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Registry No.—8 (X = H), 29376-61-2; 8 (X = Br), 51392-61-1; 8 (X = Cl), 51392-62-2; **9**, 19217-59-5; **10**, 203-85-0.

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Ion Radicals. XXIX. Reaction of Thianthrene Cation Radical Perchlorate with Some Benzene Derivatives[1,2]

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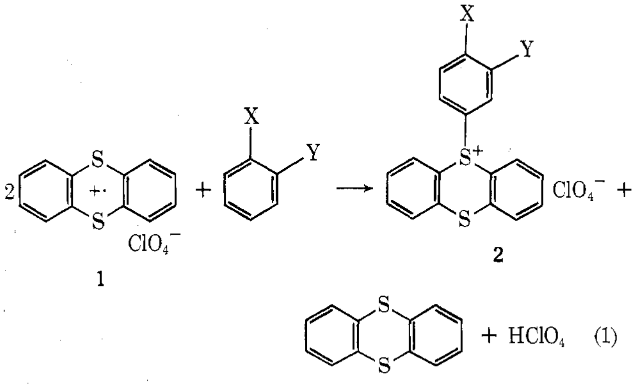
Thianthrene cation radical perchlorate ($Th\cdot^+ClO_4^-$, **1**) reacted in acetonitrile solution with acetanilide, phenol, *o*-chlorophenol, *o-tert*-butylphenol, and *N,N*-dimethylaniline to give 5-arylthianthrenium perchlorates ($ThAr^-ClO_4^-$) in which bonding is presumed to have occurred at the aryl position para to the functional group. Excellent yields were obtained, except in the case of *N,N*-dimethylaniline, which also underwent oxidative dimerization to *N,N,N′,N′*-tetramethylbenzidine. Thianthrene (Th) was formed along with the formation of the 5-arylthianthrenium perchlorates, according to the anticipated stoichiometry $2Th\cdot^+ + ArH \rightarrow Th + ThAr^+ + H^+$. Reaction of **1** with hydrazobenzene caused both oxidation to azobenzene and rearrangement (by concurrently formed acid) to benzidine monoperchlorate. Kinetics of reaction of **1** with phenol and acetanilide in acetonitrile were followed by use of the Durrum-Gibson stopped-flow spectrophotometer. Kinetics of reaction with anisole were reexamined by the same technique, allowing in each case the use of $[\mathbf{1}]_0$ in the range 10^{-6}–10^{-5} *M*. Reactions were second order in $Th\cdot^+$ and inverse order in thianthrene. Difficulties with a mechanism of reaction involving the thianthrene dication, formed in the first-stage disproportionation of the thianthrene cation radical, are discussed. No other suitable mechanism is found.

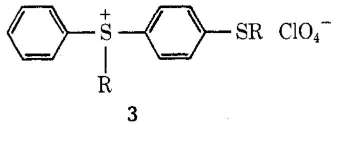
Results and Discussion

Products. The substitution reactions of organic cation radicals with aromatic substrates are not well explored. Anodic dimerizations, particularly of aromatic amines and phenols, are well known,[5] but we exclude them from the class of substitution reactions we have in mind. An earlier report[6] showed that thianthrene cation radical perchlorate (**1**) reacted with anisole to form 5-(*p*-anisyl)thianthrenium perchlorate (**2a**) according to the stoichiometry of eq 1. Compounds of this class are not well known. They may be formed in some cases (*e.g.*, X = Y = H) by reaction of thianthrene oxide with the aromatic and aluminum chloride.[6,7] Recently, analogous examples (**3**) have been made by the anodic dimerization of the sulfides C_6H_5SR (R = phenyl and alkyl).[8] We have now found that reaction of **1** with acetanilide and three phenols occurs very readily in good yield according to eq 1. Reaction with *N,N*-dimethylaniline also occurred, but in poorer yield (21%), being overshadowed by oxidative dimerization to *N,N,N′,N′*-tetramethylbenzidine (TMB) and the latter's oxidation to the corresponding cation radical ($TMB\cdot^+$). Reaction of **1** with hydrazobenzene led not only to the formation of thianthrene and azobenzene but also to benzidine; benzidine rearrangement must without doubt have occurred from the acid liberated in the redox reaction.



1 **2**

	a	**b**	**c**	**d**	**e**	**f**	**g**
X	OMe	NHAc	OH	OH	OH	NMe_2	NH_2
Y	H	H	H	Cl	*t*-Bu	H	H



3

Kinetics and Mechanism. In the earlier report the reaction of **1** with anisole was found to be second order in

Table I
Kinetic Data for the Reaction of Thianthrene Cation Radical Perchlorate (1) with Phenol, Acetanilide, and Anisole in Acetonitrile Solution at 25°

Aromatic (Ar)	10^2 $[\mathrm{Ar}]_0$, M	10^6 $[1]_0$, M	10^4 $[\mathrm{Th}]_0$, M	k_{obsd}, M^{-1} sec^{-1}	r[a]	k, M^{-1} sec^{-1}
Phenol	4.6	47	7.6	7.9×10^4	0.957	1.3×10^3
Phenol	4.6	47	7.6	6.8×10^4	0.995	1.1×10^3
Acetanilide	1.3	2.1	16	4.3×10^3	0.991	5.4×10^2
Acetanilide	1.3	4.8	16	2.2×10^3	0.994	2.8×10^2
Acetanilide	1.3	17	16	9.7×10^2	0.997	1.2×10^2
Acetanilide	1.9	3.7	4.0	1.7×10^4	0.999	3.7×10^2
Acetanilide	1.9	20	4.0	4.8×10^3	0.986	1.1×10^2
Anisole	0.87	28	8.7	5.9×10	0.980	5.9
Anisole	12	27	8.7	3.4×10^2	0.999	2.5
Anisole	12	59	8.7	3.3×10^2	0.999	2.4
Anisole	180	13	28	2.4×10^3	0.991	3.7
Anisole	180	3.2	28	1.7×10^3	0.989	2.6
Anisole	40	1.4	5.2	3.6×10^3	0.974	4.7
Anisole	83	8.1	5.2	1.6×10^3	0.989	1.0

[a] Correlation coefficient.

$\mathrm{Th}\cdot^+$ and inverse order in thianthrene. We have repeated these kinetics and also run those with acetanilide and phenol with the use of a Durrum-Gibson stopped-flow spectrophotometer, allowing us to use much lower concentrations (10^{-6}–10^{-5} M) of 1 than were possible in the earlier conventional vacuum-line spectrophotometric technique. Although the use of lower concentrations made kinetic measurements more subject to error, the new results duplicate the older ones quite well. Conventional first- and second-order rate plots indicated clearly that the reactions were second order in $\mathrm{Th}\cdot^+$. We have treated the rate data according to eq 2 and 3, and have calculated the

$$2\mathrm{Th}\cdot^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Th} + \mathrm{Th}^{2+} \quad (2)$$

$$\mathrm{Th}^{2+} + \mathrm{ArH} \xrightarrow{k_2} \mathrm{ThAr}^+ + \mathrm{H}^+ \quad (3)$$

second-order rate constants (k_{obsd}) by least-squares treatment, from which we have also calculated the rate constants, $k = k_{\mathrm{obsd}}[\mathrm{Th}]_0/[\mathrm{ArH}]_0$. For the anisole case the new results gave an average value of $k = 3.3 \pm 1.3$ M^{-1} sec^{-1}, while the earlier results gave $k = 2.4 \pm 0.34$ M^{-1} sec^{-1}, which we feel is a reasonable agreement. The relevant data are given in Table I. Similar work with acetanilide and phenol gave the data in Table I.

These and the earlier results show that the reaction of 1 with these aromatics is an aromatic substitution reaction in that reaction occurs easily when X in ArX is an electron donor.[6] At the same time, the rates for the three aromatics do not parallel the σ^+ constants for the substituents as one might have expected. Recently, the σ^+ constant for the p-acetamido group has been found to be somewhat more negative (-0.69)[9] than indicated earlier.[10] The value for the p-hydroxy group remains at -0.92. A new value for p-methoxy has not been determined,[9] but there is no reason to believe that the old ones, averaging -0.77,[10] are likely to be in error. Thus, our rate data have substituent effects in the order OH > NHAc > OMe rather than in the σ^+-constant order of OH > OMe > NHAc. Furthermore, the rate for the anisole reaction is particularly low in comparison with the other two. The data for phenol and acetanilide gave a ρ value of -2.7, which is reasonable for attack of an electrophile on the aromatics, but the data for phenol and anisole lead to a ρ value of -16.7, which is entirely unreasonable. Consequently, it may be that reaction of 1 with anisole follows a quite different mechanism from reaction with phenol and acetanilide.

Criticisms of our interpretation (eq 2 and 3) of the aromatic substitution reaction and the analogous water reaction have been made,[11] particularly on the basis that the disproportionation constant (K, eq 2) is so small that substitution rates (eq 3) must approach those of diffusion control to satisfy the rate data. Values of K have been determined from half-wave potentials for the oxidation of thianthrene to the cation radical and dication and found to be about 10^{-9}.[12,13] This requires the rate constant k_2 to be of the order 10^9–10^{12} for the three aromatics studied. These are, of course, decidedly difficult to accept. Nevertheless, no satisfactory alternative mechanism of reaction has been proposed for reactions of thianthrene cation radical which are second order in cation radical and inverse order in thianthrene. A two-step reaction analogous to parts of an electrochemical ECE process (eq 4 and 5) is

$$\mathrm{Th}\cdot^+ + \mathrm{ArH} \longrightarrow \mathrm{ThAr}\cdot + \mathrm{H}^+ \quad (4)$$

$$\mathrm{ThAr}\cdot + \mathrm{Th}\cdot^+ \longrightarrow \mathrm{ThAr}^+ + \mathrm{Th} \quad (5)$$

unattractive because the electron-transfer reaction (eq 5) would have to be rate determining and reversible, neither of which is known to be valid. Recently, Parker proposed for the water reaction that the thianthrene dimer dication may be responsible (eq 6 and 7, in which ThO represents

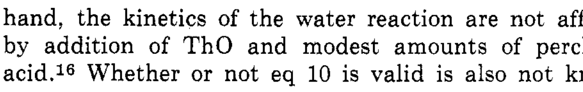
$$2\mathrm{Th}\cdot^+ \rightleftharpoons (\mathrm{Th}\cdot^+)_2 \quad (6)$$

$$(\mathrm{Th}\cdot^+)_2 + \mathrm{H_2O} \longrightarrow \mathrm{ThO} + \mathrm{Th} + 2\mathrm{H}^+ \quad (7)$$

thianthrene 5-oxide).[14] Kinetics of the water reaction and the aromatic substitution reactions require in that case that eq 7 and analogous eq 8 be reversible. It is known

$$(\mathrm{Th}\cdot^+)_2 + \mathrm{Ar} \longrightarrow \mathrm{ThAr}^+ + \mathrm{Th} + \mathrm{H}^+ \quad (8)$$

that a mixture of a sulfide and sulfoxide in acid solution will give the cation radical (eq 9). In fact, this is the way



(9)

in which Rundel and Scheffler[15] make 1. On the other hand, the kinetics of the water reaction are not affected by addition of ThO and modest amounts of perchloric acid.[16] Whether or not eq 10 is valid is also not known.

$$\mathrm{ThAr}^+ + \mathrm{Th} + \mathrm{H}^+ \longrightarrow 2\mathrm{Th}\cdot^+ + \mathrm{Ar} \quad (10)$$

Furthermore, although 1 is known to produce a dimer [*i.e.*, $(\mathrm{Th}\cdot^+\mathrm{ClO_4}^-)_2$] in propionitrile and trifluoroacetic anhydride–trifluoroacetic acid,[17] no evidence for that tetrameric aggregate has been found in acetonitrile solution.[18] Therefore, although the kinetic data for an aromatic substitution reaction may be satisfied by eq 6 and 8, there are no supporting data for them. An entirely satisfactory solution to all aspects of the mechanism of substitution is, therefore, still needed.

Experimental Section

Materials. Thianthrene cation radical perchlorate (1) was prepared by oxidizing thianthrene with perchloric acid.[4] Solvent acetonitrile was Eastman Kodak Spectrograde (<0.01% water) and was kept over molecular sieve in a septum-capped bottle. Phenol, *o*-chlorophenol, *o*-*tert*-butylphenol, and *N,N*-dimethylaniline were distilled under vacuum. Acetanilide was crystallized from hot water, hydrazobenzene was crystallized from aqueous ethanol, and *N,N,N′,N′*-tetramethylbenzidine was crystallized from ethanol after decolorizing in benzene with charcoal.

Reaction of 1 with Acetanilide. To a solution of 1.13 g (3.6 mmol) of **1** in 30 ml of acetonitrile was added 0.60 g (4.4 mmol) of solid acetanilide. As the acetanilide dissolved the purple color of the solution slowly faded to pale pink, and a white solid precipitated. This was filtered, the solution was rinsed from the flask with solvent acetone and evaporated to dryness at reduced pressure, and all solids were combined for chromatography on a column of silica gel (Merck, 30–70 mesh, 16 × 2.4 cm). Elution with benzene gave 317 mg (1.5 mmol, 83%) of thianthrene. Elution with acetone gave 362 mg (2.7 mmol) of acetanilide. Elution with ethanol gave 795 mg (1.8 mmol, 100%) of the monohydrate of 5-(*p*-acetamidophenyl)thianthrenium perchlorate (**2b**), mp 136–137° (aqueous ethanol), ultraviolet λ_{max} (acetonitrile) 282.6 nm (ϵ 1.6 × 10^4).

Anal. Calcd for $C_{20}H_{16}NS_2ClO \cdot H_2O$: C, 51.3; H, 3.87; N, 2.99; S, 13.7; Cl, 7.57. Found: C, 51.7; H, 3.93; N, 3.01; S, 13.11; Cl, 8.06.

Hydrolysis of 5-(*p*-Acetamidophenyl)thianthrenium Perchlorate (2b). A solution of 175 mg of **2b** in 10 ml of ethanol was refluxed for 24 hr after 4 drops of 30% sodium hydroxide was added. The solution was evaporated and the white solid was washed with water and benzene and dried, giving 125 mg (0.3 mmol) of crude 5-(*p*-aminophenyl)thianthrenium perchlorate (**2g**), mp 242–243° (methanol), ultraviolet λ_{max} (acetonitrile) 299 nm (10^{-3} ϵ 2.3), 265 (1.6).

Anal. Calcd for $C_{18}H_{14}NS_2ClO_4$: C, 53.0; H, 3.45; N, 3.43; S, 15.7; Cl, 8.69. Found: C, 52.7; H, 3.60; N, 3.33; S, 15.7; Cl, 8.40.

Reaction of 1 with Phenol. The reactants were 619 mg (2.0 mmol) of **1** in 30 ml of acetonitrile and 190 mg (2.0 mmol) of phenol. After work-up the residue was chromatographed and gave with benzene 217 mg (1.0 mmol, 100%) of thianthrene, with ether 68.2 mg (0.3 mmol, 15.0%) of thianthrene 5-oxide, and with acetone 572 mg of solids from which a quantitative yield of 5-(*p*-hydroxyphenyl)thianthrenium perchlorate (**2c**) was obtained by crystallization from ethanol, mp 256.5–257.5°, ultraviolet λ_{max} (acetonitrile) 316 nm (broad, 10^{-4} ϵ 2.4), 267 (sh, 1.0).

Anal. Calcd for $C_{18}H_{13}S_2ClO_5$: C, 52.9; H, 3.20; S, 15.7; Cl, 8.67. Found: C, 53.1; H, 3.37; S, 16.0; Cl, 8.98.

Reaction of 1 with *o*-Chlorophenol. The reactants were 600 mg (1.90 mmol) of **1** in 20 ml of acetonitrile and 1 ml (9.6 mmol) of *o*-chlorophenol. Work-up gave a purple, liquid residue. Chromatography gave with benzene 216 mg (1.0 mmol, 107%) of thianthrene, with ether 46.9 mg (0.20 mmol, 10.5%) of thianthrene 5-oxide, and with acetone 395 mg of solids from which crystallization from ethanol gave 5-(3-chloro-4-hydroxyphenyl)thianthrenium perchlorate (**2d**), mp 229–230°, ultraviolet λ_{max} (acetonitrile) 316 nm (10^{-4} ϵ 0.85), 289 (1.0), 250 (1.5).

Anal. Calcd for $C_{18}H_{12}S_2Cl_2O_5$: C, 48.7; H, 2.7; S, 14.5; Cl, 16.0. Found: C, 48.7; H, 2.8; S, 14.9; Cl, 15.8.

Reaction of 1 with *o*-*tert*-Butylphenol. Reactants were 757 mg (2.4 mmol) of **1** in 25 ml of acetonitrile and 0.5 ml (2.6 mmol) of *o*-*tert*-butylphenol. The pale blue solution gave a mixture of white and dark solids. Chromatography gave with benzene 343 mg of thianthrene wet with *o*-*tert*-butylphenol, with ether 59.7 mg (0.30 mmol, 12.5%) of thianthrene 5-oxide, and with acetone 511 mg of solids from which crystallization from aqueous ethanol gave quantitatively 5-(3-*tert*-butyl-4-hydroxyphenyl)thianthrenium perchlorate (**2e**), mp 205–106°, ultraviolet λ_{max} (acetonitrile) 313 nm (10^{-4} ϵ 0.67), 283 (1.1), 256 (1.5).

Anal. Calcd for $C_{22}H_{21}S_2ClO_5$: C, 56.8; H, 4.55; S, 13.8; Cl, 7.62. Found: C, 56.5; H, 4.65; S, 14.1; Cl, 8.11.

Reaction of 1 with Hydrazobenzene. Reactants were 919 mg (2.9 mmol) of **1** in 30 ml of acetonitrile and 570 mg (3.1 mmol) of hydrazobenzene. The purple solution turned yellow immediately when the hydrazobenzene was added. Elution of the silica gel column with benzene gave a mixture of thianthrene and azobenzene. Elution with ethanol gave 405 mg of the monoperchlorate of benzidine. The mixture of thianthrene and azobenzene was separated on a column of Florisil (100–200 mesh, Sigma Chemical Co.) using methanol as eluent, giving 631 mg (2.9 mmol, 100%) of thianthrene and 313 mg (1.7 mmol) of azobenzene. The amount of azobenzene corresponded with quantitative reduction of the cation radical, while the amount of benzidine monoperchlorate represents the relatively slower rearrangement of remaining hydrazobenzene, catalyzed by protons liberated in the reduction of the cation radical. Identification of benzidine monoperchlorate was made by comparing the melting point (234–245°), ultraviolet spectrum (λ_{max} 292, 242, 237 nm in acetonitrile), and the change in spectrum on adding both excess of sodium hydroxide (λ_{max} 287.5 nm) and excess of perchloric acid (λ_{max} 243 nm) with those of authentic compound.

Reaction of 1 with *N,N*-Dimethylaniline. On adding 0.8 ml (6.3 mmol) of *N,N*-dimethylaniline to a solution of 1.87 g (5.9 mmol) of **1** in 40 ml of acetonitrile, the solution turned dark green immediately, and a copious mixture of green and white solids separated. The solids were filtered and washed with benzene, whereupon the white solid dissolved. The mixed benzene and acetonitrile solutions were evaporated and the residue was chromatographed. Elution with benzene gave 937 mg (4.3 mmol, 147%) of thianthrene. Elution with ether gave 16.5 mg (0.10 mmol, 1.7%) of thianthrene 5-oxide, and elution with acetone gave 283 mg (0.60 mmol, 21%) of the dihydrate of 5-(*p*-*N,N*-dimethylaminophenyl)thianthrenium perchlorate (**2f**), mp 115–116° (aqueous ethanol), ultraviolet λ_{max} (acetonitrile) 316 nm (10^{-4} ϵ 3.2), 223 (5.2).

Anal. Calcd for $C_{20}H_{18}NS_2ClO_4 \cdot 2H_2O$: C, 49.6; H, 4.58; N, 2.89; S, 13.2; Cl, 7.32. Found: C, 50.0; H, 4.93; N, 2.98; S, 13.09; Cl, 7.10.

The green, benzene-insoluble solid was identified as tetramethylbenzidine cation radical perchlorate (**10**) by comparison with authentic **10** (see below).

Reaction of 1 with *N,N,N′,N′*-Tetramethylbenzidine (TMB). To a solution of 1.00 g (3.20 mmol) of **1** in 30 ml of acetonitrile was added 1.20 g (5.00 mmol) of TMB. The solution immediately turned dark green, and during 10 min of stirring a dark green solid separated. This was filtered and washed with benzene and ether, giving 1.14 g (3.40 mmol, 106%) of TMB cation radical perchlorate (**10**), with ultraviolet spectrum in nitromethane identical with that in the literature.[19] The behavior of **10** was also consistent with the literature. Thus, attempts to crystallize **10** from aqueous DMSO caused its reduction to TMB. Attempts to crystallize **10** from ethanol led also to reduction and the formation of impure $TMBH^{-}ClO_4^{-}$, identified by its ultraviolet spectrum.

Authentic samples of $TMBH^{+}$, ClO_4^{-}, and $TMB2H^{2+}2ClO_4^{-}$ were prepared. The former, a pale yellow solid, had mp 245–247° dec (ethanol), λ_{max} (acetonitrile) 312, 242, and 239 nm. The latter, yellow needles, had mp 280–281° dec (ethanol), λ_{max} (acetonitrile) 243 nm (broad).

Kinetics. Phenol was distilled from calcium chloride, anisole was distilled, and acetanilide was recrystallized from ethanol. Solutions of **1** and solutions of nucleophiles of known concentration were prepared on a vacuum line in septum-capped flasks from which samples could be withdrawn directly for use in the syringes of the stopped-flow apparatus. The solvent acetonitrile was used for these solutions was Eastman Kodak Spectrograde quality, and was finally dried on the vacuum line by distillation from a solution of **1**.

Kinetics were measured on a Durrum-Gibson Model D-110 stopped-flow spectrometer connected to a Tetronix Model 5103N storage oscilloscope. Solutions were transferred from the storage flasks to the spectrometer with 10-ml syringes. The injection block and cell were water jacketed at 25°. The photomultiplier voltage was adjusted to provide an output of 10.0 V when a solution of zero absorbance was in the cell. All measurements were made with the spectrometer amplifier in the absorbance mode and the oscilloscope set for as nearly full-scale output as possible. Oscilloscope traces were photographed for later data reduction. In most cases about 20 points were taken for each run and the results were analyzed by least-squares and graphic techniques. All data given in Table I are from least-squares treatment. The extinction coefficient of the cation radical at 542 nm were assumed to be 8.5 × 10^3.[4]

Registry No.—**1**, 212999-20-7; **2b**, 51608-82-3; **2c**, 51608-83-4; **2d**, 51608-85-6; **2e**, 51608-87-8; **2f**, 51608-89-0; **2g**, 51608-91-4; acetanilide, 103-84-4; phenol, 108-95-2; anisole, 100-66-3; *o*-chlorophenol, 95-57-8; *o*-*tert*-butylphenol, 88-18-6; hydrazobenzene, 122-66-7; *N,N*-dimethylaniline, 121-69-7; *N,N,N′,N′*-tetramethylbenzidine, 366-29-0.

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Ion Radicals. XXX. Reactions of Thianthrene Cation Radical Perchlorate with Amino Compounds[1,2]

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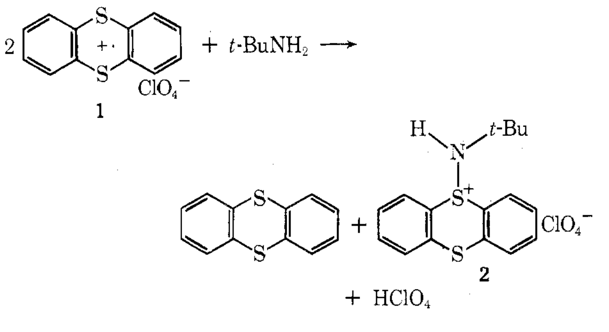
Reaction of thianthrene cation radical perchlorate (**1**) with *tert*-butylamine in acetonitrile solution gave equimolar amounts of thianthrene and 5-(*tert*-butylamino)thianthrenium perchlorate (**2**) in quantitative yields. Similarly, dimethylamine, carbazole, and cyanoacetamide gave, respectively, 5-(dimethylamino)- (**4**) and 5-carbazol-9-ylthianthrenium perchlorate (**5**) and 5-[(cyanoacetyl)imino]-5,5-dihydrothianthrene (**6**). Reaction of **1** with methylamine, ethylamine, propylamine, and cyclohexylamine gave thianthrene and 5,5-dihydro-5-(5-thianthreniumylimino)thianthrene perchlorate (**7**) in good yields. Compound **7** is ordinarily obtained by reaction of **1** with ammonia. Precautions were taken to eliminate the presence of ammonia in the amines used, and the way in which they give rise to **7** is being sought.

Very few reactions of organic cation radicals with amines are known. For the most part reactions have been of aromatic cation radicals with pyridine and methylpyridines, and many of these have been carried out electrochemically.[3-9] We have reported the reaction of the thianthrene and phenothiazine cation radicals with pyridine,[10] and the reaction of the thianthrene cation radical with ammonia.[11] There are in the literature, particularly the electrochemical, examples of oxidative dimerization of aromatic amines which may be interpreted as involving in one of the steps the reaction of the arylamine with its cation radical.[12]

As far as we know, however, reactions of cation radicals with aliphatic amines and amino compounds have not been reported. We have now found that some amines react quantitatively with the thianthrene cation radical perchlorate (**1**) to give sulfilimine derivatives. The overall stoichiometry is given for *tert*-butylamine in eq 1. The reaction occurred rapidly (too rapidly for stopped-flow kinetic measurements), and gave 5-(*tert*-butylamino)thianthrenium perchlorate (**2**). Analogous reactions with dimethylamine, carbazole, and cyanoacetamide gave the compounds **4**, **5**, and **6**.



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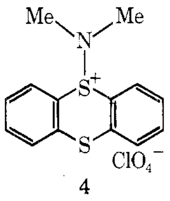

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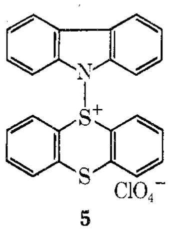

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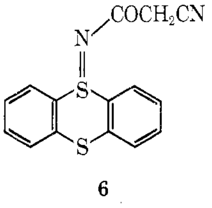

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The mechanism of these reactions is not known. We have previously interpreted the reaction of **1** with ammonia as involving the thianthrene dication, formed by disproportionation of the cation radical, but we have not been able to verify this kinetically. Reactions of **1** with ammonia, *tert*-butylamine, and dimethylamine have been too fast for us to follow even with stopped-flow techniques. Attempts to overcome the problem by going to very low concentrations of **1** ($<10^{-6}$ *M*) were made unreliable by competitive reaction of **1** with residual water in the dried solvents. By analogy with our interpretation of the ammonia reaction, the present reactions would follow eq 2 and 3, leading to the compounds **2**, **4**, **5**, and **6**, depending on whether R_1 = H or not. It is noteworthy that