Notes A department for short papers of immediate interest.

Structure of 1-Anthraquinonesulfenic Acid

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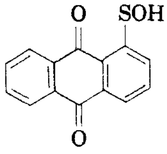
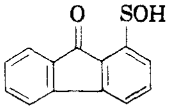
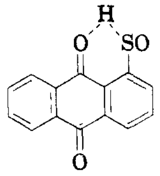
The very existence of 1-anthraquinonesulfenic acid poses a problem. This compound, first prepared by Fries[1] over 40 years ago, remains today the only known sulfenic acid[2] despite many attempts to prepare others. Even the similar 1-fluorenonesulfenic acid could not be isolated.[3]



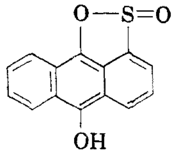


The dearth of sulfenic acids cannot be attributed to lack of synthetic methods; a search of the literature uncovered over five hundred references in which sulfenic acids were proposed as intermediates.[4]

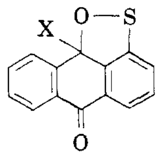
The stability of 1-anthraquinonesulfenic acid has been attributed to hydrogen bonding:[5]



Lecher and Hardy[6] account for the stability by an anthrol type structure:



A tetracyclic structure for this compound (and some of its derivatives) where X represents OH, Cl, Br, OCH_3, or OC_2H_5, could also account for the observed stability. The fourth ring would be formed by nucleophilic displacement on sulfur by the negative end of the carbonyl dipole in juxtaposition. New evidence supports the proposed structure, which is in accord with all known reactions.



Evidence for this structure was obtained by careful analysis of infrared spectra in the carbonyl region. The area of the carbonyl band has been established both theoretically and experimentally as a reliable measure of the number of carbonyl groups in a molecule.[7] There is one carbonyl group in the structure now proposed, two in the hydrogen bonded structure, and none in the anthrol structure. If the new proposal is correct, the area should be roughly half that for such compounds as 1-mercaptoanthraquinone.

EXPERIMENTAL

1-Anthraquinonesulfenic acid, the methyl ester, the methyl sulfide, the mercaptan, and the bromide were prepared from 1-anthraquinone disulfide by the methods of Fries.[1] The disulfide was prepared by reaction of 1-chloroanthraquinone with sodium sulfide and sulfur in 95% ethanol.[8] On one occasion the reaction exploded after refluxing several hours. Thereafter 50% ethanol was used as a solvent without further difficulty. The methyl ester was recovered unchanged after refluxing for six hours in absolute ethanol. Adding a few drops of conc'd hydrochloric acid caused a rapid ester interchange, and the ethyl ester was recovered in high purity.

The infrared spectrometer was a Beckman IR2 instrument equipped with a sodium chloride prism. Anhydrous alcohol-free chloroform was used as a solvent because the compounds were not soluble enough in carbon tetrachloride. Commercial chloroform stabilized by alcohol was found to react rapidly with the sulfenyl bromide. All solutions were 0.02 ± 0.001 *molar.*

The area under the carbonyl band, E, is given by

$$E = \frac{B}{Cl} \log \left(\frac{T_0}{T}\right)_\nu$$

where C is the concentration of solute in gram-moles per liter, l is the path length in centimeters, T_0 and T are the

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(1) Fries, *Ber.*, **45**, 2965 (1912).

(2) Barltrop, Hayes, and Calvin, *J. Am. Chem. Soc.*, **76**, 4348 (1954).

(3) Kharasch and Bruice, *J. Am. Chem. Soc.*, **73**, 3240 (1951).

(4) Kharasch, Paper presented at Conference on Organic Sulfur Chemistry, Indiana University, September 1951.

(5) Kharasch, Potempa, and Wehrmeister, *Chem. Revs.*, **39**, 276 (1946).

(6) Lecher and Hardy, *J. Org. Chem.*, **20**, 475 (1955).

(7) Jones, Ramsay, Keir, and Dobriner, *J. Am. Chem. Soc.*, **74**, 80 (1952); Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).

(8) German Patent 206,536, January 18, 1909.

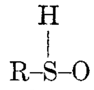
intensities of radiation transmitted by the solvent and by the solution when the spectrometer is set at frequency ν, the adsorption maximum, and B is the bandwidth in wave numbers at log $\frac{\left(\frac{T_0}{T}\right)_\nu}{2}$. Small satellite bands associated with the carbonyl band were ignored in the calculation. We thank Philip Launer for making the measurements and calculations.

DISCUSSION

The areas under the carbonyl band for four anthraquinones are:

Methyl 1-anthraquinonesulfenate	8,200
1-Anthraquinonesulfenyl bromide	7,000
1-Anthraquinonylmethyl sulfide	13,000
1-Mercaptoanthraquinone	13,000

The two compounds for which a tetracyclic structure is proposed have only about half the band area of the two that unequivocally have two carbonyl groups. The smaller area shows that one carbonyl group has disappeared. Measurements of the carbonyl band area made with the acid itself were not reproducible and were considered unreliable for the concentration of the acid was in doubt. After standing a few minutes, chloroform solutions of the acid became filled instantaneously with copious precipitate. Apparently the sulfenic acid had reacted with itself and formed a supersaturated solution. The precipitate, which melted above 300°, was probably the anhydride, which is known to form on heating a solution of the acid.[1] A tetracyclic structure for the acid is proposed by analogy.

An interesting difference between the reactions of 1-anthraquinonesulfenic acid and its salts is explained by the tetracyclic structure for the free acid. Reaction of the free acid with methyl alcohol or methyl sulfate yielded "methyl 1-anthraquinonesulfenate",[9] but reaction of the sodium or potassium salt with methyl sulfate gave exclusively methyl 1-anthraquinonyl sulfoxide. These differences in behavior had been attributed to an unlikely "pseudo" structure  $\text{R–}\overset{\overset{\text{H}}{|}}{\text{S}}\text{–O}$ for the acid.[10] The present explanation based on a gross difference in structure between the free acid and its salt accounts for the formation of different products with the same reagent more satisfactorily.

1-Anthraquinonesulfenic acid dissolves in aqueous or alcoholic solutions of sodium or potassium hydroxide, sodium carbonate, or ammonia to form solutions of characteristic color.[1] The tetracyclic structure for the acid is not incompatible with this behavior; nucleophilic attack on the sulfur would be expected to open the ring readily with formation of the sulfenic acid salt.

Failure to isolate 1-fluorenonesulfenic acid[3] does not militate against the new structure for 1-anthraquinonesulfenic acid. Divergence of the benzene rings at the carbonyl end of the fluorenone molecule results in a prohibitive bonding distance between the carbonyl oxygen and the sulfur atom. Models can be made of the structure now proposed for 1-anthraquinonesulfenic acid but not of the analogous structure for fluorenone.

A further possible method of proof of structure would be optical resolution of the sulfenic acid or a derivative. The proposed structure contains an asymmetric center; the others do not. The esters at least are probably stable enough to survive the necessary handling. The methyl ester has been refluxed in ethanol for six hours in our laboratory without change.

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The Diazotization of 3-Aminoisoquinoline[1]

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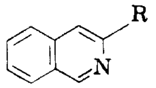
The transformation of 3-aminoisoquinoline (I) into 3-bromo- and 3-fluoro-isoquinoline was recently reported.[3,4] Diazotization of this amine and replacement of the diazo group by hydroxyl (II) and acetoxy (III) groups has now been realized.[5]



R = NH_2 (I); OH (II); $OCOCH_3$ (III); $NHCONH_2$ (IV).

In agreement with the earlier work, 3-chloroisoquinoline together with unidentified material resulted from the diazotization of the corresponding amine in dilute hydrochloric acid. Diazotization in dilute sulfuric acid, however, allowed the formation of 3-hydroxyisoquinoline in low yield together with an unidentified product in which the heterocyclic ring was apparently destroyed. This same compound was subsequently obtained upon the treatment of 3-hydroxyisoquinoline with nitrous acid.

From the combination of 3-aminoisoquinoline and isoamyl nitrite in glacial acetic acid at room

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[9] Fries and Schurmann, *Ber.*, **52**, 2182 (1919).

[10] Gutmann, *Ber.*, **41**, 1650 (1908).

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[1] A National Science Foundation Grant in support of this work is gratefully acknowledged.

[2] Texas Eastman Fellow 1955–1956.

[3] F. H. Case, *J. Org. Chem.*, **17**, 471 (1952).

[4] A. Roe and C. E. Teague, Jr., *J. Am. Chem. Soc.*, **73**, 687 (1951).

[5] An unidentified product from the decomposition of 3-isoquinoline diazonium fluoroborate was thought to be 3-hydroxyisoquinoline. It gave a strong positive ferric chloride test.[4]