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 $C_{15}H_{23}O_3N_2ClS_2$: 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.

---

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

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

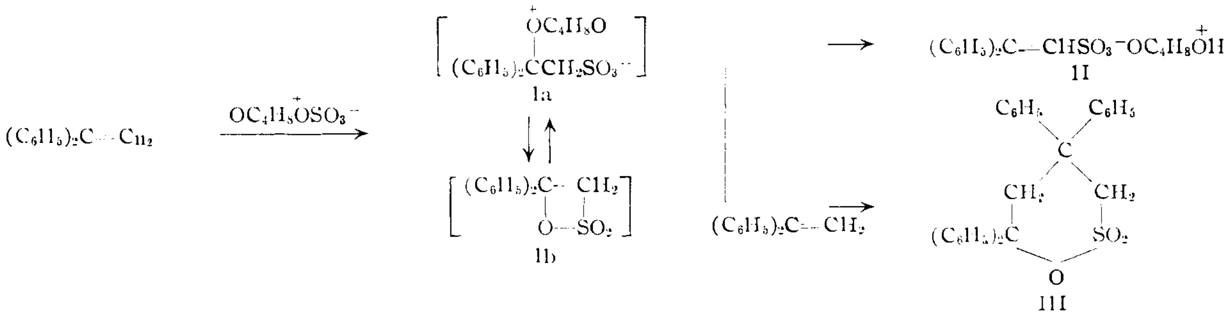
Sulfonation of Olefins. IX. Sulfonation of 1,1-Diphenylethene

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

RECEIVED OCTOBER 8, 1958

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

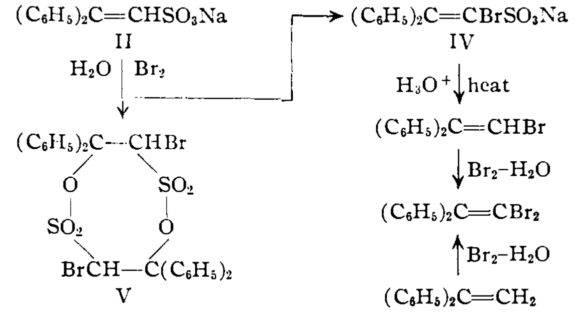
---

(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).

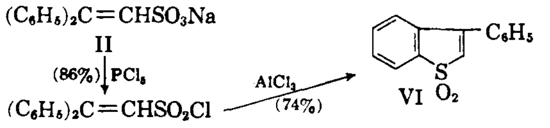
(3) (a) F. G. Bordwell and C. S. Rondestvedt, Jr., *ibid.*, **70**, 2429 (1948). (b) F. G. Bordwell, M. L. Peterson and C. S. Rondestvedt, Jr., *ibid.*, **76**, 3945 (1951).

addition product V, was also formed.[4] The salt IV is stable in neutral solution; but when boiled in aqueous acid 1,1-diphenyl-2-bromoethene

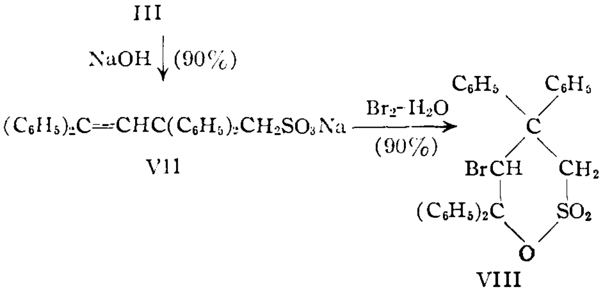


is formed. The formation of IV from II resembles the ready formation of 1,1-diphenyl-2-bromoethene from 1,1-diphenylethene.[5] We have observed that 1,1-diphenyl-2,2-dibromoethene is formed rapidly by shaking a suspension of the olefin in water containing excess bromine.

Conversion of II to its sulfonyl chloride and treatment with aluminum chloride gave 3-phenylbenzothiophene 1,1-dioxide (VI). This provides a good synthetic route to this compound.



Structure III for the sultone was assigned chiefly by analogy with that of the sultone obtained under similar conditions during the sulfonation of styrene.[3] The structure of the sultone from styrene has been proved[6] and the reaction course proposed[6] should yield III when applied to the sulfonation of 1,1-diphenylethene. The reactions of the sultone are consistent with structure III. With aqueous sodium hydroxide an unsaturated sulfonate, sodium 2,2,4,4-tetraphenyl-3-butene-1-sulfonate (VII), was formed which reacted with bromine water to give a bromosultone (VIII) in 90% yield.



These reactions are comparable to those exhibited under similar conditions by the sultone from styrene.[6]

Experimental

Sulfonation of 1,1-Diphenylethene.—Several sulfonations were carried out by the general procedure given in the previous paper.[2] The reaction mixture turns deep red almost immediately. Hydrolysis after 1-, 5- and 20-minute periods all gave approximately the same percentage of sulfonate II (70%) and sulfuric acid (20%). Sodium 2,2-diphenylethene-1-sulfonate (sodium salt of II) crystallized in needles on evaporation of the aqueous solution. Bromide–bromate titration[2] of this crystalline salt gave an unsaturation value of 97%. The bromide–bromate titration therefore gives an accurate estimate of the quantity of II present (over 90% of the sulfonates formed). A quantitative yield of S-(*p*-chlorobenzyl)-thiuronium salt of II, m.p. 179–181°, was obtained. Three crystallizations from water, in which it is but slightly soluble, gave **S-(*p*-chlorobenzyl)-thiuronium 2,2-diphenylethene-1-sulfonate**, m.p. 184–185°.

Anal. Calcd. for $C_{22}H_{21}O_3N_2S_2Cl$: C, 57.29; H, 4.59. Found: C, 57.20; H, 4.56.

Evaporation of the greenish-red organic layer from a sulfonation in which 30.8 g. (0.17 mole) of 1,1-diphenylethene and 13.7 g. (0.12 mole) of sulfur trioxide were used gave a solid. Solution in 20 ml. of acetone and dropwise addition of water gave 3.3 g. (8% of the olefin) of crystals of III, m.p. 90–93°. Several recrystallizations from acetone-alcohol induced by water gave **2,2,4,4-tetraphenyl-3-hydroxybutane-1-sulfonic acid sultone (III)**, m.p. 94–95°.

Anal. Calcd. for $C_{28}H_{24}O_3S$: C, 76.34; H, 5.49. Found: C, 76.16; H, 6.76.

Addition of water to the filtrate from the sultone isolation (above) gave 2.0 g. (11% based on olefin) of material, m.p. 55–65°. Recrystallization from acetone–water gave a hydrocarbon, m.p. 69.5–70°.

Anal. Calcd. for $C_{14}H_{12}$: C, 93.21; H, 6.79. Found: C, 93.16; H, 7.02.

An attempt was made to prepare this "dimer" by the reaction of 1,1-diphenylethene (6.4 g., 0.036 mole) and sulfuric acid (3.5 g., 0.036 mole) in 50 ml. of glacial acetic acid. After standing for 36 hr. at room temperature the reaction mixture was poured into water to give an oily solid from which 2.0 g. (57%) of colorless crystals, m.p. 100–112°, was obtained by washing with hexane. One recrystallization from methanol gave material, m.p. 111–113°, which is the m.p. reported[7] for the "dimer" (1,1,3,3-tetraphenylbutene) prepared by the action of iodine on 1,1-diphenylethene.

The residual acetone mother liquor from which III and the "dimer" had been precipitated gave a gum on evaporation of the acetone. Extraction with benzene gave material which after four crystallizations from benzene melted at 102–105°. A sodium fusion showed the presence of sulfur. No further work was done with this product.

Reaction of Sodium 2,2-Diphenyl-1-ethenesulfonate (II, Sodium Salt) with Bromine.—Bromine was added to 3.0 g. (0.011 mole) of the sodium salt of II in 30 ml. of water until the yellow color persisted. During the addition of 0.3 g. (8%) of a tan oil separated which crystallized on standing. Recrystallization from acetone-water gave colorless platelets (V), m.p. 105–106°. A sodium fusion established the presence of sulfur and bromine.

Anal. Calcd. for $C_{14}H_{11}O_3SBr$: C, 49.57; H, 3.27. Found: C, 49.89; H, 2.96.

Evaporation of the aqueous solution under reduced pressure gave 3.4 g. (89%) of sodium 2,2-diphenyl-1-bromo-1-ethenesulfonate (IV). The S-(*p*-chlorobenzyl)-thiuronium salt of IV was very slightly soluble in water and showed indications of decomposing on standing in contact with water (note the hydrolysis of IV described below). The derivative was dried and crystallized four times from chloroform to give **S-(*p*-chlorobenzyl)-thiuronium 2,2-diphenyl-1-bromo-1-ethenesulfonate**, m.p. 138–139°.

Anal. Calcd. for $C_{22}H_{20}O_3N_2S_2ClBr$: C, 48.94; H, 3.73. Found: C, 49.35; H, 4.14.

Hydrolysis of Sodium 2,2-Diphenyl-1-bromo-1-ethenesulfonate (IV).—An aqueous solution of IV prepared as above from 4.0 g. of the salt of II and bromine was heated on the steam-bath for 18 hr. during which time 3.1 g. of yellow oil separated. The oil solidified on standing in the cold room and was recrystallized from ethanol to give material, m.p. 41–42°, which did not depress the m.p. of an authentic sample[6] of 1,1-diphenyl-2-bromoethene melting at 42–43°. Addition of barium chloride to the aqueous

---

[4] A compound of similar structure is formed in the sulfonation of styrene under certain conditions (see Ref. 3b).

[5] P. Lipp and W. Ludicke, *Ber.*, **56**, 567 (1923), have shown that the dibromide loses hydrogen bromide rapidly on warming.

[6] F. G. Bordwell, F. B. Colton and M. Knell, THIS JOURNAL, **76**, 3950 (1954).

[7] E. Bergmann and H. Weiss, *Ann.*, **480**, 49 (1930).

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 $C_{36}H_{33}O_3N_2S_2Cl \cdot C_2H_6OH$: 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

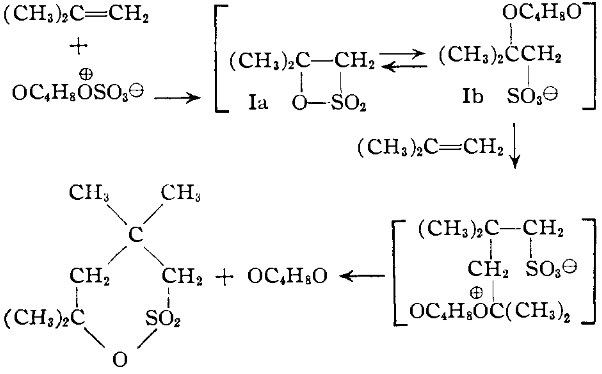
RECEIVED OCTOBER 8, 1958

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).