

Absorption of hydrogen was very rapid. The mixture was diluted with water and the insoluble portion separated, dried and distilled. Physical and analytical data for the hydrogenated product, probably somewhat impure, are given in Tables II and III.

Polymerization of Vinylacetylene to Styrene.—A solution of 5 g. of acetic acid in 104 g. of vinylacetylene was heated in a steel bomb for six hours at 105°. On distilling the mixture under reduced pressure 70 g. of vinylacetylene, 5 g. of acetic acid and 13 g. of styrene were obtained. The residue (13 g.) consisted of a soft, straw-colored resin apparently identical with the polymer obtained in the absence of acid. The styrene was purified by washing with dilute alkali, drying over calcium chloride and distilling over hydroquinone. The properties observed are: b. p. 144° (54° (30 mm.)); d_4^{20} 0.9065; n_D^{20} 1.5450. The styrene was further characterized by its dibromide, m. p. 73.5°, as compared with a recorded value of 73°,⁴ by its oxidation to benzoic acid and by its substantially quantitative conversion to meta-styrene when treated with stannic chloride.

Increase in temperature was observed to increase the rate of conversion of vinylacetylene to styrene but it failed

(4) Miller, *Ber.*, **11**, 1450 (1878).

to increase the yield on the basis of unrecovered vinylacetylene. Use of antioxidants in the reaction decreased the rate of resin formation (by-product) only slightly.

The author wishes to express his thanks to Dr. Wallace H. Carothers for his interest in this work and for his helpful suggestions.

Summary

The polymerization of vinylacetylene under various conditions is described. Evidence is presented which indicates that the dimer obtained by thermal polymerization in the absence of a catalyst is diethynylcyclobutane and that the higher polymers have polycyclobutene-cyclobutane structures. Hydrogenated derivatives of the lower polymers are characterized. Thermal polymerization of vinylacetylene in the presence of acidic materials is shown to give substantial quantities of the dimer, styrene.

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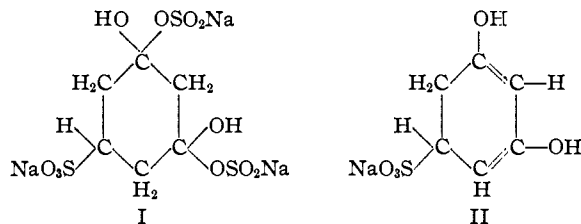
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The Action of Sodium Bisulfite on Resorcinol

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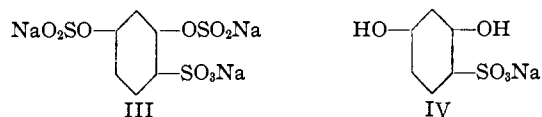
Fuchs and Elsner¹ report the formation of an isolable product resulting from the addition of three molecules of sodium bisulfite to one of resorcinol. They postulate ketonization and accordingly assign structure I to this addition product. Upon treatment with aqueous sodium hydroxide, only two of the three added bisulfite molecules are removed; consequently these investigators assign structure II to the resulting product.



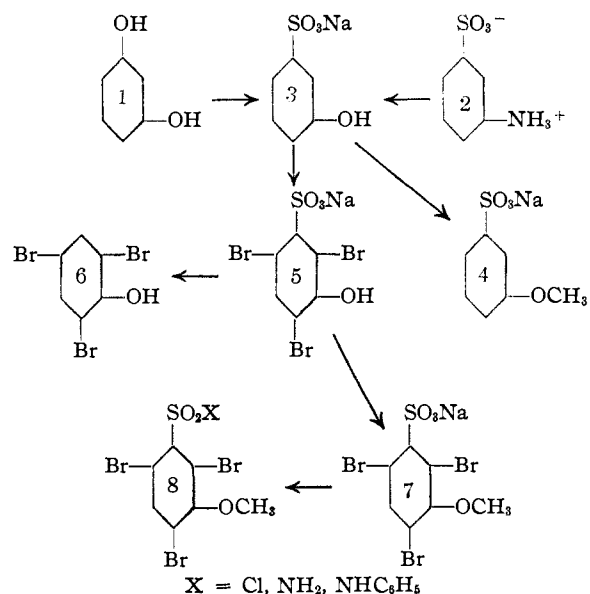
Bucherer and Hoffman² interpret the action of sodium bisulfite on resorcinol in a different manner and adopt structures III and IV for the addition product and the product obtained after hydrolysis.

(1) Fuchs and Elsner, *Ber.*, **53**, 886-898 (1920).

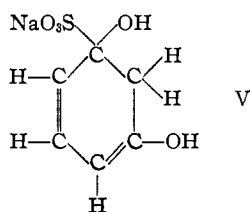
(2) Bucherer and Hoffman, *J. prakt. Chem.*, [2] **121**, 113 (1929). See also Bucherer, *ibid.*, [2] **69**, 71 and 87 (1904); *Z. angew. Chem.*, **17**, 1073 (1904); German Patent 115,335.



On treating resorcinol with bisulfite, boiling the reaction mixture first with base and then with



acid, we obtained the sodium salt of phenol-*m*-sulfonic acid instead of the sodium salt of resorcinol sulfonic acid or dihydroresorcinol sulfonic acid. The series of transformations already given establishes the constitution of our product, since the derivatives are identical whether metanilic acid or resorcinol is used as the source of the phenol-*m*-sulfonic acid. The loss of a molecule of water from Fuchs' dihydroresorcinol sulfonic acid (II) or from a compound such as V



resulting from the addition of bisulfite to the keto form of resorcinol, might account for its formation.

Experimental

The Action of Sodium Bisulfite on Resorcinol.—110 g. of resorcinol, 620 g. of sodium bisulfite and 2 liters of water were heated in a 3-liter flask under a reflux condenser on a steam cone for two weeks; 150 g. of sodium hydroxide, dissolved in the minimum quantity of water, was added to the solution slowly and heating on the steam-bath continued for one hour. One liter of concd. hydrochloric acid was then added and the reaction mixture heated for four hours to remove sulfur dioxide. After cooling, an ether extraction was made to remove any unchanged resorcinol.

(a) **Sodium Salt of Phenol-*m*-sulfonic Acid.**—The solution was then evaporated as far as possible and treated with an equal volume of alcohol. The inorganic salts were filtered off and the solution was evaporated almost to dryness. On extraction with 95% alcohol 52 g. of the sodium salt of phenol-*m*-sulfonic acid was obtained, which was purified by recrystallization from 90% alcohol.

Anal. Calcd. for $C_6H_6O_4SNa$; Na, 11.72. Found: Na, 11.71, 11.59.

(b) **Sodium Salt of 2,4,6-Tribromophenol-3-sulfonic Acid.**—The cold solution was treated with bromine until a slight excess was present. After standing for a short time, the precipitate was filtered off and dried (218 g.). It was purified by crystallization from glacial acetic acid and then absolute alcohol.

Anal. Calcd. for $C_6H_2O_4Br_3SNa$: Na, 5.31; Br, 55.39; S, 7.40. Found: Na, 5.62, 5.33; Br, 54.95, 54.83; S, 7.55, 7.3.

Hydrolysis of this compound with 50% sulfuric acid gave tribromophenol. The sulfone chloride, sulfonamide and sulfonanilide prepared from this 2,4,6-tribromophenol-3-sodium sulfonate melted at 57.6–58.8°; 176.2–177° and 159.8–160.2°, respectively. They showed no melting

point depression when mixed with the corresponding samples prepared from metanilic acid.

Identification of Product

Sodium Salt of Anisole-*m*-sulfonic Acid.—The sodium salt of phenol-*m*-sulfonic acid was methylated with dimethyl sulfate. The product was crystallized from absolute alcohol. It contained water of crystallization.

Anal. Calcd. for $C_7H_7O_4SNa \cdot H_2O$: H_2O , 7.89; OCH_3 , 13.6; Na, 10.1. Found: H_2O , 7.05; OCH_3 , 14.3; Na, 9.9.

Sodium salt of 2,4,6-tribromophenol-3-sulfonic acid was also prepared by diazotizing metanilic acid and warming the resulting solution until the evolution of nitrogen ceased. The calculated amount of bromine was then added slowly with shaking to the cooled reaction mixture after it had been saturated with sodium chloride. The precipitate was collected and crystallized from glacial acetic acid. For analysis a portion was purified further by recrystallizing from alcohol.

Anal. Calcd. for $C_6H_2O_4Br_3SNa$: Na, 5.31; Br, 55.39. Found: Na, 5.63, 5.68; Br, 55.09, 54.96.

Sodium Salt of 2,4,6-Tribromoanisole-3-sulfonic Acid.—11.6 g. of 2,4,6-tribromophenol-3-sodium sulfonate was dissolved in 15 cc. of 5 *N* sodium hydroxide and 7.5 cc. of dimethyl sulfate was added. The reaction mixture becomes warm on shaking and sets to a white crystalline mass. After the completion of the reaction, the contents of the flask were heated on the steam-bath for half an hour. The product after filtration and drying weighed 11.5 g. It was purified by crystallization from 80% alcohol as white lustrous plates.

Anal. Calcd. for $C_7H_4O_4Br_3SNa$: Na, 5.15. Found: Na, 5.20.

2,4,6-Tribromoanisole-3-sulfone chloride was obtained in quantitative yield by the action of phosphorus pentachloride on 2,4,6-tribromoanisole-3-sodium sulfonate in phosphorus oxychloride. It was crystallized from petroleum ether, m. p. 57.2–58.2°.

Anal. Calcd. for $C_7H_4O_3Br_3SCl$: C, 18.96; H, 0.90. Found: C, 19.13; H, 0.96.

2,4,6-Tribromoanisole-3-sulfonamide.—The sulfone chloride was heated with concentrated aqueous ammonia. The precipitated solid was taken up in 1 *N* sodium hydroxide and filtered. The filtrate was acidified with hydrochloric acid and the solid obtained crystallized from 50% alcohol, m. p. 176.6–178°.

Anal. Calcd. for $C_7H_6O_3Br_3NS$: C, 19.8; H, 1.42. Found: C, 20.1; H, 1.54.

The anilide after crystallization from a benzene-petroleum ether mixture melted at 160.0–160.2°.

Summary

A study of the action of sodium bisulfite on resorcinol reveals the formation of the sodium salt of phenol-*m*-sulfonic acid, a result which is not in agreement with previous work.