25-9; *cis*-5-(2-isopropyl-1,3-dioxanyl)acetic acid, 61523-26-0; *trans*-5-(2-isopropyl-1,3-dioxanyl)acetic acid, 61523-27-1; *cis*-2-isopropyl-5-(2-hydroxyethyl)-1,3-dioxane, 61523-28-2; *trans*-2-isopropyl-5-(2-hydroxyethyl)-1,3-dioxane, 61523-29-3; *cis*-2-isopropyl-5-(2-hydroxyethyl)-1,3-dioxane tosylate, 61523-30-6; *trans*-2-isopropyl-5-(2-hydroxyethyl)-1,3-dioxane tosylate, 61523-31-7; dimethyl-5-(*cis*-2-isopropyl-1,3-dioxanyl)-2-ethylsulfonium *p*-toluenesulfonate, 61523-32-8; dimethyl-5-(*trans*-2-isopropyl-1,3-dioxanyl)-2-ethylsulfonium *p*-toluenesulfonate, 61523-33-9; *cis*-2-isopropyl-5-methoxy-1,3-dioxane, 28808-16-4; *trans*-2-isopropyl-5-methoxy-1,3-dioxane, 36094-12-9; *cis*-2-isopropyl-5-(methoxymethyl)-1,3-dioxane, 28808-25-5; *trans*-2-isopropyl-5-(methoxymethyl)-1,3-dioxane, 58619-95-7; *cis*-2-isopropyl-5-(methylsulfinyl)-1,3-dioxane, 40245-31-6; *trans*-2-isopropyl-5-(methylsulfinyl)-1,3-dioxane, 40245-32-7; *cis*-2-isopropyl-5-(methylsulfonyl)-1,3-dioxane, 40245-33-8; *trans*-2-isopropyl-5-(methylsulfonyl)-1,3-dioxane, 40245-34-9; dimethyl-5-(*cis*-2-isopropyl-1,3-dioxanyl)sulfonium *p*-toluenesulfonate, 58620-17-0; dimethyl-5-(*trans*-2-isopropyl-1,3-dioxanyl)sulfonium *p*-toluenesulfonate, 58620-19-2.

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Ion Radicals. 38. Reactions of Phenoxathiin and Thianthrene Cation Radicals with Alkyl- and Dialkylamines[1,2]

B. K. Bandlish,[3] S. R. Mani,[4] and H. J. Shine*

Department of Chemistry, Texas Tech University, Lubbock, Texas 97409

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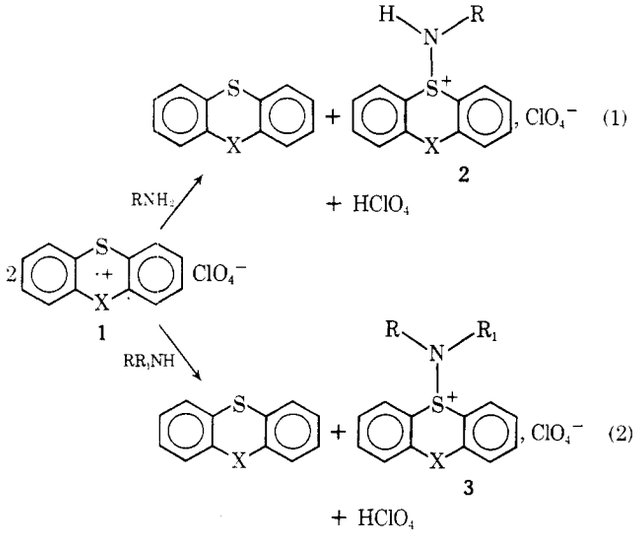
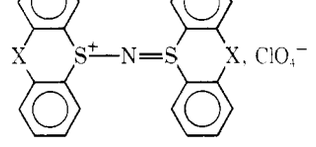
Phenoxathiin cation radical perchlorate (**1c**) reacted with alkylamines to form protonated *N*-alkylsulfilimine perchlorates (**2c**) and with dialkylamines to form *N,N*-dialkylaminosulfonium perchlorates (**3c**). Analogous reactions were obtained with thianthrene cation radical (**1d**), giving products **2d** and **3d**. Reaction of **1d** with alkylamines also gave in every case some 5,5-dihydro-5-(5-thianthreniumylimino)thianthrene perchlorate (**4d**). Only in one case, reaction with propylamine, did **1c** give the analogous **4c**. The salts **2c** were deprotonated to give the *N*-alkylsulfilimines (**5c** and **5d**) and these were methylated with methyl iodide giving *N*-alkyl-*N*-methylaminosulfonium iodides (**6c** and **6d**). Most of the sulfonium salts (**6c** and **6d**) were converted into the corresponding perchlorates (**3c** and **3d**) which were also obtained directly by reactions of **1c** and **1d** with *N*-alkylmethylamines.

It was shown recently that the cation radical perchlorates of 10-methyl-(**1a**, X = *N*-Me) and 10-phenylphenothiazine (**1b**, X = *N*-C_6H_5) react with alkyl- and dialkylamines according to eq 1 and 2.[5] We have found, subsequently, that



phenoxathiin cation radical perchlorate (**1c**, X = O) undergoes analogous reactions. Further, it was reported by Kim and Shine[6] that thianthrene cation radical perchlorate (**1d**, X = S) did not react with alkylamines according to eq 1 except in the case of *tert*-butylamine. That is, reaction of **1d** with ethyl-, propyl-, and cyclohexylamine was reported to give the dimeric product (**4d**, X = S) instead of products **2d** (R = Et, Pr, C_6H_{11}). We have found now that this report is not correct.



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4c, X = O; 4d, X = S

Reaction of alkylamines with **1d** (eq 1) is not as facile as with the analogues **1a–c**, but it does give the sulfilimine salts **2d** (X = S) although in poor yields. At the same time the dimer byproduct **4d** is formed but not exclusively as was reported earlier.[6]

Separation of products **2d** from the other products of reaction is tedious and apparently was not achieved earlier. Thus, the reactions of eq 1 and 2 are general for the series X = S, O, *N*-Me, *N*-C_6H_5, but yields vary from case to case. Data for reactions of **1c** and **1d** are given in Tables I and II. These data show that the dimer **4d** was obtained from all reactions of **1d** with alkylamines, whereas the dimer **4c** was obtained only in reaction of **1c** with propylamine. Small amounts of phenoxathiin 5-oxide and thianthrene 5-oxide were also obtained presumably from reaction of the cation radicals with water in the reagents or solvents.[7]

Deprotonation of the products **2c** and **2d** was carried out

Table I. Products of Reaction of Phenoxathiin Cation Radical Perchlorate (1c) and Thianthrene Cation Radical Perchlorate (1d) with Alkylamines in Acetonitrile

Cation radical	R in RNH_2	Registry no.	% 2[a]	Parent[b] %[c]	5-Oxide[b] %[c]	% 4[d]	Mp, °C 2
1c	Pr	107-10-8	41	47	1	6	Oil
1c	*t*-Bu	75-64-9	46	44	7		203–204
1c	C_6H_{11}	108-91-8	35	54	8		148–149
1c	$C_6H_5CH_2$	100-46-9	20	63	10		145–146
1d	Me	74-89-5	15	66	3	8	120–122
1d	Et	75-04-7	20	61	4	14	117–118
1d	Pr		21	60	5	5	Oil
1d	C_6H_{11}		19	62	6	3	Oil
1d	$C_6H_5CH_2$		18	65		8	143–144

[a] % yield means the amount of cation radical converted into product. The maximum yield of **2** is 50% (eq 1). [b] Phenoxathiin from **1c**, thianthrene from **1d**. [c] Equal amounts of parent and 5-oxide are obtained from the reaction of a cation radical with water. [d] % yield means the amount of cation radical converted into **4**.

Table II. Products of Reaction of Phenoxathiin Cation Radical Perchlorate (1c) and Thianthrene Cation Radical Perchlorate (1d) with Dialkylamines in Acetonitrile

Cation radical	R	R_1	Registry no.	% 3[a]	Parent[b] %[c]	5-Oxide[b] %[c]	Mp, °C 3
1c	Me	Me	124-40-3	7	73	8	151–152
1c	*i*-Pr	*i*-Pr	108-18-9	13	63	8	180–181
1c	Pr	Me	627-35-0	8	65	8	139–140
1c	C_6H_{11}	Me	100-60-7	11	62	8	200–201
1c	$C_6H_5CH_2$	Me	103-67-3	17	70	8	173–174
1c	$C_6H_5CH_2$	$C_6H_5CH_2$	103-49-1	27	61	11	145–146
1d	Pr	Me		22	70	10	129–131
1d	C_6H_{11}	Me		20	68	5	172–174
1d	$C_6H_5CH_2$	Me		32	67	6	154–156

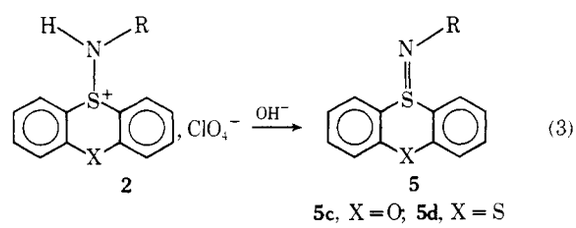
[a] % yield means the amount of cation radical converted into product. The maximum yield of **3** is 50% (eq 1). [b] Phenoxathiin from **1c**, thianthrene from **1d**. [c] Equal amounts of parent and 5-oxide are obtained from the reaction of a cation radical with water.[7]

Table III. List of Sulfilimines (5) Obtained by Deprotonation of Sulfonium Perchlorates (2), Their Adducts (6) with Methyl Iodide, and the Perchlorates (3) Obtained from 6 by Exchange with $AgClO_4$

Sulfilimine	R in 5	% yield of 5	Mp, °C of 5	% yield of 6	Mp, °C of 6	% yield of 3	Mp, °C of 3[a]
5c	Pr	87	Oil	97	132–133	86	138–139
5c	*t*-Bu	95	74–75	84	168–169	80	183–184
5c	C_6H_{11}	100	172–173	93	142–143	90	201–203
5c	$C_6H_5CH_2$	100	143–144	100	72–75	87	172–173
5d	Me	95	44–46	93	110–112	93	139–141[b]
5d	Pr	96	Oil	87	107–109	94	128–130
5d	C_6H_{11}	98	119–120	84	122–124	98	170–172
5d	$C_6H_5CH_2$	97	Oil	56	130–132	95	154–156

[a] Cf. melting points of **3c** and **3d** obtained directly, Table II. [b] Product by direct reaction, mp 139–140 °C.[6]

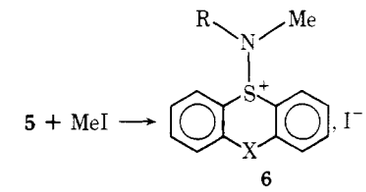
in most cases, leading to the free sulfilimines **5c** and **5d** (eq 3). Data for these reactions are given in Table III. Methylation



2 **5**

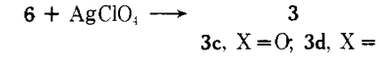
5c, X = O; **5d**, X = S (3)

of the sulfilimines with methyl iodide in dry ether gave the *N*-methylsulfonium iodides **6c** and **6d** (eq 4) in good yields, and conversion of the iodides to perchlorates was carried out (eq 5) in all cases. Thus, the compounds **3c** and **3d** (R_1 = Me)



6

6c, X = O; **6d**, X = S (4)



3c, X = O; **3d**, X = S (5)

were obtained both directly (eq 2) and indirectly (eq 5). Data for reactions 4 and 5 are also given in Table III.

The way in which the dimeric products **4c** and **4d** are formed in reactions of **1c** with propylamine and **1d** with all of the alkylamines is not known. Attempts to obtain **4d** by re-

Table IV. Absorption and NMR Spectra of Products: Sulfilimines (5), Protonated Sulfilimines (2) and Dialkylsulfonium Perchlorates (3), and Dialkylsulfonium Iodides (6)

Compd	R	R_1	λ_{max}, nm (10^{-4} ϵ)[a]	^{1}H NMR, δ (J, Hz)	Solvent
2c	Pr			8.17 (d of d, J = 7, J = unres, 2 H)[b] 8.03–7.50 (m, 6 H, arom), 6.30 (s, 1 H, –NH), 2.47 (t, 2 H, –C**H**$_2$CH$_2$CH$_3$), 1.33 (m, 2 H, –CH$_2$C**H**$_2$CH$_3$), 0.67 (t, 3 H, Me)	$CDCl_3$
2c	$C_6H_5CH_2$		234 (2.44), 299 (0.52)	7.95 (d of d, J = 8, J = unres, 2 H),[b] 7.82–7.46 (m, 6 H, arom), 7.2–7.04 (m, 5 H, C$_6$**H**$_5$CH$_2$), 3.68 (s, 2 H, C$_6$H$_5$C**H**$_2$)	$(CD_3)_2C{=}O$
2c	t-Bu		235 (3.47), 302 (0.50)	8.02 (d of d, J = 8.5, J = 2, 2 H),[b] 7.80 (m, J = 8.5, J = 7, J = 2, 2 H)[c] 7.43 (m, 4 H, arom), 1.20 (s, 9 H, t-Bu)	$(CD_3)_2C{=}O$
2c	C_6H_{11}		231 (1.72), 302 (0.48)	8.17 (d, J = 8, 2 H),[b] 7.94 (m, 2 H),[c] 7.64 (m, 4 H, arom), 1.70–0.9 (m, 10 H, C$_6$H$_{11}$)	$(CD_3)_2S{=}O$
2d	Me		221 (2.30), 253 (1.19), 294 (0.81), 328 (0.43)	8.22 (d of d, $J \simeq 7$, 2 H),[b] 7.89–7.57 (m, 6 H, arom), 6.24 (bd s, 1 H, removed with D$_2$O, –NH), 2.57 (d, becomes s with D$_2$O, 3 H, Me)	$CDCl_3$
2d	Et		222 (2.02), 252 (1.21), 293 (0.90), 326 (0.38)	8.19 (d of d, $J \simeq 7$, $J \simeq 2$, 2 H),[b] 7.93–7.57 (m, 6 H, arom), 2.96 (q, J = 7.5, 2 H, –CH$_2$–) 1.02 (t, J = 7.5, 3 H, Me)	CD_3CN
2d	Pr			8.25 (d, 2 H),[b] 7.98–7.60 (m, 6 H, arom), 6.07 (s, 1 H, removed with D$_2$O, –NH), 2.84 (q, becomes t with D$_2$O, J = 6, 2 H, –CH$_2$–), 1.44 (sext, 2 H, –CH$_2$–), 0.73 (t, J = 7, 3 H, Me)	$CDCl_3$
2d	C_6H_{11}			8.27 (m, 2 H),[b] 7.72 (m, 6 H, arom), 4.73 (bd s, 1 H, removed with D$_2$O –NH), 3.20 (bd s, 1 H, α-C$_6$H$_{11}$), 1.88–0.96 (bd m, 10 H, C$_6$H$_{11}$)	$CDCl_3$
2d	$C_6H_5CH_2$			8.16 (d of d, 2 H),[b] 7.70–7.52 (m, 6 H, arom), 7.20–7.02 (m, 5 H, C$_6$H$_5$), 4.10 (s, 2 H, –CH$_2$–)	$CDCl_3$
3c	Me	Me	239 (1.26), 279 (0.43), 304 (0.68)	8.29 (d of d, J = 8, J = unres, 2 H),[b] 8.05 (m, 2 H, arom),[c] 7.76 (m, 4 H, arom), 2.02 (s, 3 H, Me)	CD_3CN
3c	Pr	Me	238sh (1.41), 278 (0.44), 304 (0.68)	8.08 (d of d, 2 H),[b] 7.90–7.50 (m, 6 H, arom), 3.12 (t, 2 H, –C**H**$_2$CH$_2$CH$_3$), 2.52 (s, 3 H, –NMe), 1.53 (m, 2 H, –CH$_2$C**H**$_2$CH$_3$), 0.80 (t, 3 H, Me)	$(CD_3)_2C{=}O$
3c	C_6H_{11}	Me	238 (1.90), 279 (0.41), 304 (0.57)	8.33 (d of d, J = 8, J = unres, 2 H),[b] 8.05 (m, 2 H, arom),[c] 7.95–7.61 (m, 4 H, arom), remaining peaks overlapped with solvent impurity $(CH_3)_2S{=}O$	$(CD_3)_2S{=}O$
3c	$C_6H_5CH_2$	Me	239sh (1.95), 306 (0.63)	8.32 (d of d, J = 8.5, J = 2, 2 H),[b] 8.1 (m, 2 H, arom),[c] 7.75 (m, 4 H, arom), 7.42 (m, 5 H, C$_6$H$_5$), 4.56 (s, 2 H, –CH$_2$–), 2.57 (s, 3 H, Me)	$(CD_3)_2C{=}O$
3c	i-Pr	i-Pr	238sh (1.41), 275 (0.48), 303 (0.69)	8.18 (d of d, J = 8, J = 2, 2 H),[b] 8.01 (m, 2 H, arom),[c] 7.74 (m, 4 H, arom), 3.67 (hept, J = 7, 2 H, –CH–), 1.27 (d, J = 7, 12 H, Me)	$(CD_3)_2C{=}O$
3c	$C_6H_5CH_2$	$C_6H_5CH_2$	239 (2.02), 309 (0.68)	8.04 (d of d, J = 8, J = 2, 2 H),[b] 7.92 (d of d, J = 8, J = 2, 2 H, arom),[c] 7.65 (t, J = 8, 4 H, arom), 7.40–7.06 (m, 10 H, C$_6$H$_5$), 4.28 (s, 4 H, –CH$_2$–)	$(CD_3)_2S{=}O$
3d	Me	Me	222 (2.81), 255 (0.97), 298 (0.78), 330 (0.45)	8.34 (m, 2 H),[b] 7.80 (m, 6 H, arom), 2.83 (s, 6 H, Me)	$CDCl_3$
3d	Pr	Me	226 (2.74), 256 (1.32), 298 (0.85), 335 (0.43)	8.27 (d of d, J = 8, J = unres, 2 H),[b] 7.80 (s, 6 H, arom), 3.24 (t, J = 8, 2 H, –CH$_2$–), 2.65 (s, 3 H, –NMe), 1.57 (sext, 2 H, –CH$_2$–), 0.84 (t, J = 8, 3 H, Me)	$CDCl_3$
3d	C_6H_{11}	Me	225 (2.64), 258 (1.23), 296 (0.83), 334 (0.42)	8.36 (m, 2 H),[b] 7.75 (m, 6 H, arom), 2.60 (s, 3 H, Me), 2.0–1.0 (bd m, 10 H, C$_6$H$_{11}$)[d]	$CDCl_3$
3d	$C_6H_5CH_2$	Me	225 (3.61), 257 (1.35), 298 (0.90), 329 (0.64)	8.15 (d of d, J = 7, J = unres, 2 H),[b] 7.87 (s, 6 H, arom), 7.51–7.27 (m, 5 H, C$_6$H$_5$), 3.33 (s, 2 H, –CH$_2$–) 2.55 (s, 3 H, Me)	$CDCl_3$–CD_3CN
5c	t-Bu		236 sh (1.52), 277 (0.39), 297 (0.39)	7.84 (d of d, J = 7, j , 2, 2 H),[b] 7.5–7.12 (m, 6 H, arom), 0.98 (s, 9 H, t-Bu)	$CDCl_3$
5c	C_6H_{11}		237 sh (1.61), 274 (0.36), 298 (0.37)	7.86 (d of d, J = 8, 2 H),[b] 7.66–7.20 (m, 6 H, arom), 1.70–0.70 (m, 11 H, C$_6$H$_{11}$)	$CDCl_3$
5c	$C_6H_5CH_2$		239 sh (1.68), 276 (0.46), 294 (0.49)	7.83 (d of d, 2 H),[b] 7.68–7.04 (m, 11 H, arom), 3.46 (s, 2 H, –CH$_2$–)	$CDCl_3$
5d	Me		216 (2.64), 259 (1.93), 285 sh (1.62), 325 sh (0.36)	7.90 (d of d, $J \simeq 6$, $J \simeq 2$, 2 H),[b] 7.66–7.25 (m, 6 H, arom), 2.78 (s, 3 H, Me)	$CDCl_3$
5d	Pr			7.95 (d of d, J = 7, J = 2 H),[b] 7.59–7.33 (m, 6 H, arom), 2.98 (t, J = 7.5, 2 H, –CH$_2$–), 1.70 (sext, J = 7.5, 2 H, –CH$_2$–), 0.95 (t, J = 7.5, 3 H, Me)	$CDCl_3$
5d	C_6H_{11}		242 (1.38), 285 (0.43), 333 (0.08)	8.07 (d, J = 8, 2 H),[b] 7.66–7.32 (m, 6 H, arom), 3.05 (bd s, 1 H, α-C$_6$H$_{11}$), 3.04–1.0 (bd m, 10 H, C$_6$H$_{11}$)	$CDCl_3$
5d	$C_6H_5CH_2$			7.90 (d of d, 2 H),[b] 7.69–7.17 (m, 11 H, arom), 4.23 (s, 2 H, –CH$_2$–)	$CDCl_3$

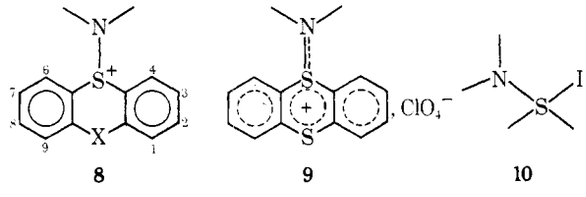
Table IV (*Continued*)

Compd	R	R_1	λ_{max}, nm (10^{-4} ϵ)[a]	^{1}H NMR, δ (J, Hz)	Solvent
6d	Me	Me		8.67 (m, 2 H),[b] 7.82 (s, 6 H, arom), 2.90 (s, 3 H, Me)	$CDCl_3$
6d	Pr	Me	225 (3.50), 244 (2.77), 298 (0.98), 334 (0.53)	8.53 (d of d, J = 8, J = unres, 2 H),[b] 7.95–7.71 (m, 6 H, arom), 3.31 (t, 2 H, $-CH_2-$), 2.71 (s, 3 H, –NMe), 1.59 (sext, J = 7, $-CH_2-$), 0.85 (t, J = 7, Me)	$CDCl_3$
6d	C_6H_{11}	Me	223 (2.87), 242 (2.27), 296 (0.80), 332 (0.41)	8.61 (d of d, J = 8, J = unres, 2 H),[b] 7.78 (s, 6 H, arom), 4.0 (bd s, 1 H, α-C_6H_{11}), 2.63 (s, 3 H, –NMe), 2.06–1.06 (bd m, 10 H C_6H_{11})	$CDCl_3$

[a] Solvent CH_3CN in all cases. [b] This assignment is to the two protons in the 4,6 positions (S is at position 5 of the ring). Each proton undergoes coupling with its ortho and meta protons. In some cases the coupling pattern was well resolved, while in others resolution was poor. [c] This assignment is to the two protons in the 3,7 positions. Each proton undergoes coupling with two ortho protons and one meta proton. [d] The α-H could not be detected.

action of **1d** with one of the protonated sulfilimine perchlorates (**2d**, R = Pr) were not successful. However, some of **4d** (3%) was obtained by reaction of the free sulfilimine **5d** (R = Me) with **1d** in acetonitrile. In this reaction the solid **1d** was added in small portions to a stirred solution of the sulfilimine, and initially the purple color of **1d** disappeared rapidly with each addition, but long before 1 equiv of **1d** was added the color of the cation radical persisted. That is, reaction between **1d** and **5d** ceased after a while. The **1d** which persisted in solution was destroyed by adding water. A recovery of 70% of the **5d** in the protonated form (i.e., **2d**, R = Me) was obtained. The amounts of thianthrene (82%) and its 5-oxide (31%) obtained indicate that some of the **5d** was also converted into thianthrene and/or its 5-oxide. The origin of **4d** in reactions of cation radicals with alkylamines may thus be from reactions of the free sulfilimines with cation radical. Although the protonated sulfilimine and perchloric acid are formed in reaction of **1d** with an alkylamine (eq 1), there is always an excess of alkylamine present, so that free sulfilimine (although a strong base) is likely to be present. However, why **1d** is converted into **4d** more easily than **1c** into **4c** (and than **1a,b** into **4a,b**),[5] and what may be the fate of the alkyl group (R), are in any event still unknown.

Given in Table IV are the ^{1}H NMR data for most of the products **2, 3, 5,** and **6.** In every case the most downfield signals are assignable to the two protons in the 4,6 positions (**8**). In



8 **9** **10**

a number of cases, particularly of phenoxathiin derivatives (X = O), the spectra were well enough resolved to give the doublet of doublets for these equivalent protons, with J values of about 8 and 2 Hz. These doublets centered at δ values of 8.16–8.28 for compounds **2,** 8.04–8.36 for compounds **3,** and 7.83–8.07 for the unprotonated compounds **5,** illustrating the deshielding effect of the formal positive charge in compounds **2** and **3.** Some variation due to the use of different solvents may have been experienced, but it is not marked. The same pattern for the 4,6 protons is seen in phenoxathiin 5-oxide (δ 7.89, J = 8 and 2 Hz) and thianthrene 5-oxide (δ 7.96) in $CDCl_3$. Thus, the deshielding effect of the S=NR group is about as great as that of the S=O group. The high value of δ 8.07 for **5d** (R = C_6H_{11}) is unusual and is not seen in the corresponding **5c** (δ 7.86).

The very interesting effect of the anion in compounds **3d** and **6d** is seen. That is, for **3d** (R = Me, Pr, C_6H_{11}) δ values for $H_{4,6}$ are 8.34, 8.27, and 8.36, respectively. The corresponding values for **6d** are 8.67, 8.53, and 8.61, resulting in downfield shifts of 0.33, 0.26, and 0.25 δ, respectively, by changing the anion from ClO_4^- to I^-. Downfield shifts of the N-methyl group in each of these compounds amounted to 0.07, 0.06, and 0.03 δ when changing from ClO_4^- to I^-, and a similar shift of 0.07 δ is seen in the α-CH_2 of the propyl groups. The data suggest that in the compounds **3** the ClO_4^- ion is separated from the charge-delocalized cation as in **9,** while in compounds **6** the iodide ion may, in fact, be well attached to sulfur (**10**) and through its inductive effect cause even greater deshielding of nearby protons.

Experimental Section

Phenoxathiin[8] and thianthrene[7a] cation radical perchlorates (**1c** and **1d**) were prepared as described earlier. The potential hazard of explosiveness of these compounds should be noted.[9] Reactions of **1c** and **1d** with amines were carried out in Eastman anhydrous grade (<0.05% water) CH_3CN stored over molecular sieve in septum-capped bottles. Solvents used for column chromatography were dry, reagent grade. The column material was E. Merck silica gel 60, ASTM 30–70 mesh. The several types of reactions are illustrated with examples and all results are tabulated in Tables I–IV. Elemental analyses were obtained on a number of products, while some were characterized by parent peak mass spectrum. Analytical data are given in Table V. All compounds were characterized by ^{1}H NMR (Table IV). Ultraviolet spectra data for most of the compounds are also given in Table IV. A Varian XL-100 NMR spectrometer and a Beckman DK-2A spectrophotometer were used.

Reaction of 1c with *tert*-Butylamine. To a stirred solution of 532 mg (1.78 mmol) of **1c** in 30 mL of CH_3CN was added 0.5 mL (~4.75 mmol) of *tert*-butylamine. The purple solution became pale yellow immediately. After 15 min the solvent was removed in a rotary evaporator, and the residue was washed well with water, dissolved in dry acetone, and dried over K_2CO_3. The acetone solution was concentrated and placed on a silica gel column. Elution with petroleum ether (bp 30–60 °C) gave 156 mg (0.78 mmol, 44%) of phenoxathiin. Elution with ether gave 26 mg (0.118 mmol, 6%) of phenoxathiin 5-oxide, and elution with acetone gave 303 mg (0.81 mmol, 46%) of **2c** (R = *t*-Bu), mp 203–204 °C (from aqueous methanol), infrared (Nujol) ClO_4^- band at 9.1–9.3 μ.

Reaction of 1d with Methylamine. Methylamine was bubbled into a solution of 601 mg (1.93 mmol) of **1d** in 50 mL of CH_3CN causing very rapid disappearance of the purple color of the cation radical. The solution was worked up as above. Elution with benzene gave 275 mg (1.27 mmol, 66%) of thianthrene. Elution with ether gave 12 mg (0.05 mmol, 2.6%) of thianthrene 5-oxide, and elution with acetone gave a mixture of **2d** (R = Me) and **4d.** These were separated with ethanol, in which **4d** is sparingly soluble, giving 43 mg (0.079 mmol, 8.2%) of **4d** and 100 mg (0.289 mmol, 15%) of **2d,** mp 120–122 °C (from CH_2Cl_2–ether).

Deprotonation of 2c. Formation of 5c (R = *t*-Bu). A mixture of

Table V. Analytical Results[a,b]

Compd	R	R_1	Formula	C	H	N	S	Cl
2c	*t*-Bu		$C_{16}H_{18}NSClO_5$	51.7	4.88	3.77	8.63	9.54
			Found	51.4	4.72	4.02	9.20	9.87
2d	Me		$C_{13}H_{12}NS_2ClO_4$	45.2	3.49	4.05	18.5	10.3
			Found	44.8	3.49	4.06	18.8	10.6
2d	Et		$C_{14}H_{14}NS_2ClO_4$	46.7	3.92	3.89	17.8	9.85
			Found	46.6	4.22	4.03	17.9	10.6
2d	$C_6H_5CH_2$		$C_{19}H_{16}NS_2ClO_4$	54.1	3.82	3.31	15.2	8.40
			Found	54.4	3.98	3.50	15.4	8.56
3c	*t*-Bu	Me	$C_{17}H_{20}NSClO_5$	52.9	5.22	3.63	8.31	9.21
			Found	52.8	5.38	3.50	8.25	
3c	Pr	Me	$C_{16}H_{18}NSClO_5$	51.7	4.88	3.92	8.95	9.54
			Found	51.6	4.84			9.53
3c	C_6H_{11}	Me	$C_{19}H_{22}NSClO_5$	55.4	5.38	3.40	7.78	8.63
			Found	55.4	5.40	3.63	7.79	
3c	$C_6H_5CH_2$	$C_6H_5CH_2$	$C_{26}H_{22}NSClO_5$	62.9	4.47	2.82	6.46	7.15
			Found	63.6	4.41	3.11	6.27	7.73
3d	Pr	Me	$C_{16}H_{18}NS_2ClO_4$	49.6	4.67	3.61	16.5	9.13
			Found	49.9	4.74	3.46	16.6	
3d	C_6H_{11}	Me	$C_{19}H_{22}NS_2ClO_4$	53.3	5.18	3.27	15.0	8.28
			Found	53.9	5.48	3.75	14.9	8.45
3d	$C_6H_5CH_2$	Me	$C_{20}H_{18}NS_2ClO_4$	55.1	4.16	3.21	14.7	8.13
			Found	55.1	4.51	3.46	14.8	8.20
5c	C_6H_{11}		$C_{18}H_{19}NSO$	72.7	6.44	4.71	10.8	
			Found	72.5	6.49	4.89	10.7	

[a] Schwarzkopf Laboratories, Woodside, N.Y. [b] Most of the sulfilimines were characterized by mass matching of the parent peak. For **5c**, R = *t*-Bu, 271.06 (calcd, 271.103); R = Pr, 257.075 (calcd, 257.085); R = $C_6H_5CH_2$, 305.078 (calcd, 305.087). For **5d**, R = Me, 245.035 (calcd, 245.034); R = C_6H_{11}, 313.096 (calcd, 313.096); R = $C_6H_5CH_2$, 321.066 (calcd, 321.065).

502 mg (1.35 mmol) of **2c** (R = *t*-Bu) in 15 mL of ethanol and 2 mL of 20% NaOH was stirred for 2 h, and concentrated to give a white solid. This was filtered, washed with water, and dried to give 346 mg (1.28 mmol, 95%) of **5c** (R = *t*-Bu), mp 74–75 °C (from aqueous ethanol).

Deprotonation of 2d. Formation of 5d (R = Me). After being stirred for 30 min a solution of 500 mg (1.45 mmol) of **2d** (R = Me) in 50 mL of ethanol and 2 mL of NaOH was poured into 300 mL of water. Extraction with ether gave 335 mg (1.37 mmol, 95%) of **5d** (R = Me), mp 44–46 °C (from ether–petroleum ether).

Methylation of 5c. Formation of 6c (R = *t*-Bu). To a suspension of 346 mg of **5c** (R = *t*-Bu) in 25 mL of dry ether was added 1 mL of CH_3I. The **5c** dissolved immediately, and after stirring for 1 h the solution began depositing white crystals. Filtration after 2 h gave 443 mg (1.07 mmol, 84%) of **6c** (R = *t*-Bu), mp 168–169 °C (from $CHCl_3$–ether).

Conversion of 6c into 3c (R = *t*-Bu; R_1 = Me). Reaction with $AgClO_4$. To a stirred solution of 103 mg (0.25 mmol) of **6c** (R = *t*-Bu) in 10 mL of acetone was added an excess of $AgClO_4$. After 15 min the precipitate of AgI was filtered through Celite filter aid. Concentration of the filtrate gave 77 mg (0.20 mmol, 80%) of **3c** (R = *t*-Bu; R_1 = Me), mp 183–184 °C dec (from ethanol).

Reaction of 1c with *N*-Methylbenzylamine. Formation of 3c (R = Benzyl; R_1 = Me). To a stirred solution of 1.11 g (3.7 mmol) of **1c** in 40 mL of CH_3CN was added 0.5 mL (≃4.10 mmol) of *N*-methylbenzylamine. Workup gave 516 mg (2.58 mmol, 70%) of phenoxathiin, 63 mg (0.29 mmol, 8%) of phenoxathiin 5-oxide, and 260 mg of **3c** (R = benzyl; R_1 = Me), mp 173–174 °C dec (from acetone–ether).

Reaction of 1d with 5d (R = Me). Formation of 4d. To a solution of 200 mg (0.816 mmol) of **5d** (R = Me) in 5 mL of CH_3CN was added 258 mg (0.816 mmol) of **1d** in small portions. The first few portions added disappeared very quickly (color), but the rate of disappearance slowed up and eventually stopped well before all of the **1d** was added. After 1 h the unreacted **1d** was destroyed by adding water, and the solution was worked up in the usual way, giving 145 mg (0.67 mmol, 82% based on **1d**) of thianthrene, 58 mg (0.25 mmol, 31%) of thianthrene 5-oxide, 12 mg (0.022 mmol, 2.7%) of **4d**, and 198 mg (0.57 mmol, 70%) of **2d**. It is noticeable that the conversion of **1d** into thianthrene and thianthrene 5-oxide totals 111%, indicating that some of the **5d** was probably converted into one or both of these compounds. In separate reactions it was found that **2d** (R = Pr) did not react with **1d**.

Registry No.—**1c**, 55975-63-8; **1d**, 35787-71-4; **2c** (R = Pr), 61558-38-1; **2c** (R = *t*-Bu), 61558-40-5; **2c** (R = C_6H_{11}), 61558-42-7; **2c** (R = $C_6H_5CH_2$), 61558-44-9; **2d** (R = Me), 61558-46-1; **2d** (R = Et), 61558-48-3; **2d** (R = Pr), 61558-50-7; **2d** (R = C_6H_{11}), 61558-52-9; **2d** (R = $C_6H_5CH_2$), 61558-54-1; **3c** (R = Me; R_1 = Me), 61558-56-3; **3c** (R = R_1 = Pr-*i*), 61558-58-5; **3c** (R = Pr; R_1 = Me), 61558-60-9; **3c** (R = C_6H_{11}; R_1 = Me), 61558-62-1; **3c** (R = $PhCH_2$; R_1Me), 61558-64-3; **3c** (R = R_1 = CH_2Ph), 61558-68-7; **3c** (R = *t*-Bu; R_1 = Me), 61558-66-5; **3d** (R = Rr; R_1 = Me), 61558-70-1; **3d** (R = C_6H_{11}; R_1 = Me), 60896-37-9; **3d** (R = $PhCH_2$; R_1 = Me), 61558-72-3; **5c** (R = Pr), 61558-73-4; **5c** (R = *t*-Bu), 61558-74-5; **5c** (R = C_6H_{11}), 61558-75-6; **5c** (R = $PhCH_2$), 61558-76-7; **5d** (R = Me), 61558-77-8; **5d** (R = Pr), 61558-78-9; **5d** (R = C_6H_{11}), 61558-79-0; **5d** (R = $PhCH_2$), 61558-80-3; **6c** (R = Pr), 61558-81-4; **6c** (R = *t*-Bu), 61558-82-5; **6c** (R = C_6H_{11}), 61558-83-6; **6c** (R = $PhCH_2$), 61558-84-7; **6d** (R = Me), 61558-85-8; **6d** (R = Pr), 61558-86-9; **6d** (R = C_6H_{11}), 61558-87-0; **6d** (R = $PhCH_2$), 61558-88-1.

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(3) Postdoctoral Fellow.
(4) Taken in part from the Ph.D. Dissertation of S. R. Mani, Texas Tech University, Aug 1976.
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