Ion Radicals. XXXIV. Preparation of Phenoxathiin Cation Radical Perchlorate. Formation and Reactions of *S*-Iminophenoxathiin (Phenoxathiin Sulfilimine)[1,2]

Serugudi R. Mani and Henry J. Shine*

Department of Chemistry, Texas Tech University, Lubbock, Texas 79409

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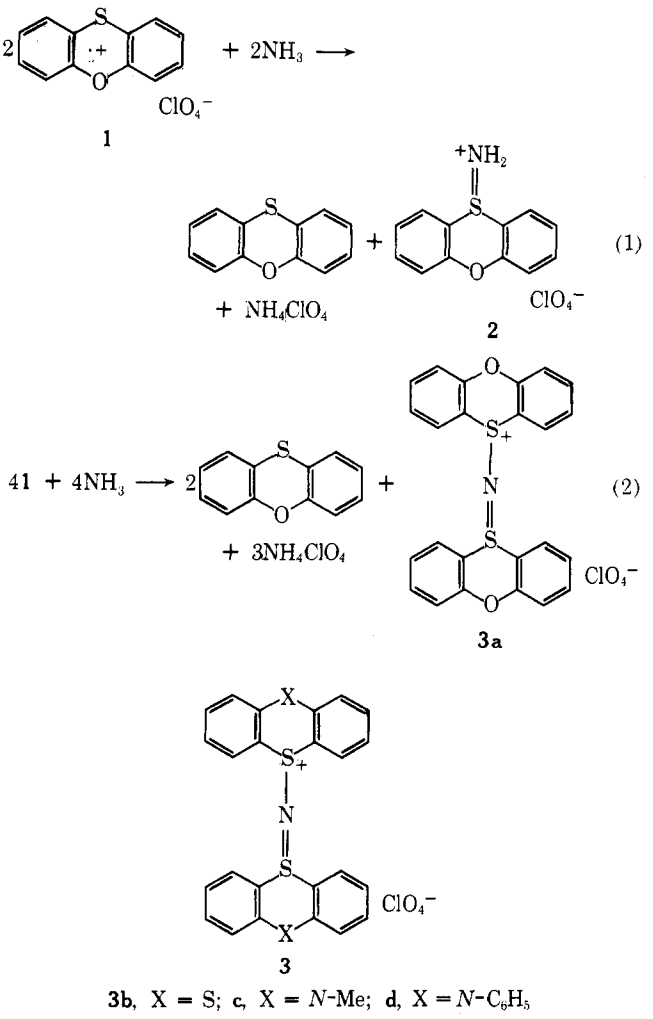
A method of preparing crystalline phenoxathiin cation radical perchlorate (1) by oxidation of phenoxathiin with perchloric acid in benzene–acetic anhydride is reported. Reaction of 1 with ammonia was controlled so as to give either phenoxathiin sulfilimine perchlorate (2) or the dimeric product 5,5-dihydro-5-(5-phenoxathiiniumylimino)phenoxathiin perchlorate (3a). Deprotonation of 2 gave phenoxathiin sulfilimine (4a). Reaction of 4a with *p*-toluenesulfonyl chloride gave the known tosyl derivative, obtainable also by reaction of phenoxathiin with chloramine-T. Methylation of 4a led to the same product obtainable by direct reaction of 1 with methylamine, i.e., 5,5-dihydro-5(methylimino)phenoxathiin perchlorate (6). Reaction of 4a with 1 led to 3a. Reaction of 4a with thianthrene cation radical perchlorate led, similarly, to 5,5-dihydro-5-(5-thianthreniumylimino)phenoxathiin perchlorate (9).

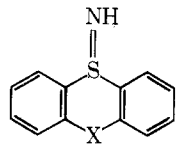
Work with the phenoxathiin cation radical has been confined in the past for the most part to characterization by ESR spectroscopy. For the most part, also, the cation radical has been made by oxidation of phenoxathiin with concentrated sulfuric acid, in which medium ESR characterization has been carried out.[3-6] The cation radical has also been made from both phenoxathiin and phenoxathiin 5-oxide by reaction with a variety of Lewis acids ($AlCl_3$, $FeCl_3$, $SbCl_5$, etc.) in haloalkane solvents for characterization by absorption spectroscopy.[7] No definitive study of the chemistry of the phenoxathiin cation radical has been reported. Ten years ago one of us[8] showed that the conversion of phenoxathiin 5-oxide into the cation radical in sulfuric acid solution was accompanied by hydroxylation reactions. The cation radical of 3-hydroxyphenoxathiin was identified by ESR, and 3-hydroxyphenoxathiin 5-oxide was isolated. Subsequently, Cauquis reported in detail on the electrochemistry of phenoxathiin, and deduced[9] that reaction of either the cation radical or the dication, formed by disproportionation of the cation radical, with water in the solvent gave the 5-oxide.[9] Phenoxathiin can be oxidized with iodine–silver perchlorate, but separation of the cation radical perchlorate (1) from the precipitated mixture of 1 and silver iodide was, in our hands, always accompanied by considerable decomposition of the cation radical. Oxidation of phenoxathiin in carbon tetrachloride with perchloric acid–acetic anhydride in the way which is so successful with thianthrene[10] was also not successful, since under those conditions 1 would not crystallize out. We are now able to make crystalline phenoxathiin cation radical perchlorate (1) quite easily, with close to 100% cation radical content, by controlled oxidation of phenoxathiin in benzene with 70% perchloric acid–acetic anhydride. This has allowed us to begin studying the chemistry of the cation radical in homogeneous solution.

An initial pleasing development is that, by controlled reaction of 1 with ammonia, we have been able to prepare not only the anticipated dimeric compound, 5,5-dihydro-5-(5-phenoxathiiniumylimino)phenoxathiin perchlorate (3a), but also phenoxathiin sulfilimine perchlorate (2). These compounds are obtained according to the stoichiometry shown in eq 1 and 2. Phenoxathiin was isolated in each case, as well as small amounts of phenoxathiin 5-oxide. In previous work with thianthrene cation radical,[11] and the cation radicals of *N*-methyl- and *N*-phenylphenothiazine,[2] it was possible to obtain the dimeric molecules (3b, 3c, and 3d) analogous to 3a. We now find that if ammonia is streamed very vigorously into a homogeneous solution of 1 in acetonitrile, the product is 2. If in contrast ammonia is bubbled gently into a suspension of 1 in acetonitrile, the product is 3a. Appropriate adjustment of conditions leads to a mixture of 2 and 3a.



3b, X = S; c, X = *N*-Me; d, X = *N*-C_6H_5

The perchlorate 2 is readily deprotonated. We have been able to prepare the hitherto unreported phenoxathiin sulfilimine (4a) and to study some of its reactions. The sulfilimines 4b and 4c have been prepared[12] by Tamura's mesitylhydroxylamine method,[13] whereas only the mesitylsulfonate of 4a was reported.[12] The sulfilimine 4a, mp 66–67°, is spectroscopically very similar to phenoxathiin 5-oxide.



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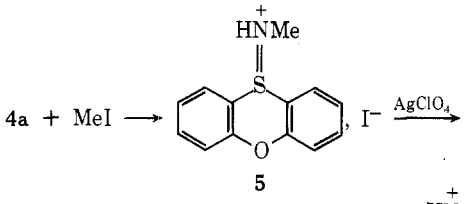
4a, X = O; b, X = S; X = *N*-Me

Reaction of 4a with methyl iodide led to 5,5-dihydro-5-(methylimino)phenoxathiin iodide (5), which was converted into the corresponding perchlorate 6 (eq 3). The latter was also prepared by reaction of methylamine with 1 (eq 4), a type of reaction reported earlier in the thianthrene[14]



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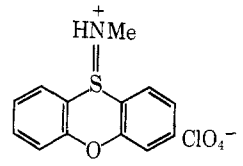
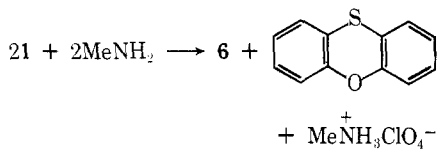


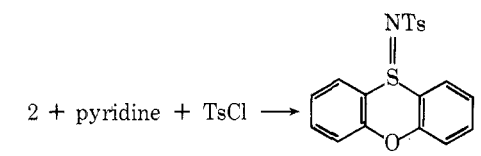
6 (3)



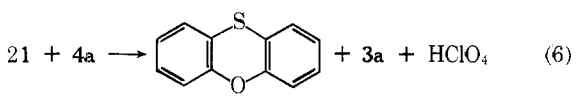
(4)

(*tert*-butylamine) and phenothiazine (various alkylamines) series.[2]

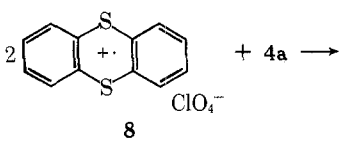
The tosyl derivative (7) of 4a has been prepared by reaction of chloramine-T with phenoxathiin.[15] Reaction of 4a (generated from treating 2 with pyridine) with tosyl chloride also gave 7, allowing us to thus characterize 4a via a known derivative (eq 5).



7 (5)



(6)



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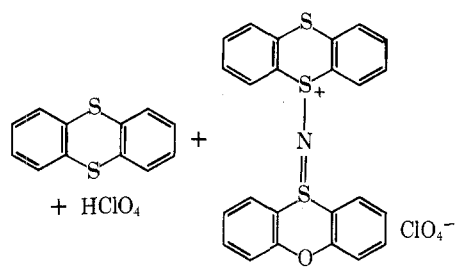

9 (7)

Finally, we have been able to prepare the dimeric compound 3a by reaction of 4a with the cation radical 1 (eq 6), and we carried out the analogous reaction of the thianthrene cation radical (8) with 4a to obtain the mixed dimer 9 (eq 7). These last two reactions obviously are related to the formation of dimeric products in the reactions of ammonia with organosulfur cation radicals[2,11] and we hope to make use of 4a in studying the mechanism of these reactions.

Experimental Section

Acetonitrile was Eastman Spectrograde. All column chromatography was performed with Merck silica gel no. 7733, 10-30 ASTM mesh. Phenoxathiin was obtained from Eastman Kodak, mp 55–57°, and was used without further purification.

Phenoxathiin cation radical perchlorate (1) was prepared by a modification of the method used for preparing thianthrene cation radical perchlorate.[10] To a solution of 500 mg (2.49 mmol) of phenoxathiin in 30 ml of dry benzene was added 1 ml of 70% perchloric acid. The acid became blue and remained undissolved in the benzene. The mixture was swirled for 10 min and acetic anhydride was added dropwise while the mixture was shaken continuously. Purple crystals of 1 began to deposit. The small purple acidic layer dissolved on the addition of acetic anhydride and the crystallization of 1 continued. The mixture was allowed to stand for 4 hr and was filtered. The crystalline 1 was washed with dry benzene until the washings were colorless, giving 501 mg (1.67 mmol, 67%) of 1 after drying under vacuum. The purity of the 1, which was determined iodimetrically, was always close to 100%.

Reactions of 1 with Ammonia. Formation of Phenoxathiin Sulfilimine Perchlorate (5,5-Dihydro-5-iminophenoxathiin Perchlorate, 2) and 5,5-Dihydro-5-(5-phenoxathiiniumylimino)phenoxathiin Perchlorate (3a). The three experiments which follow are examples of the many runs which were made seeking to understand the conditions under which 2 and 3a were formed.

A. Ammonia gas was bubbled through a suspension of 2.04 g (7.78 mmol) of 1 in 40 ml of acetonitrile. The solution turned yellow within 15 sec. The ammonia stream was continued for 5 min, and stirring for a further 15 min. The acetonitrile was removed on a rotary evaporator, and the residue was taken up in a small amount of acetone and chromatographed on a column of silica gel. Elution with benzene gave 663 mg (3.31 mmol, 49%) of phenoxathiin, and elution with chloroform gave 52 mg (0.255 mmol, 3.81%) of phenoxathiin 5-oxide. Elution with acetone gave 1.70 g (3.3 mmol, 49%) of **3a**, mp 235–238° dec (from aqueous ethanol), λ_{max} (MeCN) (10^{-4} ϵ) 314 nm (1.43), 272 (1.03), and 239 (4.48).

Anal. Calcd for $C_{24}H_{16}NS_2ClO_6$: C, 56.1; H, 3.14; N, 2.73; S, 12.5; Cl, 6.89. Found: C, 56.1; H, 3.14; N, 2.98; S, 12.7; Cl, 6.59.

B. A suspension of 1.5 g (5.0 mmol) of 1 in 30 ml of acetonitrile was stirred for 5 min after which ammonia gas was bubbled in until the purple color disappeared (within 20 sec). After stirring a further 15 min, the solution was worked up as before, giving 487 mg (2.49 mmol, 50%) of phenoxathiin and 22 mg (0.1 mmol) of phenoxathiin 5-oxide. The acetone eluate from the silica column was evaporated to give a mixture of **3a** and phenoxathiin sulfilimine perchlorate (2). The mixture was triturated with acetone to remove the more soluble 2, which was then precipitated from solution by adding ether. The two solids were crystallized to give 25 (0.05 mmol, 1%) of **3a**, mp 240–241° dec, from aqueous ethanol, and 690 mg (2.18 mmol, 44%) of 2, mp 190–191° dec, from aqueous methanol: λ_{max} (MeCN) (10^{-3} ϵ) 301 nm (5.72), 280 (3.55), and 225 (25.2).[1]H NMR (Me_2SO-d_6) δ 9.1–8.2 (m, 2 H, aromatic) and 7.75 (m, 6 H, aromatic). The NH protons could not be detected in Me_2SO solvent, presumably because of exchange, but gave rise to a 3180-cm^{-1} band in the infrared.

Anal. Calcd for $C_{12}H_{10}NSClO_5$ (2): C, 45.6; H, 3.19; N, 4.44; S, 10.2; Cl, 11.2. Found: C, 45.7, H, 3.43; N, 4.45; S, 9.85; Cl, 11.4.

C. A suspension of 1.09 g (3.63 mmol) of 1 in 40 ml of acetonitrile was stirred until all of the 1 had dissolved (20 min). Into this solution ammonia gas was introduced as a strong blast, and the solution became yellow immediately. Work-up gave 356 mg (1.77 mmol, 49%) of phenoxathin, 50.2 mg (0.232 mmol, 6.4%) of phenoxathiin 5-oxide, and 504 mg (1.60 mmol, 44%) of 2, mp 190–192° dec.

Deprotonation of 2. Formation of Phenoxathiin Sulfilimine (5,5-Dihydro-5-iminophenoxathiin, 4a). A. About 0.5 ml of triethylamine was added to a solution of 102 mg (0.322 mmol) of 2 in

5 ml of chloroform. After 10 min the solvent was removed, and the solid residue was washed well with water and crystallized from ether–petroleum ether (bp 30–60°), giving 66 mg (0.283 mmol, 88%) of **4a**: mp 66–67° dec; λ_{max} (MeCN) (10^{-3} ϵ) 298 nm (2.35), 290 (2.46), and 239 (28.2); ^{1}H NMR ($CDCl_3$) δ 7.95–7.8 (m, 2 H, aromatic), 7.3 (m, 6 H, aromatic), and 1.5 (s, 1 H, NH). The NH band was at 3200 cm^{-1}.

Anal. Calcd for $C_{12}H_9NOS \cdot H_2O$: C, 61.8; H, 4.75; N, 6.00; S, 13.7. Found: C, 61.9; H, 4.81; N, 5.86; S, 13.8.

B. Compound **4a** was also obtained by adding 10% sodium hydroxide solution to a suspension of **2** in ethanol and working up as before.

Methylation of 4a. Formation of 5,5-Dihydro-5-(methylimino)phenoxathiin Iodide (5). To a solution of 110 mg (0.511 mmol) of **4a** in ether was added 2 ml of methyl iodide. Pale yellow crystals of **5** deposited during 15 min of stirring, giving 149 mg (0.42 mmol, 81.5%), mp 121–122° dec.

Conversion of 5 into 5,5-Dihydro-5-(methylimino)phenoxathiin Perchlorate (6). An excess of silver perchlorate was added to a stirred solution of 100 mg (0.28 mmol) of **5** in acetonitrile. After 10 min the precipitated silver iodide was filtered, the solution was evaporated, and the residue was washed with water and crystallized from aqueous methanol, giving 88 mg (0.27 mmol, 96%) of **6**, mp 160–162° dec, mmp with authentic **6** (see below) 159–160° dec.

Reaction of 1 with Methylamine. Formation of 6. A suspension of 1.02 g (3.41 mmol) of **1** in acetonitrile was stirred for 10 min and methylamine gas was bubbled in until the purple color disappeared. Reaction was slower than with ammonia. Work-up and chromatography, as earlier, gave 457 mg (2.28 mmol, 67%) of phenoxathiin, 31 mg (0.144 mmol, 4%) of phenoxathiin 5-oxide, and 143 mg (0.433 mmol, 13%) of **6**, mp 158–159° dec, from aqueous acetone: λ_{max} (MeCN) (10^{-3} ϵ) 302 nm (5.43), 280 (3.54), and 233 (20.0); ^{1}H NMR (Me_2SO-d_6) δ 8.0–8.2 (m, 2 H, aromatic), 7.7 (m, 6 H, aromatic), and 2.2 (s, 3 H, Me). The NH proton could not be detected in Me_2SO solvent, presumably because of exchange, but gave rise to a 3280-cm^{-1} band in the infrared.

Anal. Calcd for $C_{13}H_{12}NSClO_5$: C, 47.3; H, 3.67; N, 4.25; S, 9.72; Cl, 10.7. Found: C, 47.3; H, 3.42; N, 4.39; S, 9.92; Cl, 10.7.

Reaction of 4a with Tosyl Chloride. Formation of *N*-Tosyl Phenoxathiin Sulfilimine (7). A suspension of 53 mg (0.17 mmol) of **2** in ether was deprotonated by addition of 1 ml of pyridine. Tosyl chloride (42 mg, 0.22 mmol) was added, and after 1 hr of stirring the solvent was removed. The residue was washed well with water and crystallized from aqueous ethanol to give 26 mg (0.07 mmol, 41%) of **7**, mp 166–168°, infrared identical with that of an authentic sample, mp 168–170°, made by reaction of phenoxathiin with chloramine-T according to method B of Tsujihara et al.[15]

Reaction of 1 with 4a. Preparation of 3a. A suspension of 139 mg (0.463 mmol) of **1** in 10 ml of acetonitrile was stirred for 10 min and a solution of 51 mg (0.237 mmol) of **4a** in 3 ml of acetronitrile was added. The disappearance of the color of **1** was quite slow. After 20 min the pale purple color was discharged by adding 1 drop of water. The solution was stirred with a small amount of sodium carbonate (to neutralize perchloric acid) and evaporated. Column chromatography gave 47.6 mg (0.237 mmol, 51%) of phenoxathiin (benzene), 19 mg (0.09 mmol) of phenoxathiin 5-oxide (chloroform), and 101 mg (0.196 mmol, 42%) of **3a** (acetone), mp 236–238° dec, from aqueous methanol.

Reaction of 4a with Thianthrene Cation Radical Perchlorate (8). Formation of 5,5-Dihydro-5-(5-thianthreniumylimino)phenoxathiin Perchlorate (9). Reaction was carried out as with the reaction of **4a** with **1**, using 52 mg (0.165 mmol) of **8** and 19.5 mg (0.091 mmol) of **4a**. After stirring with sodium carbonate the solution was poured into water and the precipitate was taken up in acetone and precipitated with ether. Crystallization from aqueous methanol gave 41 mg (0.077 mmol, 47%) of **9**, mp 208–210° dec.

Anal. Calcd for $C_{24}H_{16}NS_3ClO_5$: C, 54.4; H, 3.04; N, 2.64; S, 18.2; Cl, 6.69. Found: C, 54.1; H, 3.02; N, 2.47; S, 18.4; Cl, 6.56.

The acetone–ether filtrate from the precipitation of **9** was evaporated, and the residue was taken up in chloroform and subjected to TLC on silica gel with benzene development, giving 19.5 mg (0.09 mmol, 55%) of thianthrene and 7 mg (0.03 mmol) of thianthrene 5-oxide.

Registry No.—**1**, 55975-63-8; **2**, 55975-55-8; **3a**, 55975-57-0; **4a**, 54002-03-8; **5**, 55975-58-1; **6**, 55975-60-5; **7**, 54462-91-8; **8**, 35787-71-4; **9**, 55975-62-7; phenoxathiin, 262-20-4; methyl iodide, 74-88-4; silver perchlorate, 7783-93-9; methylamine, 74-89-5; tosyl chloride, 98-59-9.

References and Notes

(1) Supported by Grant GP-25989X from the National Science Foundation, and Grant D-028 from the Robert A. Welch Foundation.
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Dimethyl Sulfoxide–Trifluoroacetic Anhydride. A New and Efficient Reagent for the Preparation of Iminosulfuranes[1]

Ashok K. Sharma, Thomas Ku, Arthur D. Dawson, and Daniel Swern*

Fels Research Institute and Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122

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The scope and limitations are described of the recently reported dimethyl sulfoxide–trifluoroacetic anhydride (DMSO–TFAA) reagent for the preparation of iminosulfuranes. Yields range from 40 to 90% with aryl amines, including ortho-substituted ones, aryl amides, aryl sulfonamides, and urea. Previously uncharacterized iminosulfuranes have been prepared from sulfanilamide (mono- and diylides) and sulfadiazine. Relatively basic amines (cyclohexylamine, benzylamine), *o*- and *p*-diaminobenzenes, anthranilamide, ansidine, and 2- and 4-aminopyridines failed to yield isolable iminosulfuranes.

This paper defines the scope and limitations of the recently reported dimethyl sulfoxide–trifluoroacetic anhydride (DMSO–TFAA) reagent for the efficient preparation of iminosulfuranes (sulfilimines) and compares the reagent's utility with that of other "activated" DMSO reagents. In our preliminary communications[1a] only a few iminosulfuranes were reported and no information was then available on the limitations of the new reagent.