Fractions A and E were combined and recrystallized from 50 ml. of hot water, using Norit, to yield 0.90 g. (22%) of 2-amino-3,6,7-trimethyl-4(3H)pteridinone (III) which contained only a trace of the starting material. Fractions D and F were combined and recrystallized from 350 ml. of boiling water to give 0.65 g. (16%) of 2-amino-1,6,7-trimethyl-4(1H)pteridinone (II) containing only traces of I and III. The identities of these recrystallized products were corroborated by ultraviolet and infrared comparisons with authentic samples[6] of II and III.

The infrared spectra of these two products are distinctively different in the C=O and C=N regions. The 3-methyl derivative (III) has bands at 5.78, 6.07, and 6.43 μ while the 1-methyl derivative (II) has bands at 5.92 (shoulder), 6.0, 6.18, 6.25 (shoulder), and 6.51 μ.

2-Acetamido-1,6,7-trimethyl-4-(1H)pteridinone (V). 2-Amino-1,6,7 trimethyl-4-(1H)pteridinone (1.0 g., 4.9 mmoles) and 20 ml. of acetic anhydride were mixed and heated to reflux for 4 hr. The solution was then cooled well and the crystalline product was collected; yield 0.4 g. The filtrate was evaporated to dryness. The residue was slurried with ether and the solid product was collected; yield 0.5 g. (combined yield 75%).

The two products were combined and recrystallized from 7 ml. of ethanol; yield 0.45 g. (37%); m.p. 171–172°. R_f 0.90 (0.5% sodium carbonate); R_f 0.79 (3% ammonium chloride). Ultraviolet absorption spectra in 0.1N sodium hydroxide 262 mμ (ϵ 15,100), 338 mμ (ϵ 12,700); methanol λ_{max} 230 mμ (ϵ 15,800), 278 mμ (ϵ 20,800), 325 mμ (ϵ 13,300).

Anal. Calcd. for $C_{11}H_{13}N_5O_2$ (247)· C, 53.4; H, 5.3; N, 28.3. Found: C, 53.3; H, 5.3; N, 28.3.

Acid hydrolysis of 2-acetamido-1,6,7-trimethyl-4-(1H)pteridinone (V). 2-Acetamido-1,6,7-trimethyl-4-(1H)-pteridinone (100 mg., 0.4 mmole) was dissolved in 100 ml. of 0.1N hydrochloric acid and heated on the steam bath for 20 min. This was cooled overnight and the crystalline product was collected; yield 30 mg. (36%). Infrared absorption spectra and chromatography showed this to be 1,6,7-trimethyl-2,4-(1H,3H)pteridinedione.[6]

Anal. Calcd. for $C_9H_{10}N_4O_2$ (206): C, 52.4; H, 4.9; N, 27.2. Found: C, 52.3; H, 5.1; N, 26.9.

Chromatographic and spectroscopic examination of the filtrate indicated that no other product was present.

2-Acetamido-4-hydroxy-6,7-dimethylpteridine. 2-Amino-4-hydroxy-6,7-dimethylpteridine (1.0 g., 5.2 mmoles) and 40 ml. of acetic anhydride were mixed and heated to reflux for 4.5 hr. After cooling for several hours the crystalline product was collected and washed with ether; yield 0.9 g. (75%).

A portion (0.5 g.) of this material was recrystallized once from 10 ml. of water and a second time from 15 ml. of water; yield 0.4 g.; light yellow needle-like crystals; m.p., placed in a bath at 250° it melts and resolidifies and melts at 298–299° dec. R_f 0.71 (0.5% sodium carbonate), R_f 0.62 (3% ammonium chloride). Ultraviolet absorption spectra in 0.1N sodium hydroxide, λ_{max} 252 mμ (ϵ 29,400), 342 mμ (ϵ 9700); 0.1N HCl, λ_{max} 280 mμ (ϵ 17,000), 331 mμ (ϵ 10,700).

Anal. Calcd. for $C_{10}H_{11}N_5O_2.6H_2O$: C, 35.2; H, 6.8; N, 20.5; H_2O, 31.7. Found: C, 35.3; H, 7.1; N, 20.6; H_2O (Karl Fischer) 35.2.

2-(N-Methylacetamido)-4-hydroxy-6,7-dimethylpteridine. 2-Methylamino-4-hydroxy-6,7-dimethylpteridine (0.65 g., 3.2 mmoles) and 15 ml. of acetic anhydride were mixed and heated to reflux for 3 hr. The solution was filtered to remove a trace of insoluble material and cooled overnight; yield of crystalline product 0.49 g. This was recrystallized from 20 ml. of ethanol; yield 0.28 g. (36%); m.p. 222–225°; R_f 0.88 (0.5% sodium carbonate), 0.74 (3% ammonium chloride); ultraviolet absorption spectra in 0.1N hydrochloric acid, λ_{max} 280 m, (ϵ 12,100), 327 mμ (ϵ 8000); methanol, λ_{max} 279 mμ (ϵ 11,600), 330 mμ (ϵ 7900); 0.1M sodium tetraborate, 248 mμ (ϵ 21,800), 333 mμ (ϵ 8000).

Anal. Calcd. for $C_{11}H_{13}N_5O_2$ (247): C, 53.4; H, 5.3; N, 28.3. Found: C, 53.5; H, 5.4; N, 28.4.

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Reductive Halogenation of Thiaxanthene 5-Oxide

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During an investigation of the orientation of monosubstituents in the 10-thiaxanthenone[1] nucleus, we had occasion to allow aqueous hydrobromic acid to react with thiaxanthene-5-oxide (I) in an attempt to halogenate reductively thiaxanthene-5-oxide. It was found that treatment of I with a 33% solution of hydrobromic acid gave a 26% yield of 10-thiaxanthenone (V) and a 29% yield of thiaxanthene (II).

Hilditch and Smiles[2] originally studied the intramolecular acid-induced rearrangements of thiaxanthene-5-oxide and 10-thiaxanthenol compounds. These workers found, for example, that the reaction of alcoholic hydrogen chloride on thiaxanthene-5-oxide afforded a colored thiaxanthylium salt which slowly changed to a colorless 10-chlorothiaxanthene. By treating thiaxanthene-5-oxide with hydrobromic acid, we isolated almost equimolar quantities of II and V.

A possible mechanistic interpretation of the reaction of hydrobromic acid on thiaxanthene-5-oxide is presented below.

Initial protonation of the sulfoxide grouping in I with subsequent reduction would form II and one molar equivalent of bromine (or hypobromous acid). The reductive halogenation of other systems in which the sulfoxide grouping is reduced to a sulfide have been reported.[3–5] An electrophilic attack by bromine on II would then yield the unstable 10-bromothiaxanthene (III) which could readily hydrolyze under the conditions of the experiment giving 10-thiaxanthenol (IV). Disproportionation of IV would afford the observed products,

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[1] The numbering and nomenclature is that recommended by *Chemical Abstracts*.

[2] T. P. Hilditch and S. Smiles, *J. Chem. Soc.*, **99**, 145 (1911).

[3] H. J. Page and S. Smiles, *J. Chem. Soc.*, **97**, 1112 (1910).

[4] H. Gilman and J. Eisch, *J. Am. Chem. Soc.*, **77**, 3862 (1955).

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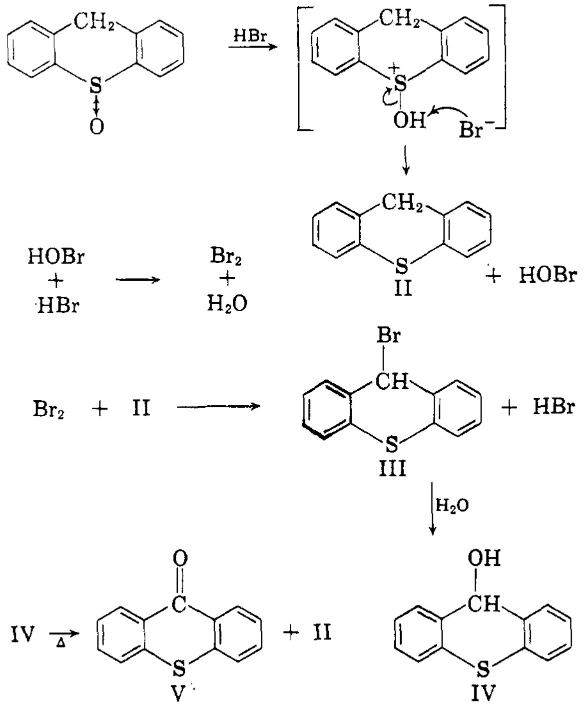

10-thiaxanthenone (V) and thiaxanthene (II). Schönberg and Mustafa[6] noted that heating of 10-thiaxanthenol in a stream of carbon dioxide gave thiaxanthene, 10-thiaxanthenone, and some dithiaxanthylene. Similar disproportionations of 10-thiaxanthenol[7–9] and 9-xanthenol[10] have been reported.

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]

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.

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

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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

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