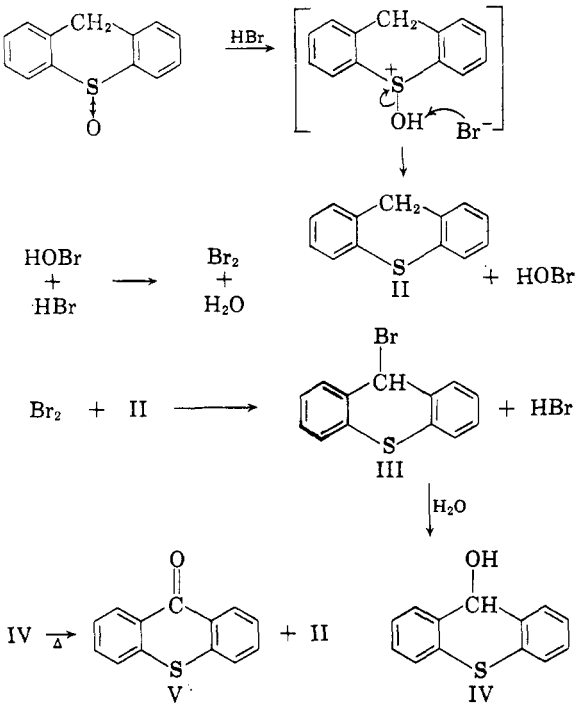

10-thiaxanthenone (V) and thiaxanthene (II). Schönberg and Mustafa[6] noted that heating of 10-thiaxanthenol in a stream of carbon dioxide gave thiaxanthene, 10-thiaxanthenone, and some dithiaxanthylene. Similar disproportionations of 10-thiaxanthenol[7-9] and 9-xanthenol[10] have been reported.

It is possible that 10-thiaxanthenol (IV) does not disproportionate and is merely oxidized to 10-thiaxanthenone (V). The thiaxanthene (II), found as a product, would thus be material that was reduced but not brominated. Hilditch and Smiles[2] in preparing 10-thiaxanthenol reported that it could be easily oxidized by atmospheric oxygen to 10-thiaxanthenone.

The reaction of either thiaxanthene-5,5-dioxide or 10-thiaxanthenone-5,5-dioxide with aqueous hydrobromic acid gave high recoveries of starting materials. The oxidation of 10-thiaxanthenone with 30% hydrogen peroxide in ethanolic solution was unsuccessful. This inability to synthesize 10-thiaxanthenone-5-oxide might be traced to the large dipole moment of 10-thiaxanthenone.[11] There have been other instances of this rather large dipole moment in 10-thiaxanthenone retarding normal carbonyl addition reactions.[12]

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EXPERIMENTAL[13]

Reaction of thiaxanthene-5-oxide with hydrobromic acid. A mixture of 4.0 g. (0.0187 mole) of thiaxanthene-5-oxide,[2] 10 ml. of water, and 20 ml. of 48% hydrobromic acid was stirred at room temperature for 2 hr. and then at gentle reflux for 1 hr. At the end of this time the pink solid was filtered, washed, and dried to give 3.5 g. of material melting over the range 105–175°.

Recrystallization from ethanol gave 1.0 g. (26%) of 10-thiaxanthenone, m.p. 215–217°, identified by a mixed melting point and a comparison of the infrared spectra. The ethanolic filtrate was poured over ice to give 1.1 g. (29%) of thiaxanthene, m.p. 126–129°, identified by the method of mixture melting points. A repeat of this experiment gave essentially the same results.

Reaction of thiaxanthene-5,5-dioxide[2] and 10-thiaxanthenone-5,5-dioxide[14] with hydrobromic acid under analogous conditions gave a 90% and 93.4% recovery of starting materials.

10-Thiaxanthenone-5-oxide (attempted). Seven grams (0.033 mole) of 10-thiaxanthenone was dissolved in 250 ml. of refluxing absolute ethanol. Ten milliliters of 30% hydrogen peroxide was added and stirring was continued at reflux for 5 hr. One hundred and seventy milliliters of the solvent was then removed by distillation and the remaining undistilled portion was poured into about 500 ml. of water which had been previously heated to 80°. Upon cooling, 6.5 g. (93%) of 10-thiaxanthenone, m.p. 215.5–217°, was separated. A mixed melting point with the starting material was undepressed. A second attempt at the preparation of 10-thiaxanthenone-5-oxide gave a 94% recovery of starting material.

Acknowledgment. Infrared analyses were obtained through the courtesy of the Institute for Atomic Research, Iowa State University, and special acknowledgment is made to Dr. V. A. Fassel and Mr. R. Kniseley for the spectra.

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N-Sulfinylamines. Effect of Structure on the Alcoholysis Reaction[1]

WALTER T. SMITH, JR., AND LOWELL D. GRINNINGER

Received August 1, 1960

In previous work,[2] the ultraviolet absorption spectra of *N*-sulfinylaniline and 4-nitro-*N*-sulfinylaniline were determined in several alcohols and the extent of any reaction was estimated from the absorption data. It was shown that, while *N*-sulfinylaniline reacted only with methyl alcohol

(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-49. Reproduction in whole or in part is permitted for any purpose of the United States Government.

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and the more acidic 2-chloroethanol, 4-nitro-*N*-sulfinylaniline reacted with all of the alcohols studied. These results suggested that the rate of reaction of *N*-sulfinylaniline with alcohols is apparently increased by the substitution of an electron withdrawing group on the aromatic nucleus. In view of a recent report[3] indicating that 4-methoxy-*N*-sulfinylaniline does not react with ethyl alcohol, we wish to report the results of our continuing study which show that a variety of *N*-sulfinylanilines react rapidly and completely with methyl alcohol.

The ultraviolet spectra of both aromatic and aliphatic *N*-sulfinylamines have been determined in anhydrous methyl alcohol to determine the reactivity of these compounds with this solvent. The spectra of aromatic *N*-sulfinylamines indicated rapid and complete reaction. The *N*-sulfinylanilines studied were: 2- and 3-nitro-; 4-bromo-; 4-iodo-; 4-methyl-; 2,4-dimethyl-; 2,6-dimethyl-; and 4-*sec*-amyl-. This study shows that even highly hindered *N*-sulfinylanilines containing electron donating groups (*e.g.*, 2,6-dimethyl-*N*-sulfinylaniline) can undergo rapid reaction. The rapid rate of reaction of all of the above compounds precluded a study of the effect of substituents on the rate of reaction.

The aliphatic *N*-sulfinyl amines showed little or no reaction with methyl alcohol. The aliphatic *N*-sulfinylamines studied were: *n*-heptyl-; *tert*-butyl-; cyclohexyl-; 2-chloroethyl-; and 3-chloropropyl-.

To account for this difference in reactivity of the aromatic and aliphatic *N*-sulfinylamines it is proposed that an increase in the base strength of the *N*-sulfinylamino group of the aliphatic *N*-sulfinylamines causes a decrease in the reaction rate. *N*-Sulfinyl-*tert*-butylamine showed no reaction with methyl alcohol. This can be attributed to both the increased basicity of the amine and to steric hindrance of the bulky *tert*-butyl group.

EXPERIMENTAL

The ultraviolet spectra were determined using either a Beckman DU spectrophotometer or a Beckman DK recording spectrophotometer. Solutions of the *N*-sulfinylamines containing about 5×10^{-3} g./l. were measured in 1- or 2-cm. cells.

When each of the *N*-sulfinylanilines discussed above was dissolved in anhydrous methyl alcohol the spectrum obtained was essentially identical with that of the parent aniline dissolved in methyl alcohol.

SPECTRA OF RNSO

R	In CH_3OH		In cyclohexane	
	log ϵ		log ϵ	
tert-Butyl	233	3.10	233	3.03
n-Heptyl	232–234	3.24	235	3.67[a]
Cyclohexyl	237–238	2.99	235	3.83[a]
$ClCH_2CH_2$—	230	3.27	233	3.55
$Cl(CH_2)_3$—	231	3.49	231	3.82

[a] In ether solution.

The spectra of the aliphatic *N*-sulfinylamines discussed are given below.

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Reaction of Styrylquinolines with Sulfhydryl Compounds[1]

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Received October 19, 1960

The observation that 4-(4-dimethylaminostyryl)-quinoline (I)[2-4] and its methiodide[5] caused regression of Lymphoma 8 tumors in rats led to a study of the fate of these compounds in the animals. It was discovered that the deep purple quaternary salt was converted into a nearly colorless compound in the small intestine.[6] An aqueous solution of the latter compound produced a spot on filter paper which became deeply colored again after exposure to air and heat, especially in the presence of a trace of base. It was suggested that the original dye was reduced to a leuco form, or that amino acids in the contents of the small intestine might be reacting with it. Glycine did not decolorize a solution of the hydrochloride of I, but cysteine and mercaptoacetic acid each did. Glutathione, cysteineamine, and *p*-thiocresol also decolorized acid solutions of I.

Gilman, Towle, and Ingham[7] were able to reduce the ethylene double bond in 4-styrylquinoline and in 2-styrylquinoline, but not in 2-(4-dimethylaminostyryl)-8-methylquinoline, by a boiling solution of *p*-thiocresol in xylene. When their method was applied to I, a white crystalline reduction product melting at approximately 110° was obtained. The same compound was obtained by reduction with hydrogen and Raney nickel at room temperature and 45 p.s.i., or by reduction with a boiling solution

(1) This research was supported by grants from the National Institutes of Health, the American Cancer Society, and Health Research, Inc. We are indebted to Dr. Charles Milligan, Dr. Harold Lyons, and Dr. Granvil Kyker for helpful suggestions. A portion of this report was presented at the Southeastern Regional Meeting in Richmond, Va., Nov. 5–7, 1959.

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