulfate in Table II). The barium sulfonate solution was treated with excess sodium sulfate and filtered. The weight of the precipitate, dried at 150°, gave the amount of sulfonic acids as barium sulfate (recorded in Table II as % sulfonic acids).

The solution containing the sodium sulfonates and sodium sulfate was evaporated to dryness and extracted repeatedly with methanol or 95% ethanol. Evaporation of the solvent gave the sodium sulfonates. In most cases where the salts were discolored, it was found that treatment with activated charcoal of alcoholic solutions (but not aqueous solutions) gave colorless products. The weights of sodium sulfonates isolated varied from about 60 to 100% of the theoretical as indicated by the % of sulfonic acids present.

Bromide-Bromate Titrations.—About 0.5 g. of the sodium sulfonate was dissolved in 50 ml. of water, and the solution was made 1 N with respect to hydrochloric acid. Then 1.0 g. of potassium bromide was added, and the solution titrated with 0.03333 M (0.1000 N to double bond) potassium bromate solution until a yellow color persisted for five minutes. About 10 ml. more of the bromate solution was then added. After the mixture had stood in the dark for 30 min., 1.0 g. of potassium iodide was added, and the liberated iodine back-titrated with freshly standardized sodium thiosulfate solution.

Titration of samples from sulfonations is often complicated by the presence of hydroxy sulfonates. If titration values greater than 100% were obtained it was assumed that hydroxy sulfonates were absent. In one instance (sulfonates from 2,4,4-trimethyl-1-pentene) this assumption was shown to be justified. If values of less than 100% were obtained an average molecular weight was assumed in the calculation of the percentage unsaturation.

Infrared Spectra.—A mixture containing 98% desiccated potassium bromide and 2% sodium sulfonate was ground to a fine powder and pressed into a clear window, and the spectrum taken. The absorption band found to be most useful was that in the 11.2 μ region (disubstituted terminal double bond) since it is both strong and sharp. In all instances where the sodium sulfonates were obtained from reaction mixtures there was a medium to strong hydroxyl band in the 2.8 μ region. However, for branched sulfonates this is more likely to indicate water of hydration than hydroxy sulfonate (see below).

Sulfonation of 2,4,4-Trimethyl-1-pentene.—A 16.9-g. sample of the olefin was sulfonated by the procedure described above using an equimolar quantity (12.1 g.) of sulfur trioxide, 15 g. of dioxane and 100 ml. of methylene chloride. After hydrolysis only a black tar was obtained from the organic layer. The aqueous layer contained 6% of sulfate and 75% of sulfonates by barium sulfate determinations (see above procedure). Extraction of the sodium sulfonate–sulfate mixture with 95% alcohol, decolorization three times with charcoal and evaporation yielded 60% of colorless sodium sulfonates, which gave a bromide-bromate titration value of 147%. There was no absorption in the 11.2 μ region.

Treatment of an aqueous solution containing 1.0 g. of sodium sulfonate with an alcoholic solution containing 1.1 g. of S-(p-chlorobenzyl)-thiuronium chloride gave 1.7 g. of derivative, m.p. 175–185°. Two recrystallizations from water gave 1.0 g. (54%) of **S-(p-chlorobenzyl)-thiuronium 2,4,4-trimethyl-1-pentene-1-sulfonate**, m.p. 187–188°.

Anal. Calcd. for $C_{16}H_{25}O_3S_2N_2Cl$: C, 48.90; H, 6.41. Found: C, 48.85; H, 6.21.

The S-(p-chlorobenzyl)-thiuronium salt in methanol was passed over Dow-X-50 cation exchange resin. Methanol was used to elute the column. Titration of the solution with standard sodium hydroxide showed a quantitative conversion to 2,4,4-trimethyl-1-pentene-1-sulfonic acid. Bromide-bromate titration gave a value of 148% unsaturation as compared to 147% for the original sulfonate, which indicates that the original was relatively pure sodium 2,4,4-trimethyl-1-pentene-1-sulfonate. The salt exhibited a strong hydroxyl band in the infrared indicating water of hydration.

A sample of sodium 2,4,4-trimethyl-1-pentene-1-sulfonate (dried for 8 hr. under vacuum at 20°) lost 85% of its water of hydration (assuming a monohydrate) on heating at 135° at 0.3 mm. to constant weight. The salt still showed a strong hydroxyl band in the infrared. This may be due to adsorption of water while preparing the potassium bromide pellet, since on standing open to the atmosphere at room temperature the salt readsorbed 12% of the original water of hydration in 30 min. and 44% in 20 hr.

2,3,3-Trimethyl-1-butene.—Crude 2,3,3-trimethyl-2-butanol was obtained by the reaction of methylmagnesium iodide and pinacolone in the usual manner. It was found to be advantageous to remove the ether prior to dehydration as the olefin tends to co-distil with ether. After dehydration, by refluxing the crude alcohol for 4 hr. over iodine, a 72% yield (1 mole run) of 2,3,3-trimethyl-1-butene, b.p. 78–78.5°, n^{25}_{D} 1.3985, was obtained; reported[18] b.p. 77.9° (760 mm.), n^{20}_{D} 1.4029.

2-Chloromethyl-3,3-dimethyl-1-butene (I).—Chlorine (20 g., 0.29 mole) was dissolved in 400 ml. of methylene chloride, and this solution was added with stirring over a period of one hour to 29.4 g. (0.30 mole) of 2,3,3-trimethyl-1-butene and 42.0 g. (0.50 mole) of sodium carbonate in 50 ml. of methylene chloride cooled in an ice-bath. The reaction mixture was washed with three 50-ml. portions of aqueous sodium bicarbonate and with one 50-ml. portion of water. After drying over anhydrous sodium sulfate the solvent was removed and the residue distilled under vacuum to give 13.5 g. (35%) of material, b.p. 63–65° (60 mm.), n^{25}_{D} 1.4420, and 6.5 g. of material, b.p. 104–106° (60 mm.), n^{25}_{D} 1.4738. The latter (dichloride) failed to decolorize bromine in carbon tetrachloride and was not investigated further.

After 0.5617 g. (4.237×10^{-3} mole) of the first fraction had been refluxed for 2 hr. in 25 ml. of 95% alcohol containing 1.0 g. of sodium hydroxide and acidified with nitric acid, 0.4854 g. (3.388×10^{-3} mole) of silver chloride (79.97%) was precipitated by addition of alcoholic silver nitrate. Under the same conditions 0.2966 g. (3.274×10^{-3} mole) of methallyl chloride gave 0.3713 g. (2.591×10^{-3} mole) of silver chloride (79.13%). Since 2-chloromethyl-3,3-dimethyl-1-butene is the only allylic chloride of the carbon skeleton of 2,3,3-trimethyl-1-butene, this determination serves as a structure proof and analysis.

Sodium 2,3,3-Trimethyl-1-butene-1-sulfonate (II).—2-Chloromethyl-3,3-dimethyl-1-butene (3 g., 0.0226 mole) was added to a solution of 2.85 g. (0.0226 mole) of sodium sulfite in 25 ml. of water, and the mixture was stirred and refluxed for 4 hr. The mixture was extracted with methylene chloride, evaporated to 10 ml. and cooled to give 2.3 g. of sodium sulfonates, which gave negative tests for chloride and sulfite. The mother liquor was evaporated to dryness and extracted with boiling 95% alcohol. An additional 0.75 g. of sodium sulfonate free of chloride and sulfite was obtained from the alcohol, bringing the total yield to 68%. Bromide–bromate titration of these salts gave a value of 168% unsaturation. The S-(p-chlorobenzyl)-thiuronium salt, m.p. 165–167°, was obtained in practically quantita-

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(16) Microanalyses were by Miss Hilda Beck.

(17) L. F. Fieser, "Experiments in Organic Chemistry," 2nd edition, D. C. Heath and Co., New York, N. Y., 1941, p. 368.

(18) J. P. Wibaut, H. Hoog, S. L. Langedijk, J. Overhoff and J. Smittenburg, *Rec. trav. chim.*, **58**, 329 (1939).

tive yield. Two recrystallizations from aqueous alcohol (68 and 71% recoveries) gave *S*-(*p*-**chlorobenzyl**)-**thiuronium 2,3,3-trimethyl-1-butene-1-sulfonate**, m.p. 168–169°.

Anal. Calcd. for $C_{15}H_{25}O_3N_2ClS_2$: C, 47.54; H, 6.12; N, 7.40. Found: C, 47.85; H, 5.74; N, 7.70.

Sulfonation of 2,3,3-Trimethyl-1-butene.—2,3,3-Trimethyl-1-butene (25.0 g., 0.255 mole) was sulfonated using 20.4 g. (0.255 mole) of sulfur trioxide, 25.0 g. (0.284 mole) of dioxane and 200 ml. of ethylene chloride. Hydrolysis with 100 ml. of ice-cold water was carried out as rapidly as possible (4 min.) in order to minimize hydrolysis of the sultone.

Evaporation of the organic layer gave 34.2 g. (75.5%) of sultone, m.p. 140–143°. Recrystallization from ether–ethanol gave 29.0 g. of **2,2,3-trimethyl-3-hydroxy-1-butanesulfonic acid sultone**, m.p. 145–146°.[19]

Anal. Calcd. for $C_7H_{14}O_3S$: C, 47.14; H, 7.92. Found: C, 47.16; H, 7.81.

Analysis of the water layer showed 7% of sulfuric acid and 17% of sulfonic acids to be present. The yield of sodium sulfonates was 4.4 g. (100%). Bromide–bromate titration gave an unsaturation value of 85%. An S-(*p*-chlorobenzyl)-thiuronium salt, m.p. 155–158°, was obtained in 43% yield (82% of the unsaturated sulfonate, see below). One recrystallization gave a derivative, m.p. 167–168°, which did not give a mixed m.p. depression with the authentic sample of S-(*p*-chlorobenzyl)-thiuronium 2,3,3-trimethyl-1-butene-1-sulfonate described above. The infrared spectra were identical. Since sodium 2,3,3-trimethyl-1-butene-1-sulfonate gives a bromide–bromate titration value of 168%, about 52% of this material is probably present in the sodium sulfonates. The remainder may be hydroxy sulfonate from the hydrolysis of the sultone.

EVANSTON, ILL.

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(19) The reactions of this sultone will be discussed in a succeeding paper.[11]

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

Sulfonation of Olefins. IX. Sulfonation of 1,1-Diphenylethene

BY F. G. BORDWELL AND M. L. PETERSON[1]

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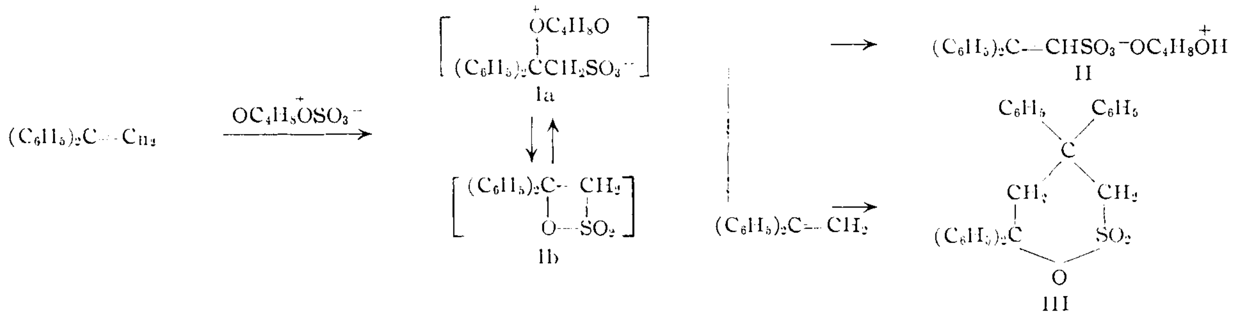
Sulfonation of 1,1-diphenylethene with dioxane–sulfur trioxide gave about 70% of 2,2-diphenyl-1-ethene-1-sulfonic acid, 10% of 2,2,4,4-tetraphenyl-4-hydroxybutane-1-sulfonic acid sultone and 10% of a dimer of 1,1-diphenylethene.

Most α-olefins with a β-methyl branch react with dioxane–sulfur troxide to give unsaturated sulfonic acids as the principal products.[2] These have been shown to be formed chiefly by way of carbonium-sulfonate or β-sultone intermediates (like Ia and Ib), although it is possible that they are formed to a minor extent by a concerted mechanism involving a quasi six-membered ring transition state.[2] Styrene gives 10–20% of unsaturated sulfonic acid under ordinary sulfonation conditions.[3] It appeared to be of interest to investigate the behavior of 1,1-diphenylethene, which has a β-branch, but cannot give an unsaturated sulfonic acid by a quasi six-membered ring type of concerted mechanism.



Like other α-olefins with β-branches[2] the reaction of 1,1-diphenylethene with an equimolar quantity of dioxane–sulfur trioxide gave an unsaturated sulfonic acid, 2,2-diphenyl-1-ethenesulfonic acid (II), as the major product (about 70%). About 20% of the sulfur trioxide was recovered as sulfuric acid and about 10% was converted to the sultone of 2,2,4,4-tetraphenyl-4-hydroxybutane-1-sulfonic acid (III). Formation of the latter utilizes two moles of olefin to one of sulfur trioxide; the other 10% of olefin was converted to an unidentified dimer of 1,1-diphenylethene. The apparent absence of a hydroxy sulfonate in the products is consistent with the behavior of other β-branched α-olefins on sulfonation.[2]

The formation of high yields of II is explicable in terms of intermediates Ia or Ib and shows that the formation of unsaturated sulfonic acids from β-branched α-olefins can occur in cases where the quasi six-membered ring mechanism is inoperative. This supports the conclusion that this type of process is not common in sulfonations.[2]

The formation of II and its reactions provide further examples of the known tendency for the maintenance of the double bond in 1,1-diaryl systems. Thus the sodium salt of II reacted with bromine in aqueous solution to give sodium 2,2-diphenyl-1-bromoethene-1-sulfonate (IV) as the major product (89%). A small amount (8%) of a water-insoluble product, which is probably the dimeric

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(1) Procter and Gamble Fellow, 1948–1951.

(2) See paper VIII in this series, F. G. Bordwell and C. E. Osborne, THIS JOURNAL, **81**, 1995 (1959).

(3) (a) F. G. Bordwell and C. S. Rondestvedt, Jr., *ibid.*, **70**, 2429 (1948). (b) F. G. Bordwell, M. L. Peterson and C. S. Rondestvedt, Jr., *ibid.*, **76**, 3945 (1954).