powder formed was isolated by filtration, washed thoroughly with water and dried in air. The yield was 1.74 g. (5 mmoles; 100%); m.p. 122.5–124.5—undepressed when admixed with authentic material as prepared under *A*. The infrared spectrum was the same as that of authentic.

Acid stability of triphenylcarbethoxymethylene phosphorane (IV). Triphenylcarbethoxymethylene phosphorane (0.348 g.; 1 mmole) was dissolved in 10 ml. of 10% hydrochloric acid. Immediately upon attaining a clear solution, the pH was adjusted to the phenolphthalein end-point with a 10% sodium hydroxide solution. The white solid which formed was filtered, washed with water and dried in air. It weighed 0.330 g. (0.95 mmole; 95%) and was shown to be starting material by a mixed melting point determination and the congruency of infrared spectra.

Acid hydrolysis of triphenylcarbethoxymethylene phosphorane (IV). Triphenylcarbethoxymethylene phosphorane (3.48 g.; 10 mmoles) was dissolved in 100 ml of 10% hydrochloric acid and set aside to evaporate. One month later, 3.55 g. (10 mmoles; 100%) of yellowish crystals were obtained. Two recrystallizations from absolute ethanol-ether gave 1.63 g. (4.6 mmoles; 46%) of white crystals; m.p. 218° dec. When mixed with authentic triphenylcarbethoxymethylphosphonium chloride (m.p. 219.5°), the melting point was 218.5° dec. The infrared spectrum was identical with authentic material.

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Bisulfite Adducts of Acrolein

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One molecular equivalent of sodium bisulfite reacts with acrolein to form a product which on hydrogenation and ring closure yields small amounts of 1,3-propanesultone.[1] As methacrolein and mesityl oxide by similar reactions yield 2-methyl - 1,3 - propanesultone[1] (3 - oxy - 2 - methylpropane - 1 - sulfonic acid sultone), and 1,1,3-trimethyl-1,3-propanesultone,[2] both in good yield and as the mesityl oxide adduct is known to be sodium 2-methyl-4-pentanone-2-sulfonate[3]; it might be assumed that the acrolein product is also the double bond adduct, sodium propanal-3-sulfonate. In contrast, the reaction of cinnamaldehyde with one equivalent of sodium bisulfite yields the carbonyl adduct, sodium 3-phenyl-2-propene-1-hydroxy-1-sulfonate.[4]

We have now obtained evidence that the initial product of the reaction between acrolein and sodium bisulfite at *p*H below 5 is the unsaturated carbonyl adduct, sodium 1-hydroxy-2-propene-1-sulfonate. The addition of sodium bisulfite to the carbonyl group in this *p*H range is rapid and not strongly exothermic:

$$NaHSO_3 + CH_2{=}CH{-}CHO \longrightarrow CH_2{=}CH{-}CH(OH)SO_3Na$$

This adduct, at *p*H below 5, slowly adds a second sodium bisulfite, yielding sodium 1-hydroxy-1,3-propane disulfonate:

$$CH_2{=}CH{-}CH(OH)SO_3Na + NaHSO_3 \longrightarrow NaSO_3{-}CH_2{-}CH_2{-}CH(OH)SO_3Na$$

In the *p*H range above about 5.2 two reactions occur: The unsaturated carbonyl adduct disproportionates to the diadduct and a second mole of bisulfite adds either to the original unsaturated carbonyl adduct or to acrolein produced in the disproportionation. This reaction system is exothermic

$$2CH_2{=}CH{-}CH(OH)SO_3Na \longrightarrow NaSO_3{-}CH_2{-}CH_2{-}CH(OH)SO_3Na + CH_2{=}CH{-}CHO$$

$$CH_2{=}CH{-}CH(OH)SO_3Na + NaHSO_3 \longrightarrow NaSO_3{-}CH_2{-}CH_2{-}CH(OH)SO_3Na$$

$$CH_2{=}CH{-}CHO + 2\,NaHSO_3 \longrightarrow NaSO_3{-}CH_2{-}CH_2{-}CH(OH)SO_3Na$$

As shown in the first equation above, the unsaturated carbonyl adduct alone disproportionates with evolution of heat at *p*H of about 5.2 or higher yielding the diadduct. In this case the expected amount of free acrolein is not obtained because acrolein reacts with the diadduct:

$$NaSO_3{-}CH_2CH_2CH(OH)SO_3Na + xCH_2{=}CH{-}CHO \longrightarrow \left[NaSO_3{-}CH_2{-}CH_2{-}\underset{\displaystyle SO_3Na}{\underset{|}{CH}}{-}O{-}\left(CH_2{-}\underset{\displaystyle CHO}{\underset{|}{CH}}{-}\right)_x + NaSO_3{-}CH_2{-}CH_2{-}CHO\right]$$

This last reaction has been carried out independently using a neutral, aqueous solution of recrystallized sodium 1-hydroxy-1,3-propane disulfonate, and aqueous acrolein. The product probably contains a small amount of sodium propanal-3-sulfonate.

So far it has not been possible to isolate sodium 1-hydroxy-2-propene-1-sulfonate from water solution. The identification of the compound is based on examination of the water solution by NMR spectroscopy, on the Raman spectrum of the solution, on ultraviolet determination of residual acrolein, and on chemical analysis. These data indicate the presence of the $CH_2{=}CHR$ and $R{-}CH(OH)SO_3Na$ groups.

Sodium 1-hydroxy-1,3-propane disulfonate when treated with aqueous hydrochloric or sulfuric acid splits out sulfur dioxide yielding sodium propanal-

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3-sulfonate, a white solid soluble in water, methanol, and 80% ethanol:

$$NaSO_3—CH_2—CH_2—CH(OH)SO_3Na + H^+ \longrightarrow NaSO_3—CH_2CH_2—CHO + H_2SO_3 + Na^+$$

The 2,4-dinitrophenylhydrazone and the oxime of this aldehyde are water-soluble, high-melting solids. Hydrogenation of the aldehyde over Raney nickel, conversion to free sulfonic acid, and cyclization by vacuum distillation gives 1,3-propanesultone in 79% over-all yield based on acrolein.

EXPERIMENTAL

Preparation of sodium 1-hydroxy-1,3-propanedisulfonate. Acrolein, 27.6 g. (0.493 mole), was added over a period of 20 min. to a stirred solution of sodium metabisulfite, 95 g. (1 mole as sodium bisulfite), in 200 ml. of water. The temperature was maintained at 17–20° by cooling and the *p*H of the reaction mixture was held at 3.6–4.0 by addition of small amounts of sulfur dioxide gas. Analysis of the reaction mixture at this point indicated the presence of 0.495 mole of C=C and 0.473 mole of bisulfite ion. The reaction mixture was left in an ice box over night (*p*H 3–4) after which analysis indicated 0.009 mole of C=C and 0.070 mole of bisulfite ion. Ethanol was added until the mixture became cloudy. On standing, colorless needles were deposited. The catalysts were recrystallized from aqueous ethanol, yield 120 g.

Anal. Calcd. for $C_3H_6S_2O_7Na_2 \cdot 3H_2O$: C, 11.3; H, 3.8; S, 20.1. Found: C, 11.6; H, 3.7; S, 20.7.

The infrared spectrum of a Nujol mull of the crystals showed no carbonyl bond (5.8 μ). The high resolution NMR spectrum (40 mc./sec.) of a water solution of the crystals showed higher field multiplets at 127 cps (S—CH_2—C) and 163 cps (C—CH_2—C) from a benzene external standard. No resonances were observed in the region from 20-60 cps from benzene.

Preparation of sodium 1-hydroxy-2-propene-1-sulfonate. Acrolein, 56.0 g. (1 mole), and a solution of sodium metabisulfite, 95.1 g. (1 mole as sodium bisulfite), in 200 ml. of water, were added with stirring from separate burettes over a period of 45 min. to 50 ml. of water at 18–22°. The *p*H of the reaction mixture was held at 2.2 by addition of small amounts of sulfur dioxide gas. Feed rates were adjusted to maintain stoichiometric amounts of reactants in the reaction mixture. Analysis of the product indicated the presence of 0.046 mole of bisulfite ion and 0.975 mole of C=C. The ultraviolet spectrum of the solution indicated less than 0.6 wt. % acrolein in the product. The Raman spectrum indicated the presence of C=C (1648 cm.$^{-1}$) and the RCH(OH)SO_3Na group (1046 cm.$^{-1}$). No carbonyl band (1750 cm.$^{-1}$) was observed. The high resolution NMR spectrum (40 mc./sec.) showed two higher field multiplets at 28 and 54 c.p.s. (CH_2=C and C=CHR) from a benzene external standard. No resonances were found in the range from 120–170 c.p.s. from benzene.

Dilution of the reaction product with ethanol containing sulfur dioxide gave a cloudy solution which slowly deposited crystals of sodium 1-hydroxy-1,3-propanedisulfonate. Evaporation of water from the crude reaction mixture at 0° under vacuum gave a dry salt which smelled strongly of acrolein and contained 0.158 mole of C=C/100 g. (Calcd. for $C_3H_5SO_4Na$: 0.625 mole/100 g.)

Disproportionation of sodium-1-hydroxy-2-propene-1-sulfonate. A solution (90 ml.) of sodium-1-hydroxy-2-propene-1-sulfonate was prepared as above from 31.2 g. (0.327 moles as sodium bisulfite) of sodium metabisulfate and 18.3 g. (0.327 mole) of acrolein. Analysis of this solution indicated the presence of 0.0146 mole/100 ml. of bisulfite ion and 0.318 mole/100 ml. of C=C. Aqueous sodium hydroxide was added dropwise to the stirred solution and the *p*H and temperature were observed. At a *p*H of 5.2 an increase in temperature occurred and a strong acrolein odor developed in the solution. Analysis of the solution at this point indicated the presence of 0.002 mole/100 ml. of bisulfite ion and 0.086 mole/100 ml. of C=C. The solution was evaporated to dryness at room temperature under vacuum yielding a white crystalline residue and distillate containing a total of 0.050 mole of acrolein. Recrystallization of the residue from aqueous ethanol gave white needles.

Anal. Calcd. for $C_3H_6S_2O_7Na_2 \cdot 3H_2O$: C, 11.3; H, 3.8; S 20.1; C=C, 0.0 mole/100 g. Found: C, 11.6; H, 3.6; S, 21.8; C=C, 0.005 mole/100 g.

The NMR spectrum of an aqueous solution of the crystals was identical with that of sodium 1-hydroxy-1,3-propanedisulfonate.

In a related experiment 280 ml. of a solution of sodium 1-hydroxy-2-propene-1-sulfonate prepared from 58.6 g. of acrolein and 95.0 g. of sodium metabisulfite at *p*H 3.4 was diluted with 500 ml. of ethanol containing sulfur dioxide and left at −15°. Crystals (51 g., 32% yield on sodium bisulfite) of sodium 1-hydroxy-1,3-propanedisulfonate were slowly deposited.

Reaction of sodium 1-hydroxy-1,3-propanedisulfonate with acrolein. A solution of 79.5 g. of sodium 1-hydroxy-1,3-propanedisulfonate (0.25 mole) in 100 ml. of water (*p*H 6.6) was added over 35 min. to a stirred solution of 84.0 g. (1.5 moles) of acrolein in 350 ml. of water at 20°. After stirring for 1 hr. at 20°, the reaction mixture was evaporated to dryness at room temperature, 1 mm. pressure, yielding 150.2 g. of water-soluble solid. Analysis of the distillate from the evaporation indicated the presence of 0.105 mole of carbonyl (5.9 g. as acrolein). Attempts to separate unchanged sodium 1-hydroxy-1,3-propanedisulfonate from the solid by recrystallization from water and from aqueous ethanol were unsuccessful.

Anal. Found: C, 37.9; H, 5.3; S, 10.9; H_2O, 5.56; hydroxyl value 0.166 eq./100 g., carbonyl value 0.291 eq./100 g.

Hydrolysis of sodium 1-hydroxy-1,3-propanedisulfonate. A solution of 10.2 g. (0.032 mole) of sodium 1-hydroxy-1,3-propanedisulfonate in 100 ml. of water was treated with 3.5 g. of 95% sulfuric acid in 25 ml. of water. The mixture was boiled to expel sulfur dioxide and was then neutralized to *p*H 7.1 with sodium hydroxide. The solution was evaporated to dryness under vacuum (50°, 1 mm.) and the solid was extracted with boiling 80% ethanol. The dry residue, 5.4 g., contained 0.0013 mole of carbonyl by analysis. The extract was evaporated to dryness yielding 5.1 g. of white solid, soluble in water and methanol, carbonyl value 0.409 eq./100 g. (calcd. for $NaSO_3CH_2—CH_2—CHO$ .625 eq./100 g). A solution of 0.6 g. of this solid in water reacted with 0.4 g. of 2,4-dinitrophenylhydrazine yielding 0.4 g. of 2,4-dinitrophenylhydrazone, a yellow, water-soluble solid which was recrystallized from ethanol-water, m.p. 227–229° dec.

Anal. Calcd. for $C_9H_9N_4O_7SNa \cdot H_2O$: C, 30.2; H, 3.08; S, 8.94. Found: C, 29.5; H, 3.1; S, 9.0.

The infrared spectrum indicated the presence of water of crystallization.

The oxime of the aldehyde was prepared as follows. A solution of 5.5 g. of sodium 1-hydroxy-1,3-propanedisulfonate in 50 ml. of water was treated with 2.5 g. of 95% sulfuric acid. The solution was boiled to eliminate sulfur dioxide and neutralized to xylene cyanol–methyl orange indicator. Hydroxylamine hydrochloride, 1.2 g., was added and the solution was again neutralized (0.0163 eq. of sodium hydroxide required, 94% of the sodium 1-hydroxy-1,3-propane disulfonate charged). The solution was evaporated to dryness (50°, 1 mm.) and the dry solid was extracted with boiling ethanol. On cooling the extract crystals were deposited. These were recrystallized from 80% ethanol yielding white crystals, m.p. 215–220° with decomposition.

Anal. Calcd. for $C_3H_6O_4NSNa \cdot H_2O$: C, 18.6; H, 4.15; S, 16.6. Found: C, 19.0; H, 4.2; S, 16.9; SO_4^{--}, 0.8.

The infrared spectrum indicated the presence of water of crystallization.

Conversion of sodium 1-hydroxy-1,3-propanedisulfonate to 1,3-propanesultone. A solution of 50.0 g. of crude sodium 1-hydroxy-1,3-propanedisulfonate (prepared from 8.9 g. of 95% acrolein and 29.8 g. of sodium metabisulfite) in 200 ml. of water was treated with 20.0 g. of 36% hydrochloric acid. The solution was boiled until the odor of sulfur dioxide was gone from the vapors (30 min). The solution was cooled, neutralized to *p*H 7.05 with aqueous sodium hydroxide, and hydrogenated over Raney nickel at 32–80° and 1300–770 p.s.i.g. Hydrogen adsorption amounted to 0.16 mole. The catalyst was removed by filtration. The filtrate was passed over Dowex 50 (H^+) ion exchange resin to remove sodium ion. The solution was concentrated under vacuum and the bottoms were distilled, yielding 14.6 g. of propanesultone b.p. 96° (1 mm.), ester value, 0.819 eq./100 g., calcd. ester value 0.820 eq./100 g. (79% conversion on acrolein).

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Reactions of Hindered Phenols. III.[1] Reaction of Nitrous Acid with Hindered Phenols

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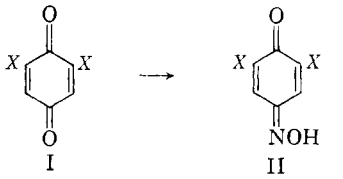
The tautomeric behavior of nitrosophenols (quinone oximes) is well known and on the basis of electronic spectra, Havinga and co-workers[4] have shown that *p*-nitrosophenol exists in solution as the phenol along with the quinone monoxime, whereas in the solid state it occurs as the oxime. Hadzi has recently shown on the basis of infrared studies that in the solid state it could be represented as the monoxime and in chloroform solution, the oxime structure predominates.[5] X-ray determination of 3-chloroquinone-4-oxime and 3-methyl-6-chloroquinone-4-oxime has indicated that the molecules exist in the quinone oxime form.[6]

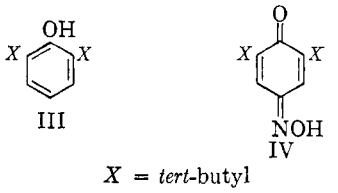
If the quinone is sterically hindered by substituents in the *ortho* position as in I, then the product obtained by the action of hydroxylamine has the structure II.[7] Hodgson and co-workers have carried



I II

X = Cl, Br, CH_3, i-C_3H_7

out a large amount of work on the nitrosation of substituted phenols.[8] We were interested in studying the reaction of nitrous acid on sterically hindered phenols. 2,6-Di-*tert*-butylphenol (III) gave on treatment with nitrous acid, an excellent yield of a compound melting at 221–222°. The ultraviolet spectrum showed λ_{max} 302,418 mμ, ϵ_{max} 15,300 and 3700, respectively, which indicates predominantly a monoxime structure.[4] The infrared spectrum (Nujol mull), 3330 cm.$^{-1}$ (OH), 1613 cm.$^{-1}$ (C=O), 1560 cm.$^{-1}$ (C=N), and 1042 cm.$^{-1}$ (N–OH stretching), supports an

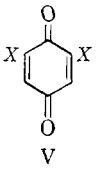


III IV

X = *tert*-butyl

oxime structure (IV).[5] Metro[9] obtained a compound melting at 219–220° by treating 2,6-di-*tert*-butylbenzoquinone with hydroxylamine hydrochloride. This obviously has the identical structure (IV).

A number of methods are known for the preparation of 2,6-di-*tert*-butylbenzoquinone (V).[10–14] Since the oxime (IV) was obtained in almost quantitative yield, the hydrolysis of the same appeared to be



V

X = *tert*-butyl

a simple route for the preparation of V. Thus by the hydrolysis of the oxime (IV) with 20% hydrochloric acid in the presence of cuprous oxide, a 75% yield of V was obtained.

Hart and Cassis[15] found that the action of nitric acid and acetic acid on 2,6-di-*tert*-butylphenol

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