tinction 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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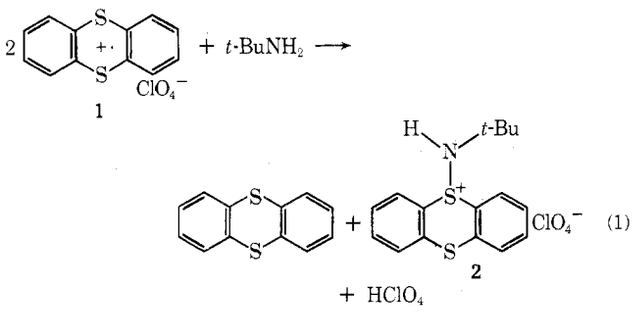
Reaction of thianthrene cation radical perchlorate (**1**) with *tert*-butylamine in acetonitrile solution gave equimolar amounts of thianthrene and 5-(*tert*-butylamino)thianthrenium perchlorate (**2**) in quantitative yields. Similarly, dimethylamine, carbazole, and cyanoacetamide gave, respectively, 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.

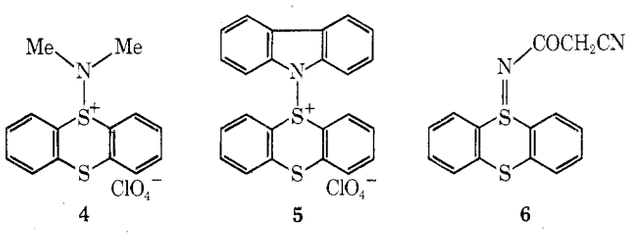
Very few reactions of organic cation radicals with amines are known. For the most part reactions have been of aromatic cation radicals with pyridine and methylpyridines, and many of these have been carried out electrochemically.[3-9] We have reported the reaction of the thianthrene and phenothiazine 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

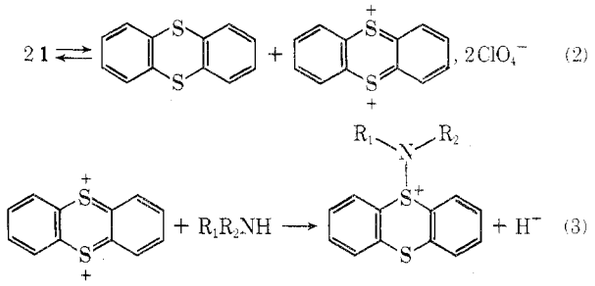


(1)

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**.



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

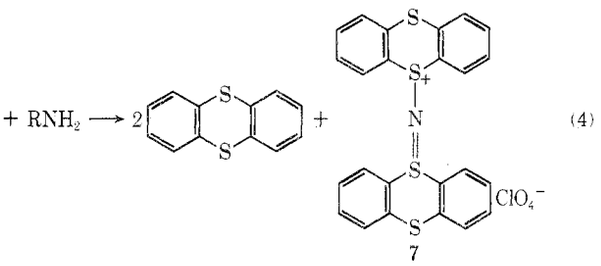


(2)

(3)

the sulfilimine **3** must be significantly basic, since the product isolated from reaction with *tert*-butylamine is protonated **3** (*i.e.*, **2**).

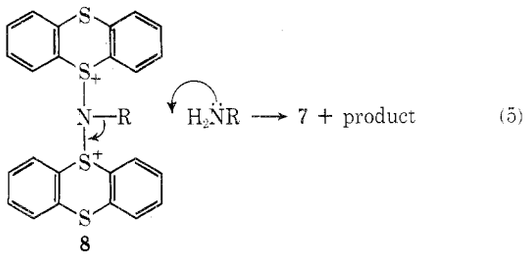
We are surprised that reaction with so weak a base as cyanoacetamide occurs. We were also surprised to find that reaction with methylamine, ethylamine, propylamine, and cyclohexylamine gave not analogs of **2** and **4** but the dealkylated product 5,5-dihydro-5-(5-thianthreniumylimino)thianthrene perchlorate (**7**), eq 4. We have



(4)

7

tried to eliminate the likelihood that **7** was formed from reaction with ammonia as an impurity in the amines. The amines were stored over ammonia-absorbing molecular sieve, methylamine was used directly from a commercial supply and also generated from its recrystallized hydrochloride, and propylamine and cyclohexylamine were redistilled. It is possible that the product of reaction of these amines with **1** has initially the structure **8**, from which the alkyl group is eliminated, as shown in eq 5, as



(5)

8

an olefin or dialkylamine. Searches for dimethylamine, dicyclohexylamine, and cyclohexene as products in the appropriate cases, however, have been so far unsuccessful.

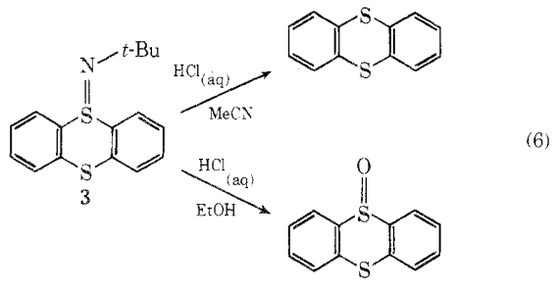
Reaction of **1** with carbazole gave not only **5** but also a green solid which gave an esr signal and is thought to be the cation radical perchlorate of a carbazole dimer. This product was not examined further.

Reaction of **1** with urea gave a product whose identity is still unknown to us.

Compound **2** was deprotonated by sodium hydroxide, giving the *tert*-butylsulfilimine **3**.

Reaction of **3** (and **2**) in acetonitrile solution with cold dilute hydrochloric acid gave thianthrene, while warming **3** in ethanol with concentrated hydrochloric acid gave 90% of thianthrene 5-oxide and only 8% of thianthrene (eq 6).

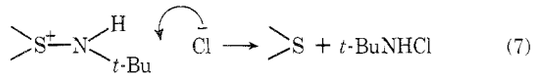
Alkyl-substituted sulfilimines are not readily made[13] and their chemistry has not been explored very much.[14] Diethylsulfilimine is reported to form *N*-chlorodiethylsulfilimine when treated with 0.1 *N* hydrochloric acid,[15] and diphenylsulfilimine to be hydrolyzed to diphenyl sulfoxide



(6)

3

when heated with 20% sulfuric acid.[16] Our present experience suggests that displacement of thianthrene from the protonated sulfilimine by chloride ion may occur (eq 7), and we are exploring this possibility.



(7)

Experimental Section

Thianthrene cation radical perchlorate (**1**) was prepared as described earlier.[17] Acetonitrile was Eastman Kodak Spectrograde and was stored over Linde 4A molecular sieve in a septum-capped bottle. Nitromethane was Eastman Kodak Spectrograde and was also stored over molecular sieve after drying over phosphorus pentoxide and distilling twice. Methylamine, dimethylamine, and ethylamine were Matheson anhydrous gases. Propylamine (98%), *tert*-butylamine (99+%), and carbazole (99+%) were from Aldrich. Cyclohexylamine and cyanoacetamide were from Eastman Organic Chemicals.

All column chromatography was performed with Merck silica gel either 30–70 ASTM mesh, 0.2–0.5 mm (Cat. No. 7733), or 70–325 ASTM mesh, 0.05–0.2 mm (Cat. No. 7734).

Reaction of 1 with *tert*-Butylamine. To a stirred solution of 1.37 g (4.30 mmol) of **1** in 40 ml of acetonitrile, protected by a drying tube, was added 1 ml (*ca.* 9.52 mmol) of *tert*-butylamine. The purple solution became pale yellow immediately and thianthrene precipitated. After 5 min the solution was rinsed from the flask with solvent acetone and evaporated, and the residue was chromatographed. Elution with benzene gave 480 mg (2.2 mmol, 102% of theory) of thianthrene. Elution with ether gave 10 mg (0.043 mmol, 1%) of thianthrene 5-oxide. Elution with acetone gave 820 mg (2.1 mmol, 100% of theory) of 5-(*tert*-butylamino)thianthrenium perchlorate (**2**), mp 203.5–204.5° (aqueous ethanol), ultraviolet λ_{max} (acetonitrile) 224 nm (10^{-4} ϵ 2.0), 254 (1.0), 289 (0.54), and 326 (0.34).

Anal. Calcd for $C_{16}H_{18}NS_2ClO_4$: C, 49.5; H, 4.67; N, 3.71; S, 16.5; Cl, 9.14. Found: C, 49.6; H, 4.81; N, 3.69; S, 16.3; Cl, 9.21.

Reaction of 2 with Base. Formation of 5-(*tert*-Butylimino)-5,5-dihydrothianthrene (3). A mixture of 98 mg (0.25 mmol) of **2** in 10 ml of ethanol and 3 ml of 30% aqueous sodium hydroxide was refluxed for 5 hr. Concentration gave a white solid, which was filtered, washed with water, and dried to give 72 mg (0.25 mmol, 100%) of **3**: mp 148–149° (aqueous DMSO); parent mass peak *m/e* 287.08; ultraviolet λ_{max} (acetonitrile) 249 nm (ϵ 1.8×10^3), 288 (weak, broad).

Anal. Calcd for $C_{16}H_{17}NS_2$: C, 66.8; H, 5.96; N, 4.87; S, 22.3. Found: C, 66.9; H, 6.16; N, 4.88; S, 22.1.

Reaction of 3 with Acids. Addition of 1 drop of concentrated hydrochloric acid to a 3-ml cuvette containing **3** in acetonitrile (4.23×10^{-5} *M*) caused within the time of recording the spectrum a change of the spectrum from that of **3** (249 nm) to that of thianthrene (256 nm). Addition of 1 drop of 1.2% hydrochloric acid to a similar solution caused the spectrum to become immediately that of protonated **3** (*cf.* **2**) and then to change slowly to that of thianthrene, going through an isosbestic point at 236 nm. Addition of 1 drop of 70% perchloric acid to a similar solution caused the spectrum to change to that of **2**. Addition of 1 drop of 0.15% hydrochloric acid gave also the spectrum of the protonated ion (**2**), namely λ_{max} 225, 255, 289, and 326 nm. In contrast, a solution of 58 mg (0.20 mmol) of **3** in 15 ml of ethanol containing 10 drops of concentrated hydrochloric acid was warmed for 20 min on the water bath. The solution was then evaporated in the rotary evaporator at reduced pressure, and the white solid residue was washed with water several times, dried, and chromatographed on silica gel to give 3.7 mg (0.017 mmol, 8%) of thianthrene and 43.4 mg (0.19 mmol, 95%) of thianthrene 5-oxide, identified by its ultraviolet spectrum and mp 140–143°.

Reaction of 1 with Dimethylamine. A stream of dry dimethylamine was bubbled into a solution of 1.65 g (5.2 mmol) of 1 in 80 ml of acetonitrile. The purple solution became pale yellow almost instantly. The reaction mixture was worked up as before to give 834 mg (3.9 mmol, 156%) of thianthrene, 70 mg (0.3 mmol, 5.8%) of thianthrene 5-oxide, and 465 mg (1.3 mmol, 57%) of 5-(dimethylamino)thianthrenium perchlorate (4), mp 139–140° (aqueous ethanol), ultraviolet λ_{max} (acetonitrile) 226 nm (10^{-3} ϵ 0.29), 259 (9.0), 300 (7.0), 332 (4.0).

Anal. Calcd for $C_{14}H_{14}NS_2ClO_4$: C, 46.7; H, 3.92; N, 3.89; S, 17.8; Cl, 9.85. Found: C, 46.4; H, 4.01; N, 4.07; S, 17.9; Cl, 9.97.

Reaction of 1 with Carbazole. To a solution of 1.01 g (3.2 mmol) of 1 in 30 ml of acetonitrile was added 552 mg (3.3 mmol) of solid carbazole. The solution turned green immediately and a copious dark green precipitate formed. This was filtered after stirring for 10 min and washed with benzene. The green solid (178 mg) gave a single-line esr spectrum. Evaporation of filtrate and washings gave a yellow-green residue. Chromatography gave with benzene 766 mg of a mixture of thianthrene and carbazole which could not be separated; with ether 19 mg (0.08 mmol, 2.5%) of thianthrene 5-oxide; and with acetone 932 mg (1.9 mmol, 121%) of crude 5-carbazol-9-ylthianthrenium perchlorate (5), mp 264–265° dec (methanol), ultraviolet λ_{max} (acetonitrile) 275 nm (10^{-3} ϵ 43), 318 (sh, 6.4).

Anal. Calcd for $C_{24}H_{16}NS_2ClO_4$: C, 59.6; H, 3.34; N, 2.91; S, 13.3; Cl, 7.35. Found: C, 59.6; H, 3.73; N, 3.06; S, 13.7; Cl, 7.23.

Reaction of 1 with Cyanoacetamide. A solution of 1.03 g (3.3 mmol) of 1 in 30 ml of acetonitrile and 340 mg (4.0 mmol) of solid cyanoacetamide were used. The purple color of the solution became pale purple only after 40 min of stirring. Much white solid formed. Evaporation gave a mixture of white and purple solids, which became pale yellow on trituration with acetone. Chromatography gave, with benzene, 381 mg (1.8 mmol, 110%) of thianthrene; with ether, 17.7 mg (0.076 mmol, 3%) of thianthrene-5-oxide; with ether–acetone (1:1) 162 mg (1.9 mmol) of cyanoacetamide; and with acetone 508 mg (1.6 mmol, 103%) of 5-[(cyanoacetyl)imino]-5,5-dihydrothianthrene (6): mp 214–215° dec (DMSO); ultraviolet λ_{max} (acetonitrile) 282 nm (ϵ 4.0×10^3); parent mass peak m/e 282.02.

Anal. Calcd for $C_{15}H_{10}N_2S_2O$: C, 58.4; H, 3.26; N, 9.08; S, 20.8. Found: C, 58.8; H, 3.68; N, 9.05; S, 21.2.

Compound 6 was recovered quantitatively after being refluxed for 24 hr in 10 ml of ethanol containing 1 ml of 30% sodium hydroxide. In contrast, treatment of 3 ml of a solution of 6 in acetonitrile with 1 drop of 10% hydrochloric acid caused the rapid appearance of the thianthrene ultraviolet spectrum.

Reaction of 1 with Methylamine. A. Methylamine gas (Matheson), dried by passage through calcium chloride, was bubbled into a solution of 601 mg (1.9 mmol) of 1 in 50 ml of acetonitrile until the purple color was gone. Work-up and chromatography gave 247 mg (1.1 mmol, 118%) of thianthrene; 30.4 (0.1 mmol, 5.3%) of thianthrene 5-oxide; and 437 mg (0.80 mmol, 94%) of 5,5-dihydro-5-(5-thianthreniumylimino)thianthrene perchlorate (7), mp 239–240° dec (aqueous DMSO).

Anal. Calcd for $C_{24}H_{16}NS_4ClO_4$: C, 52.8; H, 2.93; N, 2.56; S, 23.5; Cl, 6.49. Found: C, 52.7; H, 2.94; N, 3.14; S, 23.4; Cl, 6.56.

B. Methylamine gas was generated by addition of 50% sodium hydroxide solution to solid methylamine hydrochloride, dried by passage through calcium sulfate, and used as above with 1.06 g (3.40 mmol) of 1 in 80 ml of acetonitrile. Work-up gave with benzene 389 mg (1.80 mmol) of thianthrene, with chloroform 37.1 mg (0.16 mmol) of thianthrene 5-oxide, and with acetone 575 mg (1.10 mmol) of 7.

Reaction of 1 with Ethylamine. Ethylamine gas (Matheson) was used as above with 1.44 g (4.6 mmol) of 1 in 50 ml of nitromethane. Work-up gave 570 mg (2.6 mmol, 114%) of thianthrene, 47.1 mg (0.20 mmol, 4.3%) of thianthrene 5-oxide, and 611 mg (1.1 mmol, 52%) of 7.

Reaction of 1 with Propylamine. Propylamine, 0.106 g (1.8 mmol), was added to a solution of 2.19 g (6.9 mmol) of 1 in 75 ml of acetonitrile. The purple color disappeared only slowly. Work-up gave 1.05 g (4.9 mmol, 143%) of thianthrene, 21.4 mg (0.09 mmol, 1.5%) of thianthrene 5-oxide, and 1.13 g (2.1 mmol, 63%) of 7.

Reaction of 1 with Cyclohexylamine. A. Reaction of 572 mg (1.8 mmol) of 1 in 30 ml of nitromethane with 0.8 ml (*ca.* 7.0 mmol) of cyclohexylamine gave immediately a pale yellow solution. Work-up gave 226 mg (1.0 mmol, 111%) of thianthrene, 7.2 mg (0.03 mmol, 1.7%) of thianthrene 5-oxide, and 326 mg (0.6 mmol, 69%) of 7.

B. Cyclohexylamine was redistilled and passed through a column packed with Linde molecular sieve (Type 4A). Enough of the amine was added to a solution of 1.1 g (3.5 mmol) of 1 in 25 ml of acetonitrile until the color of the solution was discharged. The solution was evaporated under vacuum and the pale brown residue was chromatographed on silica gel. Elution with benzene gave 514 (2.4 mmol) of thianthrene; elution with ether gave 34 mg (0.1 mmol) of thianthrene 5-oxide; and elution with acetone gave 707 mg (1.3 mmol) of 7.

Registry No.—1, 35787-71-4; 2, 51608-74-3; 3, 51608-75-4; 4, 51608-77-6; 5, 51608-79-8; 6, 51608-80-1; 7, 35612-51-2; *tert*-butylamine, 75-64-9; dimethylamine, 124-40-3; carbazole, 86-74-8; cyanoacetamide, 107-91-5; methylamine, 74-89-5; ethylamine, 75-04-7; propylamine, 107-10-8; cyclohexylamine, 108-91-8.

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