4-Dimethylaminobenzoyl Formic Acid (VIII).—In another hydrolysis of VIb, the acid solution was allowed to stand at room temperature overnight. The mixture was made alkaline with 5 N sodium hydroxide solution and the N,N-dimethyl-p-phenylenediamine that separated was removed by extraction with ether–benzene. The aqueous phase then was cooled in ice water and acidified to pH 2 by means of dilute hydrochloric acid to obtain 0.5 g. of greenish yellow crystals, that melted with liberation of gas and darkening at 173–175°. Recrystallization from ethyl alcohol gave 0.4 g. (42%) of greenish yellow needles, and raised the melting-decomposition point to 175–176°. The pure keto acid[11] is finally obtained in golden yellow needles, m.p. 180° dec. from ethanol.

Anal. Calcd. for $C_{10}H_{11}NO_3$: C, 62.2; H, 5.7; N, 7.3. Found: C, 62.8; H, 6.0; N, 7.5.

4-Dimethylaminobenzalaniline (X).—Further proof of 4-dimethylaminobenzoylformic acid as one of the degradation products from the hydrolysis VIb was obtained by decarboxylation of its anil according to a method described by Bouveault.[12] Thus, 0.95 g. (0.05 mole) of the keto acid and

(11) H. Staudinger and H. Stockmann, *Ber.*, **42**, 3485 (1909), prepared it from dimethylaniline and oxalyl chloride or oxalyl monoester chloride, m.p. 187°.

(12) L. Bouveault, *Bull. soc. chim.* **15**, 1020 (1896); **17**, 363 (1897).

2.0 g. (0.02 mole) of freshly distilled aniline were boiled for 10 min. Excess aniline was then distilled under reduced pressure, leaving a yellow oily residue that solidified upon cooling. Two crystallizations from ethyl alcohol gave 0.4 g. of micro, yellow crystals, m.p. 98.5–99.5°. This substance did not depress the melting point of an authentic specimen of the anil (m.p. 98–99°) derived from 4-dimethylaminobenzaldehyde.

Anal. Calcd. for $C_{15}H_{16}N_2$: C, 80.35; H, 7.15; N, 12.5. Found: C, 80.35; H, 7.24; N, 12.2.

N′-Benzoyl-N,N-dimethyl-p-phenylenediamine (IX).—The acid filtrate obtained upon precipitation of the 4-dimethylaminobenzoyl cyanide was evaporated to dryness by heating on a steam bath under a stream of air until most of the water was driven off, and finally by heating in a vacuum oven at 50°. The 1.1 g. of white salt that remained was dissolved in 2 ml. of water and, with ice cooling, was treated successively with 1 ml. each of benzoyl chloride and 5 N sodium hydroxide. The tan benzoyl derivative formed was recrystallized from benzene–ethyl alcohol to give 0.45 g. (37%) of white needles, m.p. 228–229°. These did not depress the melting point of the benzoyl derivative (m.p. 226–228°) of an authentic specimen of N,N-dimethyl-p-phenylenediamine.

Dienone–Phenol Rearrangements of 4-Dichloromethyl- and 4-Trichloromethyl-4-methyl-2,5-cyclohexadien-1-one[1]

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4-Dichloromethyl-4-methyl-2,5-cyclohexadien-1-one and 4-trichloromethyl-4-methyl-2,5-cyclohexadien-1-one undergo the normal dienone–phenol rearrangement in 80% sulfuric acid. The latter compound, in addition to the normal product, gives 10% of a cresotic acid derivative resulting from a 1,3-shift of the trichloromethyl group.

The dienone–phenol rearrangement is generally acknowledged to proceed through migration of a hydrocarbon radical with its pair of bonding electrons.[2] Consistent with this mechanism are indications that the rearrangement may proceed with difficulty or be prevented altogether if the site from which the migrating group must leave is made electron-deficient by the introduction of electron-attracting groups. Thus, 4 - dichloromethyl - 4 - methyl-2,5-cyclohexadien-1-one (I)[3] and its naphthalenic analog, 4-dichloromethyl-4-methyl-1(4H)-naphthalenone,[4] fail to rearrange when treated with a catalytic amount of sulfuric acid in acetic anhydride, a medium which serves well for similar unchlorinated compounds.[5]

Results reported in two papers indicate that 2,5-cyclohexadien-1-ones with an electron-withdrawing group in the *gem* position may, in fact, rearrange

abnormally.[6] Compound II has been found to give III upon treatment with 60% sulfuric acid,[7]
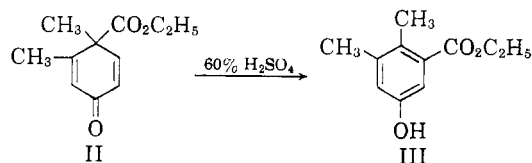
and Newman and Wood have described a rearrangement of IV in polyphosphoric acid in which the trichloromethyl group undergoes a 1,3-shift.[8] The same authors report that in polyphosphoric acid, V undergoes only the normal rearrangement in addition to complete loss of the trichloromethyl group.[8]
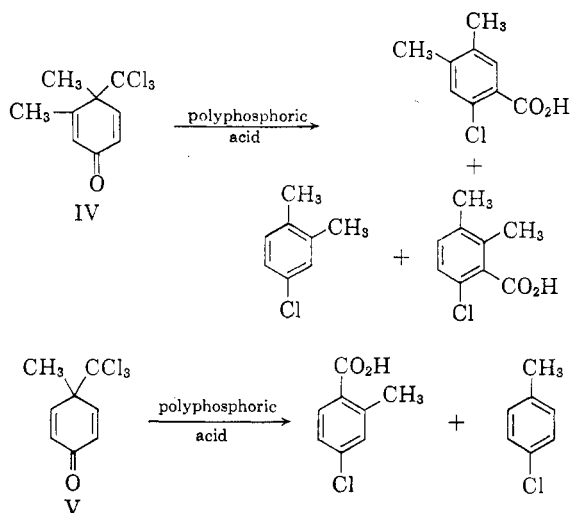
(1) The author is indebted to the National Science Foundation for support of this work under NSF-G6578.

(2) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, 1959, p. 639.

(3) K. v. Auwers and G. Keil, *Ber.*, **35**, 4207 (1902).

(4) R. C. Fuson and T. G. Miller, *J. Org. Chem.*, **17**, 316 (1952).

(5) R. T. Arnold, J. S. Buckley, and J. Richter, *J. Am. Chem. Soc.*, **69**, 2322 (1947).

(6) Migratory aptitudes in the rearrangement of carbonium ions generally increase as the electron-releasing ability of the group increases, unless steric factors are predominant—see ref. 2, p. 609. The term "abnormal rearrangement" is thus used here to indicate that the poorest electron donor of the *gem*-substituents has migrated.

(7) H. Pleininger and T. Suehiro, *Ber.*, **89**, 2789 (1956).

(8) M. S. Newman and L. L. Wood, Jr., *J. Am. Chem. Soc.*, **81**, 6450 (1959). Although these rearrangements do not give phenolic products, the nature of the starting materials and the reagent used suggest their comparison to the conventional dienone–phenol rearrangement.

Two cyclohexadienones with electron-attracting groups in the *gem* position, compounds I and V, are being used in this laboratory as starting materials, and it was deemed worthwhile to investigate their behavior when treated with strong sulfuric acid. The results on V differ significantly from those Newman and Wood obtained using polyphosphoric acid as the reagent.

The dichloromethyl compound (I) was found to rearrange normally when warmed with 80% sulfuric acid. Rearrangement is followed by hydrolytic removal of the chlorine to give the corresponding aldehyde. Yields are limited by the
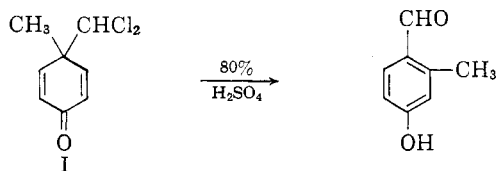
formation of higher molecular weight dyes from the product. Heating for twenty-four hours at 60° gives 31% of the aldehyde in addition to 42% recovered starting material and 22% of a red, ether-insoluble dye. More vigorous conditions result in increased conversion of the ketone but also give higher yields of the dye at the expense of the original rearrangement product. That the dye was formed from the final product and not from I or an intermediate was shown by an experiment in which the hydroxyaldehyde alone was converted completely to the dye by heating it for eighteen hours at 85° with 80% sulfuric acid. Sulfonation of the hydroxytolualdehyde did not occur to any appreciable extent. Moreover, the crude aldehyde isolated gave a negative ferric chloride test and colorless solution in aqueous sodium hydroxide, indicating that a 1,3-migration of the dichloromethyl group did not take place. The hydroxyaldehyde formed was identical to a sample of 4-hydroxy-*o*-tolualdehyde prepared by the Reimer-Tieman procedure.[9]

4-Trichloromethyl-4-methyl-2,5-cyclohexadien-1-one (V) rearranges completely when heated at 90–95° for twenty-four hours in 80% sulfuric acid to give a mixture containing 90% of *m*-cresolsulfonic acids (VI) and 10% of 3-sulfo-2,5-cresotic acid (VII). In addition, a very small amount of unsulfonated 2,5-cresotic acid was
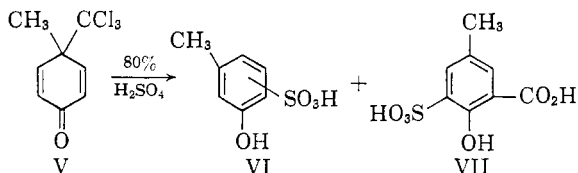
isolated. The use of lower acid concentrations or temperatures resulted in incomplete conversion of the ketone. Compound VI results from normal rearrangement of V, followed by hydrolysis to the carboxylic acid, decarboxylation, and sulfonation. An authentic sample of 4,2-cresotic acid,[10] the expected normal rearrangement product, when heated to 90° with 80% sulfuric acid undergoes decarboxylation and sulfonation to give a cresolsulfonic acid whose infrared spectrum is identical to that of the compound VI formed in the rearrangement. Direct sulfonation of *m*-cresol gives a compound whose infrared spectrum differs from that of the rearrangement product only by the appearance of a very weak band at 827 cm.$^{-1}$. Since the isomer content of sulfonated *m*-cresol varies with the conditions of sulfonation,[11] it is probable that the samples compared differed somewhat in this respect. The lack of absorption at 3400 cm.$^{-1}$, beyond that contributed by VII, by the crude sodium sulfonates isolated from the rearrangement indicates that no appreciable amount of 6-hydroxy-*m*-toluenesulfonic acid was present. Hence loss of the trichloromethyl group without rearrangement does not occur in 80% sulfuric acid as it does in polyphosphoric acid. 3-Sulfo-2,5-cresotic acid (VII) has not previously been described in the literature. Sulfonation of an authentic sample[9] of 2,5-cresotic acid gives a compound identical in infrared spectrum and chemical behavior to the rearrangement product. Structure VII is assigned because the sulfonation product does not couple with *p*-nitrobenzenediazonium chloride.

VI and VII were isolated by adjusting the diluted reaction mixture to *p*H 3 with ammonia, saturating with ammonium sulfate, and extraction with 2-butanol. Compound VII crystallized preferentially from the 2-butanol solution on evaporation, leaving the ammonium salt of VI in solution. A more complete estimation of yields in the rearrangement was obtained by adjusting the diluted reaction mixture to *p*H 4 with sodium

(9) H. H. Hodgson and T. A. Jenkinson, *J. Chem. Soc.*, 469 (1929).

(10) F. Tiemann and C. Schotten, *Ber.*, **11**, 767 (1878).

(11) R. P. Haworth and A. Lapworth, *J. Chem. Soc.*, **125**, 1299 (1924).

hydroxide, evaporating to dryness, and extracting VI and VII as the sodium salts by anhydrous methanol. An analysis of this product mixture was achieved by a colorimetric determination of the ferric chloride complex of VII at pH 1.72, where VII forms a colored complex, but VI does not.

Newman and Wood ascribe the difference in behavior of IV and V in polyphosphoric acid to crowding by the extra methyl group in IV which was said to cause rearrangement of the bulkier *gem*-substituent, the trichloromethyl group.[8] The work reported here indicates that such crowding is not always necessary for trichloromethyl group migration, but that electronic factors are also involved. It is apparent that migration of a methyl group with its bonding pair would become increasingly difficult as the site from which it must leave is made more electron deficient by the introduction of electron-attracting substituents such as —CCl_3. In such cases aromatization might occur instead by one of the following schemes:
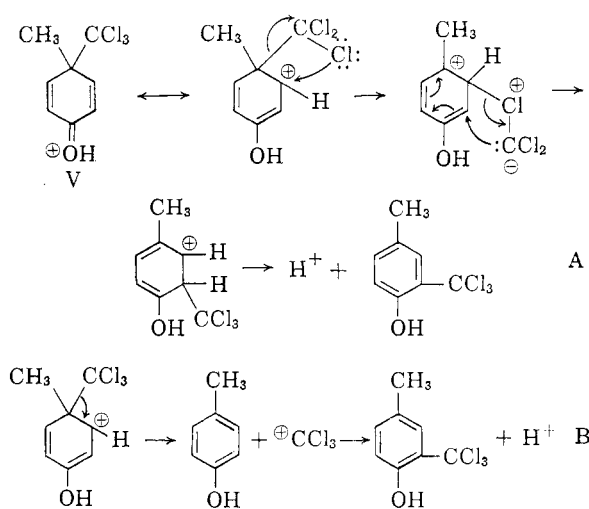
The trichloromethyl group is well adapted for either path. Scheme A is suggested by the immediate proximity of one of the chlorine atoms of V to the neighboring carbon atom on the ring, while B-strain and resonance stabilization in the trichloromethyl carbonium ion may favor path B.

Experimental

Rearrangement of 4-Dichloromethyl-4-methyl-2,5-cyclo-hexadien-1-one (I).—A solution of 5 g. of 4-dichloromethyl-4-methyl-2,5-cyclohexadien-1-one[8] in 20 g. of 80% sulfuric acid was heated in an oil bath at 60° for 24 hr. During this time the solution became dark red and hydrogen chloride was evolved. The mixture was diluted with 75 ml. of ice water, adjusted to pH 9–10 with 30% sodium hydroxide solution, and extracted with three 25-ml. portions of ether. On evaporation, the ether solution yielded 2.1 g. (42%) of starting material.

The basic aqueous solution was acidified with dilute sulfuric acid and filtered to give 0.8 g. (*ca.* 22%) of an acid-insoluble red dye.[12] The acidic aqueous solution was ex-

tracted with six 25-ml. portions of ether and the ether evaporated to give 1.1 g. (31%) of 4-hydroxy-*o*-tolualdehyde, m.p. 105–107° crude, 109–110° (reported[10] 109–110°) after recrystallization from water. The infrared spectrum was identical with that of an authentic sample.[10] The absence of a ferric chloride test and the formation of a colorless, basic solution indicated that the crude hydroxyaldehyde did not contain any 5-methylsalicylaldehyde, which would have been formed by a 1,3-migration of the dichloromethyl group.

Neutralization of the remaining aqueous solution, evaporation to dryness, extraction of the powdered residue with anhydrous methanol, and evaporation of the solvent gave only a negligible weight of solid, proving that sulfonation of the 4-hydroxy-*o*-tolualdehyde did not occur.

A 31% yield of 4-hydroxy-*o*-tolualdehyde was also obtained, in addition to 58% of recovered starting material and 7% dye, by heating the ketone in 60% sulfuric acid at 85–90° for 17 hr. Longer heating periods or higher temperatures in 60% or 80% sulfuric acid increased the conversion of ketone, but also increased the amount of hydroxyaldehyde converted to the red dye. When the ketone was treated with 80% sulfuric acid at 80° for 19 hr., conversion to the dye was virtually complete.

Rearrangement of 4-Trichloromethyl-4-methyl-2,5-cyclo-hexadien-1-one (V).—A solution of 5 g. of the ketone[13] in 20 g. of 80% sulfuric acid was heated in an oil bath at 90–95° for 24 hr. During this time the mixture became brown in color and hydrogen chloride was evolved. The solution was diluted with 60 ml. of ice water and extracted with two 20-ml. portions of ether. Evaporation of the ether yielded a few milligrams of a solid acid which was proved, by melting point and comparison of the infrared spectrum with that of an authentic sample,[10] to be 2,5-cresotic acid. The aqueous solution was made basic with 30% sodium hydroxide solution, adjusted to pH 4–5 with hydrochloric acid, and then evaporated to dryness on a steam bath. The powdered residue was extracted with 100 ml. of anhydrous methanol and the methanol evaporated to give, after drying at 140° in vacuum, 5.3 g. of white solid, a mixture of sodium chloride and the sulfonates of *m*-cresol and 2,5-cresotic acid.

A gravimetric analysis for chloride ion in the mixed sulfonates indicated the presence of 8.9% sodium chloride. No sulfates were present. After correction for sodium chloride the yield was thus 4.8 g. Colorimetric analysis of the mixture for 3-sulfo-2,5-cresotic acid by the method described below showed it to contain 90% of the *m*-cresol sulfonate and 10% of the 2,5-cresotic acid sulfonate. The infrared spectrum of the crude sodium sulfonate mixture was entirely consistent with its representation as consisting of the sodium sulfonates of *m*-cresol in large amount and 2,5-cresotic acid as a minor component.

Isolation of 6-sulfo-2,5-cresotic acid was accomplished by salting it out of an acidic aqueous solution of the mixed sulfonates with sodium chloide. The compound thus isolated was identical in chemical behavior and infrared spectrum to the direct sulfonation product of 2,5-cresotic acid (see below).

Evaporation of the salted solution and extraction with anhydrous methanol gave the sodium salt (contaminated with sodium chloride) of *m*-cresolsulfonic acid. The infrared spectrum of this material was identical to that of the reaction product of 4,2-cresotic acid and 80% sulfuric acid, and virtually identical to the direct sulfonation product of *m*-cresol.

For identification purposes, the sulfonates were separated as follows: 5 g. of the cyclohexadienone was allowed to re-

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(12) Because the structure of the dye is not known, it is impossible to calculate exact percentage yields. If the same molecular weight, or a multiple of it, as 4-hydroxy-*o*-tolualdehyde is assigned, the yield given should not be in error significantly, since the aldehyde is converted to the dye by 80% sulfuric acid with little loss in weight.

(13) M. S. Newman and A. G. Pinkus, *J. Org. Chem.*, **19**, 978 (1954).

arrange as described above. The mixture was diluted with 75 ml. of ice water, adjusted to pH 4–5 with 28% ammonia, saturated with ammonium sulfate, and then extracted with three 25-ml. portions of ether to remove a small amount of unsulfonated 2,5-cresotic acid. The aqueous solution was then extracted with six 25-ml. portions of 2-butanol, and the combined 2-butanol extracts were washed with water saturated with ammonium sulfate and 2-butanol until the washings were neutral to Congo red. Partial evaporation of the 2-butanol solution yielded the 3-sulfo-2,5-cresotic acid. On complete evaporation of the 2-butanol the ammonium salt of m-cresolsulfonic acid remained. The total yield of sulfonates recovered by this method was ca. 40%. No chlorides or sulfates were co-extracted by the 2-butanol.

Analysis for 3-Sulfo-2,5-cresotic Acid in the Presence of m-Cresolsulfonic Acid.—At pH 2.2 the cresotic acid derivative forms a purple complex with ferric chloride, and the cresolsulfonic acid mixture gives a much weaker rose color. At pH 1.72, however, only the cresotic acid derivative forms a colored complex. Beers law was followed at 547 mμ by solutions 2.96×10^{-3} M in ferric chloride and ranging from 1.05×10^{-4} M to 6.04×10^{-4} M in 3-sulfo-2,5-cresotic acid. The pH was adjusted to 1.72 by making all dilutions with a solution of sulfuric acid of pH 1.72 (ca. 0.015 M). The extinction coefficient at 547 mμ was 1280. There was no interference from widely varying quantities of m-cresolsulfonic acid, p-cresolsulfonic acid, or 6-sulfo-4,2-cresotic acid.

Sulfonation of 4,2-Cresotic Acid with 80% Sulfuric Acid.—A solution of 1 g. of 4,2-cresotic acid[10] and 10 g. of 80% sulfuric acid was heated to 90° for 24 hr. Carbon dioxide was evolved rapidly. The brownish solution was poured into 50 ml. of water. Efforts to obtain the sodium salt by salting the neutralized solution were unsuccessful. The ammonium salt was obtained by adjusting the diluted solution to pH 4 with ammonia, extracting with four 20-ml. portions of 2-butanol, washing the 2-butanol solution with saturated ammonium sulfate, and evaporation of the 2-butanol. The tan residue, after trituration with ether, weighed 0.80 g. (60%). A mixture of isomers was undoubtedly present; however, no effort was made to determine the isomer composition or to separate the components.

The infrared spectrum of this mixture in a Nujol mull is characterized by strong bands at 3120, 1170 (very broad), 1086, and 1018 cm.$^{-1}$. Assignment of the first band to the phenolic OH and the second to an unresolved combination of —OH and —SO$_3$$^-$ bands seems justified.[14] The latter two bands are both in the region assigned to the —SO$_3$$^-$ function[14] and whether both, or just one, are due to this group is not known. As expected because of the evolution of carbon dioxide during sulfonation, no carbonyl absorption was present. The infrared spectrum of the sodium salt, obtained by evaporation of a weakly basic solution and extracting the residue with methanol, was identical except for a slight shifting in the bands in the —SO$_3$$^-$ region and loss of a shoulder at 1410 cm.$^{-1}$ due to the ammonium ion.

Hydroxytoluene Sulfonic Acids by Sulfonation of m-Cresol. A solution of 10 g. of m-cresol in 50 ml. of concentrated sulfuric acid was allowed to stand at ambient temperature for 1 hr. and then poured onto 100 g. of ice. The sodium and ammonium salts were isolated as described directly above. No effort was made to determine the isomer distribution; however, it should not have differed greatly from the 1:2.7 ratio of p-hydroxy- to o-hydroxysulfonic acid reported by Haworth and Lapworth for the sulfonation of m-cresol under similar conditions.[11] The infrared spectra of these salts (Nujol mulls) were identical to those of the corresponding compounds resulting from the reaction of 4,2-cresotic acid with 80% sulfuric acid except that they contained one additional weak band at 827 cm.$^{-1}$. With ferric chloride at pH 2.15

the isomer mixture developed a rose color, while at pH 1.72 the test was negative.

3-Sulfo-2,5-cresotic Acid (6-Hydroxy-5-sulfo-m-toluic Acid) (VII).—A solution of 2.5 g. of 2,5-cresotic acid[10] in 20 ml. of concd. sulfuric acid was allowed to stand for one day at room temperature, then heated to 60–70° for 3 hr., cooled, and poured onto 100 g. of ice. The mixture was brought to room temperature and 5 g. of salt was added. Upon standing the mixture deposited a fibrous precipitate of the free sulfonic acid. This was washed with saturated sodium chloride solution and dried; yield 2.4 g. The sulfonic acid does not couple with p-nitrobenzenediazonium chloride, fluoroesces strongly in a neutralized aqueous solution, and gives a strong purple color with ferric chloride at pH 2.15 and at pH 1.72.

The infrared spectrum (Nujol mull) of the free sulfonic acid is characterized by bands at 3430 (—OH), 1680 (>C=O), 1600, 1250, 1210, 1117, 1052 (SO$_3$H), 857, and 806 cm.$^{-1}$. When a solution of the acid is adjusted to pH 4–6 with sodium hydroxide and the salt isolated by evaporation to dryness (the procedure used to isolate the sodium salts of the rearrangement products of V), the infrared spectrum reveals partial to complete conversion of the carboxyl group to its anion—i.e., partial to complete loss of the 1680-cm.$^{-1}$ band and emergence of a strong band at 1580 cm.$^{-1}$. Other shifts in intensities and wave lengths throughout the spectrum were also noticeable, especially in the 1050–1200-cm.region where —SO$_3$H and —OH absorb.[14] This spectral behavior is consistent with that of the sulfocresotic acid isolated in the rearrangement of V.

6-Hydroxy-m-toluenesulfonic Acid.—In order to obtain samples of this compound for comparison of infrared spectra p-cresol was sulfonated by the method given above for m-cresol. The sodium salt was isolated by salting it out of the diluted reaction mixture, followed by extraction of the sodium cresolsulfonate from coprecipitated sodium sulfate with anhydrous methanol. Evaporation of the methanol gave a white solid which contained no sulfate and only traces of chloride. The infrared spectrum (Nujol mull) contained strong bands at 3420, 1255, 1230, 1210, 1180, 1115, 1043, 868, 813, and 737 cm.$^{-1}$. The spectrum was similar in overall nature to that of m-cresolsulfonic acid and of the product obtained from the rearrangement of V, the most notable difference being a strong —OH absorption at 3420 cm.$^{-1}$ in the p-cresol derivative, which was lacking in the m-cresol sulfonates.

p-Cresol is also sulfonated completely in 80% sulfuric acid under the conditions of rearrangement of V.

This compound gave a strong purple color with ferric chloride at pH 2.15, but none at pH 1.72.

5-Sulfo-4,2-cresotic Acid (4-Hydroxy-5-sulfo-o-toluic acid).—This compound was not isolated as a rearrangement product of V. However, it was needed for comparison with those compounds which were isolated and, since it is not described in the literature, its preparation is given here. A solution of 1 g. of 4,2-cresotic acid[10] in 10 ml. of concentrated sulfuric acid was allowed to stand for 3 days at room temperature. There was no evidence of decarboxylation. The mixture was poured into 50 ml. of water and the solution saturated with salt. The solid was collected by filtration and recrystallized from 10% sodium chloride solution to give an 82% yield of the sodium salt. Although sulfonation of 4,2-cresotic acid may give a mixture of isomers, it is probable that the crystallized salt consisted largely of the expected 5-sulfo compound. The infrared spectrum of this compound in a Nujol mull is characterized by strong bands at 3420 (—OH), 1710 (C=O), 1255, 1230, 1188, 1120, and 1055 (—SO$_3$$^-$) cm.$^{-1}$. In contrast with the sulfocresotic acid obtained from the rearrangement of V, it couples easily with p-nitrobenzenediazonium chloride to give a purple color, does not fluoresce in aqueous solutions, and forms a rose-colored complex with ferric chloride at pH 2.15 which is destroyed if the pH is reduced to 1.72.

(14) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley & Sons, Inc., New York, 1958.