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CATION RADICALS. XXVII. SULFILIMINE DERIVATIVES FROM REACTION OF THIANTHRENE AND N-PHENYLPHENOTHIAZINE CATION RADICALS WITH t-BUTYLAMINE AND DIMETHYLAMINE

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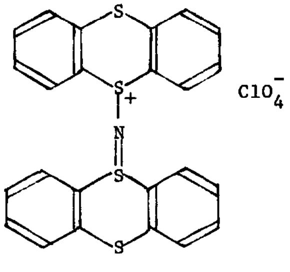
Although N-tosyl sulfilimines, *e.g.*, Ar_2S=NTs and R_2S=NTs are reasonably easily made from reaction of diaryl, dialkyl, and alkyl aryl sulfides with chloramine-T,[1-3] neither sulfilimines themselves nor N-alkyl- and N-aryl sulfilimines are as easily made. Reaction between dimethylsulfoxide and arylamines in the presence of P_2O_5 and triethylamine leads to N-aryl dimethylsulfilimines, Me_2S=NAr.[4,5] Dialkylsulfilimines, R_2S=NH, are formed by reaction of dialkyl sulfides with hydroxylamine O-sulfonic acid and sodium methoxide.[6] Decomposition of N-tosyl derivatives in concentrated sulfuric acid leads to sulfilimines, *e.g.*, $(C_6H_5)_2S$=NH, and this is reported as the first general method of preparing sulfilimines.[7] A general method for preparing N-substituted sulfilimines has recently been published by Martin and consists of reaction of a diphenyldialkoxysulfurane with amides[8] or amines[9] in DMF solution.

It was found recently that the thianthrene cation radical perchlorate (1) reacted with ammonia to form 5,5-dihydro-5-(5-thianthreniumylimino)-thianthrene perchlorate (2).[10] An entirely analogous reaction occurs with N-phenylphenothiazine cation radical perchlorate (3).[11] We now find that 1 and 3 react with *t*-butylamine in acetonitrile solution to form the N-*t*-butyl derivatives (4) and (5) of the corresponding sulfilimines. The stoichiometry of



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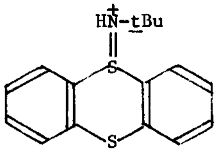

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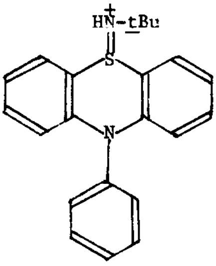

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these reactions follows equation (1), in which $R_2S^{\cdot +}$ represents the cation radical. Based on

$$2R_2S^{\cdot+}ClO_4^- \;+\; 2\underline{t}BuNH_2 \;\rightarrow\; R_2S \;+\; R_2S{=}\overset{+}{N}H\underline{t}BuClO_4^- \;+\; \underline{t}Bu\overset{+}{N}H_3ClO_4^- \qquad (1)$$

this stoichiometry, 1 gave 100% of the anticipated thianthrene and 97% of 4. Reaction of 3 gave quantitative yields of N-phenylphenothiazine and 5. Each pair of products was separated by column chromatography.

Compound 4 had mp 203.5-204.5 (aqueous ethanol).

Anal. Calcd. for $C_{16}H_{18}NS_2ClO_4$: C, 49.54; H, 4.67; N, 3.71; S, 16.53; Cl, 9.14.

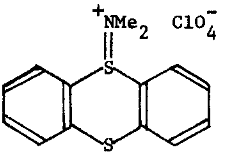
Found: C, 49.58; H, 4.81; N, 3.69; S, 16.26; Cl, 9.21.[12]

Compound 5 had mp 198-199° (ethanol-ether).

Anal. Calcd. for $C_{22}H_{23}N_2SClO_4$: C, 59.12; H, 5.18; N, 6.26; S, 7.17; Cl, 7.93.

Found: C, 58.78; H, 5.10; N, 6.49; S, 7.45; Cl, 8.23.

Reaction of 1 with excess of dimethylamine in acetonitrile led to the perchlorate of the N,N-dimethyl derivative (6), mp 139-140° (aqueous ethanol).



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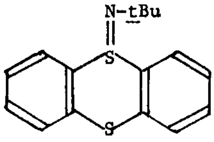

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Anal. Calcd. for $C_{14}H_{14}NS_2ClO_4$: C, 46.72; H, 3.92; N, 3.89; S, 17.81; Cl, 9.85.

Found: C, 46.41; H, 4.01; N, 4.07; S, 17.90; Cl, 9.97.

In this reaction it appears that some of the cation radical is reduced to thianthrene. That is, the amount of 6 isolated was 56.5% of that anticipated from equation (1), whereas the amount of thianthrene was 152% of that anticipated. The isolations accounted for all of the 1 used.

The formation and isolation of compounds 4, 5 and 6 by column chromatograph were carried out without difficulty, and may represent a method of preparing analogous compounds. Instead of using isolated cation radical salts, it may be possible to prepare the cation radical *in situ*, as in some reactions of the perylene cation radical.[13] This approach will be explored.

The chemistry of N-substituted sulfilimines is not well documented.[4] Compound 4 is neutralized by base to form the N-*t*-butylsulfilimine (7), mp 148-149° (aqueous DMSO).

Anal. Calcd. for $C_{16}H_{17}S_2N$: C, 66.85; H, 5.96; N, 4.87; S, 22.30.

Found: C, 66.93; H, 6.16; N, 4.88; S, 22.07.

This sulfilimine is stable to boiling in aqueous ethanolic NaOH, but is readily decomposed by HCl. A few drops of aqueous HCl converts 7 in MeCN into thianthrene. The reaction can be followed spectroscopically and shows the conversion of protonated-7 (λ_{max} 225 nm) into thianthrene (λ_{max} 256 nm) via a clean isosbestic point. The mechanism of this reductive deamination is being explored. In contrast, warming 7 with a few drops of conc. HCl in ethanol gave 90% of thianthrene 5-oxide and only 8% of thianthrene.

In contrast with reaction of 1 with the two title amines, reaction with methylamine gave 2 ; the course of this reaction is being studied.

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