

Reactions of Thianthrene Cation radical Perchlorate with 1-Alkyl-4-Arenesulfonylaminobenzenes

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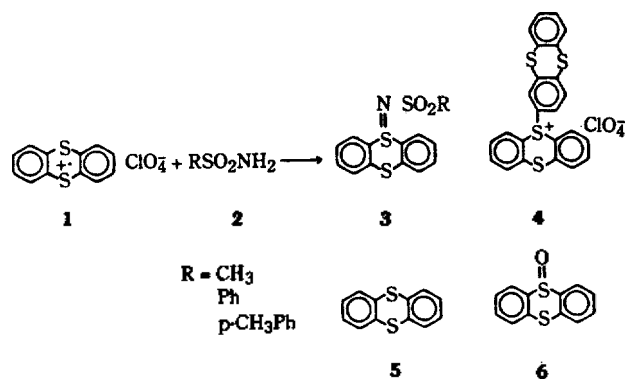
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Reaction of thianthrene cation radical perchlorate (**1**) with 1-methyl-4-benzenesulfonylaminobenzene (**10**) afforded thianthrene (**5**), *N*-(4-tolyl)-*N*-thianthrenylbenzenesulfonamide (**14**), 1-methyl-3-[*N*-(4-tolyl)-*N*-benzenesulfonyl-amino-4-benzenesulfonylaminobenzene (**16**), *cis*-thianthrene-5,10-dioxide (**17**), 5-(3'-methyl-6-benzenesulfonylaminobenzene)thianthrenium perchlorate (**18**), and benzenesulfonate. In the meantime, reaction of **1** with 1-ethyl-4-benzenesulfonylaminobenzene (**12**) afforded **5**, 1-ethyl-3-[*N*-(4-ethylphenyl)-*N*-benzenesulfonyl]amino-4-benzenesulfonylaminobenzene (**19**), 1-benzenesulfonyl-amino-4-[1-(2-benzenesulfonylamino-5-ethylphenyl)ethyl]benzene (**20**), and 1-(1-acetamidoethyl)-4-benzenesulfonylaminobenzene (**21**). The formations of these products except for **18** and benzenesulfonate could be rationalized by assuming a sulfonamidyl radical as an intermediate.

Introduction

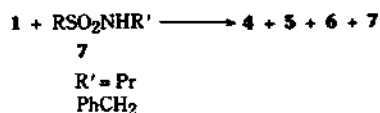
Thianthrene cation radical perchlorate (**1**) is one of the most stable crystalline sulfur containing cation radical, so that reactions with **1** have been much exploited.¹

We have previously reported the reactions of **1** with *N*-free sulfonamides (**2**) in which *N*-alkyl- or arylsulfonylsulfonamides (**3**) were obtained in good yields, although it took 3 months to observe complete discharge of dark purple color of **1** in acetonitrile (Scheme 1).



Scheme 1

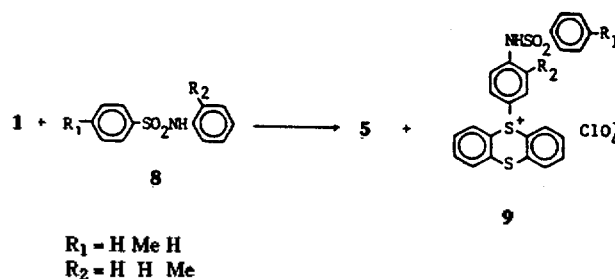
N-Alkylsulfonamides (**7**), however, did not react with **1** and the unreacted sulfonamides were recovered quantitatively, along with the isolation of **4**, **5**, and **6** (Scheme 2).



Scheme 2

When *N*-arenesulfonylamines (**8**) without having any substituent at para position of a *N*-aryl group³ were allowed to react with **1** at the same conditions as in the previous reactions foregoing, 5-(*p*-arenesulfonylaminophenyl)thianthrenium perchlorates (**9**) were formed within an hour (Scheme 3).

Since benzene does not react with **1**, one may realize that arenesulfonylamino groups activate the benzene ring. In order to see a substituent effect present at para position of a



Scheme 3

N-aryl group, methyl, ethyl, isopropyl, and nitro group were introduced at the para position of a *N*-aryl group. The results obtained are described in this report.

Experimental

Materials and Apparatus. Thianthrene (**5**) was synthesized from the reaction of benzene and sulfur powder in the presence of anhydrous aluminum chloride according to the literature.⁴ Thianthrene cation radical perchlorate (**1**) was prepared by the method previously described.⁵ Acetonitrile was dried by refluxing over P_2O_5 for 3 h, followed by refluxing over calcium hydride and distilled twice. The distillate was stored over molecular sieve (4 Å) in a septum-capped bottle. All solvents used for the column chromatography were distilled before use.

Infrared spectra were recorded using a Perkin-Elmer model 283 infrared spectrometer. ^1H NMR spectra were obtained using a Varian EM 360A spectrometer and chemical shifts were represented in ppm relative to an internal standard (TMS). UV spectra were recorded on Beckman 5270 spectrometer. Melting points were measured using Fisher-Johns melting point apparatus and are not calibrated.

Thin layer chromatography was performed with Merck silica gel (Art. 7739) and the chromatogram was visualized by a mineral uv lamp. Column chromatography was carried out using Merck silica gel (Art. 7733). All solvents were specified in each case.

(1) 1-Methyl-4-benzenesulfonylaminobenzene (10). To a solution of 2.01 g (18.7 mmol) of *p*-toluidine in 50 ml of 10% potassium hydroxide was added 2.4 ml (18.8 mmol) of benzenesulfonyl chloride. The mixture was stirred until the

odor of benzenesulfonyl chloride disappeared, followed by adjusting pH of the solution to be 4 using 25% aq. hydrochloric acid. Yield was 3.92g (16.8 mmol, 90%); mp 123-123.5°C (aq. ethanol) (lit.⁶ 121°C); IR (KBr) 3260 (NH stret.), 1330 (SO₂ stret.), 1160 (SO₂ stret.) cm⁻¹; ¹H NMR (CDCl₃) δ 2.23 (s, 3H, CH₃), 7.00-7.83 (m, 10H, NH and aromatic).

(2) **1-Nitro-4-(p-toluenesulfonylamino)benzene (11)**. To a solution of 3.82 g (20.0 mmol) of p-toluenesulfonyl chloride and 2.73 g (19.8 mmol) of p-nitroaniline was added 5 ml of pyridine. The mixture was warmed for 20 min in a water bath, followed by washing with water. Dark yellow solid (4.77 g, 17.2 mmol, 86%) was decolorized and recrystallized from ethanol: mp 189-190°C (lit.⁷ 191-192°C); IR (KBr) 3320 (NH stret.), 1520, 1330 (SO₂ stret.), 1160 (SO₂ stret.) cm⁻¹; ¹H NMR (CDCl₃ + DMSO-d₆) δ 2.39 (s, 3H, CH₃), 7.31-8.21 (m, 8H, aromatic), 10.40 (s, 1H, NH).

(3) **1-Ethyl-4-benzenesulfonylamino benzene (12)**. To a solution of p-ethylaniline in 40 ml of pyridine was added the same number of moles of benzenesulfonyl chloride. The reaction mixture was allowed to stand at room temperature for 24 h. The red solution was poured to a large volume of an ice-water containing excess hydrochloric acid enough to neutralize the pyridine and allowed to stand overnight. The crude sulfonamide was filtered and washed with water, followed by dissolving in 5% NaOH solution. The sulfonamide was recovered by adding slowly hydrochloric acid with vigorous stirring until the solution was acidic to litmas paper. Recrystallization from aq. ethanol afforded a white needle type crystals: Yield 95%; mp 79.5-80°C; ¹H NMR (CDCl₃) δ 1.14 (t, 3H, CH₃), 2.53 (q, 2H, CH₂), 6.90-7.20 (s, 4H, aromatic), 7.30-7.60 (m, 3H, aromatic), 7.70-8.00 (m, 3H, NH and aromatic); IR (KBr) 3200 (NH stret.) 1310 (SO₂ stret.), 1130 (SO₂ stret.) cm⁻¹.

(4) **1-Isopropyl-4-benzenesulfonylamino benzene (13)**. Using the same procedure as described in (3), was obtained 95% yield of the desired compound: mp 110-110.5°C (aq. ethanol); ¹H NMR (CDCl₃) δ 1.17 (d, 6H, 2CH₃), 2.90 (m, 1H, CH), 6.93-7.20 (s, 4H, aromatic), 7.33-7.68 (m, 4H, NH and aromatic), 7.68-8.00 (m, 2H, aromatic); IR (KBr) 3260 (NH stret.), 1150 (SO₂ stret.), 1330 (SO₂ stret.) cm⁻¹.

(5) **Reaction of 1 with 1-Methyl-4-benzenesulfonylaminobenzene (10)**. To a stirred solution of 1.395 g (4.42 mmol) of **1** in 25 ml of acetonitrile was added 2.165 g (8.75 mmol) of **10**. After the reaction flask was stoppered with a septum, stirring was continued until the color of **1** had completely disappeared. It took 13 days and the solution of the reaction mixture was dark green. The solvent was stripped off and the residue was extracted by adding chloroform (100 ml) and water (100 ml). The residue from chloroform layer was chromatographed on silica gel column (1.9 × 16 cm). Elution with hexane (50 ml × 5) gave 0.662 g (3.06 mmol) of **5**, while elution with benzene (50 ml × 8) gave 0.827 g of a mixture with three components and 0.772 g (3.31 mmol) of **10**. This mixture was rechromatographed on alumina (Merck active basic, Art. 1076, 1.9 × 12 cm) column. Elution with hexane (50 ml × 5) gave 0.078 g (0.36 mmol) of **5**, while elution with benzene (50 ml × 4) gave 0.088 g (0.19 mmol) of a white solid, identified as N-(4-tolyl)-N-thianthrenylbenzenesulfonamide (**14**): mp 171-172°C (aq. ethanol); λ_{max}^{EtOH} (log ε) 264 (4.32), 243 (4.00) nm; ¹H NMR (CDCl₃) δ 2.31 (s, 3H, CH₃), 7.05-7.87 (m, 16H, aromatic); IR (KBr) 1165 (SO₂ stret.), 1350 (SO₂ stret.) cm⁻¹; MS, m/e (rel. intensity)

320(B), 461 (44.3, M⁺). From the other benzene fraction was obtained 0.012 g (0.048 mmol) of thianthrene-5,5-dioxide (**15**): 168-169°C mp (aq. ethanol) (lit.⁸ 168-169°C); IR (KBr) 1450, 1310 (SO₂ stret.), 1160 (SO₂ stret.) cm⁻¹. Elution with acetonitrile (50 ml × 4) gave 0.70 g of a mixture of **10** and one unknown compound, which was rechromatographed on alumina (Merck active acidic, Art 1078, 1.9 × 8 cm). Elution with benzene (50 ml × 4) gave 0.157 g (0.32 mmol) of a white solid, identified as 1-methyl-3-[N-(4-tolyl)-N-benzenesulfonylamino]-4-benzenesulfonylamino benzene (**16**): mp 108-109°C (hexane-ether), ¹H NMR (CDCl₃, 100 MHz) δ 2.25 (s, 6H, 2CH₃), 6.85 (s, br, 1H, -NH, exchangeable in D₂O), 7.00-7.82 (m, 17H, aromatic); IR (KBr) 3250 (NH stret.), 1340 (SO₂ stret.), 1165 (SO₂ stret.) cm⁻¹. Elution with ether (50 ml × 5) gave 0.589 g (2.52 mmol) of **10** and 0.282 g of mixture of cis-thianthrene-5,10-dioxide (**17**) and a sticky material. Compound **17** was identified based on physical and spectral data: mp 247-248°C (aq. ethanol) (lit.⁹ 249°C); λ_{max}^{EtOH} 210 nm; ¹H NMR (CDCl₃) δ 7.63-8.17 (m, aromatic), IR (KBr) 1080 (S = O stret.), 1020 (S = O stret.) cm⁻¹. Elution with acetone gave 1.178 g of a dark brown sticky material from which 0.030 g of yellow solid was obtained by adding 1 ml of acetone. Repeat of this treatment three times afforded 0.068 g (0.12 mmol) of yellow solid containing some brown materials, which was decolorized and then recrystallized from aq. ethanol to give pale yellow solid, identified as 5-(3'-methyl-6-benzenesulfonylamino benzene)thianthrenium perchlorate (**18**): mp 168-169.5°C; λ_{max}^{EtOH} 222, 260, 315-280(sh) nm; ¹H NMR (CDCl₃) δ 2.45 (s, 3H, CH₃), 6.62 (s, 1H, NH), 7.53-8.56 (m, 15H, aromatic), 8.95-9.13 (m, 2H, 2H of 4 and 6 positions of thianthrene moiety); MS, m/e (rel. int.) 77(31.2), 212(22.9), 213(5.0), 273(22.8), 274(6.5), 286(14.9), 287(100, B), 288(31.2), 289(9.6), 305(15.8), 320(50.3), 321 (18.1), 461(31.7), 462(9.2), 463(6.1). Elution with methanol gave 0.115 g of benzenesulfonate, identified by comparing IR spectrum with that of authentic sample.

(6) **Reaction of 1 with 1-Nitro-4-(p-toluenesulfonylaminobenzene (11)**. To a stirred solution of 1.053 g (3.33 mmol) of **1** in 45 ml of acetonitrile was added 2.395 g (8.64 mmol) of **11**. This mixture was treated as in the reaction of **10** with **1**. The color of the reaction mixture was pale red after 50 days stirring. Thin layer chromatography (Kiesel gel 60, PF₂₅₄) with benzene showed four spots of which R_f values were 0.61, 0.33, 0.12 and 0, corresponding to **5**, **6**, **9**, and an unknown, respectively. The reaction mixture was worked up and the residue was chromatographed on silica gel column (3.1 × 11 cm). Elution with hexane (50 ml × 9) gave 0.272 g (1.26 mmol) of **5**, while elution with benzene (50 ml × 5) afforded 0.026 g (0.11 mmol) of **6**. Elution with ether (50 ml × 13) gave 2.322 g (7.94 mmol) of **11**. Finally elution with acetone (50 ml × 3) gave 1.103 g of dark brown sticky materials. Washing the materials with water gave 0.570 g of yellow solids, which were dissolved in a warm ethyl acetate. The ethyl acetate insoluble, white solid (0.293 g) was identified as **4** in view of physical and spectral data of the authentic sample.

(7) **Reaction of 1 with 1-Ethyl-4-benzenesulfonylaminobenzene (12)**. To a stirred solution of 2.481 g (7.86 mmol) of **1** in 50 ml of dried acetonitrile was added 2.322 g (8.88 mmol) of **12** at room temperature. The reaction was completed in 7 days and the color of the reaction mixture became pale purple. The reaction mixture was worked up as

usual and the residue was chromatographed on silica gel column (4.5 × 5 cm). Elution with n-hexane (400 ml) gave 1.494 g (6.81 mmol) of **5**, while elution with benzene (400 ml) gave a mixture of 0.50 g of unknown, showing two spots on tlc and 0.362 g (1.39 mmol) of **12**. This mixture was rechromatographed on silica gel column (0.9 × 19 cm). From benzene fractions (200 ml) was obtained 0.122 g (0.23 mmol) of a white solid, identified as 1-ethyl-3-[N-(4-ethylphenyl)-N-(benzenesulfonyl)]amino-4-benzenesulfonylamino benzene (**19**); mp 103-103.5 °C (n-hexane-cyclohexane); UV λ_{max}^{MeOH} 272 (shoulder) nm; $^1\text{H NMR}$ (CDCl_3 , 100 MHz) δ 1.08 (t, 6H, 2CH₃), 2.47 (q, 4H, CH₂), 6.84 (s, 1H, NH), 6.90-7.07 (m, 5H, aromatic), 7.22-7.58 (m, 8H, aromatic), 7.58-7.80 (m, 4H, aromatic); IR (KBr) 3290 (NH, stret.), 1353 (SO₂ stret.), 1180 (SO₂ stret.); Anal. Calcd. for C₂₉H₂₉N₂O₄S₂: C, 67.22; H, 5.42; N, 5.38; O, 12.29. Found: C, 67.51; H, 5.37; N, 4.98; O, 11.37. Later benzene fractions (200 ml) gave 0.310 g (1.19 mmol) of **12**. Elution of the original reaction mixture with methylene chloride (400 ml) gave 0.735 g of an unknown white solid: $^1\text{H NMR}$ (CDCl_3) δ 1.23(q), 2.53(q), 3.96(q), 6.23-6.57(d, aromatic), 6.67-7.14(m, aromatic), 7.14-8.00(m, aromatic). When the compound was dissolved in n-propyl alcohol for the recrystallization, purple color appeared and new good crystals 0.666 g (1.28 mmol) were obtained by the addition of n-hexane to the alcoholic solution. This compound was assigned as 1-benzenesulfonylamino-4-[1-(2-benzenesulfonylamino-5-ethylphenyl)ethyl]benzene (**20**): mp 206-206.5 °C; $\lambda_{max}^{CH_3CN}$ 264 (shoulder), 272 (shoulder) nm; $^1\text{H NMR}$ (CDCl_3 + DMSO-d₆) δ 1.22(q, 6H, 2CH₃), 2.45(q, 2H, CH₂), 4.46(q, 1H, CH), 6.56-6.78(d, 3H, aromatic), 6.78-7.00(s, 4H, aromatic), 7.18-7.80(m, 10H, aromatic), 8.62(s, 1H, NH), 9.62(s, 1H, NH); IR (KBr) 3260 (NH stret.), 1340 (SO₂ stret.), 1150 (SO₂ stret.) cm⁻¹; Anal. Calcd. for C₂₈H₂₉N₂O₄S₂: C, 64.59; H, 5.42; N, 5.38. Found: C, 64.43; H, 6.32; N, 5.21. Elution with acetone (100 ml) gave 1.51 g of a mixture with many spots on tlc. Repeated chromatography on silica gel using ethyl acetate gave 0.113 g (0.37 mmol) of a white solid, identified as 1-(1-acetamidoethyl)-4-benzenesulfonylamino benzene (**21**): mp 127.5-128 °C (isopropanol-n-hexane); UV λ_{max}^{MeOH} 265 (shoulder), 271 (shoulder) nm; $^1\text{H NMR}$ (CDCl_3 + DMSO-d₆) δ 1.22 (d, 3H, CH₃), 1.90 (s, 3H, CH₃), 4.93 (q, 1H, CH), 6.90-7.31 (s, 4H, aromatic), 7.40-7.69 (m, 3H, aromatic), 7.69-8.20 (m, 3H, NH and aromatic), 10.09 (s, 1H, NH); IR (KBr) 3290 (NH stret.), 1685 (C=O stret.), 1350 (SO₂ stret.), 1180 (SO₂ stret.) cm⁻¹. Anal. Calcd. for C₁₆H₁₆N₂O₃S: C, 60.36; H, 5.70; N, 8.80; O, 15.07. Found: C, 60.50; H, 5.87; N, 9.03; O, 15.81.

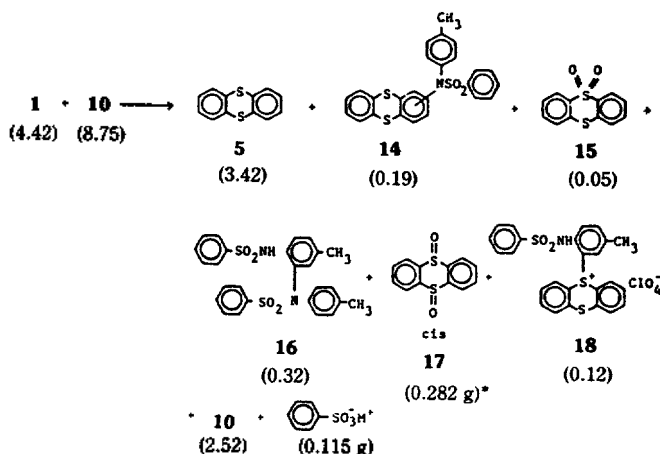
(8) Reaction of 1 with 1-isopropyl-4-benzenesulfonylamino benzene (13). To a stirred solution of 1.705 g (5.40 mmol) of **1** in 25 ml of anhydrous acetonitrile was added 2.646 g (9.61 mmol) of **13** at room temperature. The purple color of **1** turned blue in one days, followed by pale red in additional 2 days and finally colorless solution was obtained in additional 3 days. Tlc (benzene) of the reaction mixture showed four spots (R_f , 0.69, 0.49, 0.28, 0) corresponding to **5** (0.69), and **13** (0.28). However, tlc ($\text{CH}_3\text{CN}/\text{CHCl}_3$, 1/3, v/v) showed seven spots (R_f , 0.92, 0.90, 0.78, 0.21, 0.18, 0.14, 0.04). After the solvent was evaporated, in vacuo, the residue was chromatographed on silica gel column (1.9 × 10 cm). Elution with hexane (795 ml) gave 0.833 g (3.85 mmol) of **5**, while elution with benzene (600 ml) gave 1.403 g of a mixture consisting of **13** as a major and an unknown as a minor. Elution was continually performed using chloroform, methylene

chloride, acetone, and methanol. It was unsuccessful to purify any of these fractions. $^1\text{H NMR}$ spectra of each fraction did not indicate the presence of an isopropyl group.

Results and Discussion

(a) Reaction with 10

Reaction of **1** with **10** afforded several products as shown in Scheme 4.



The numbers in the parenthesis represent millimoles of the reactants and the isolated products unless otherwise specified.

*: Sticky materials included.

: M is not identified.

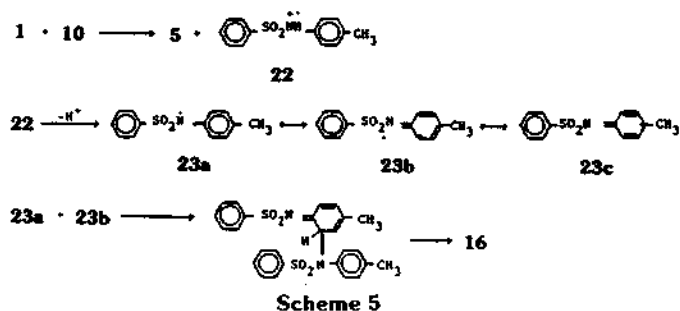
Scheme 4

Reaction of **1** with **10** proceeded rather slowly and afforded several products which were not formed in the reaction with **8**. Of these, the formation of compounds, **14**, **16**, and benzenesulfonate as well as the oxides of **5**, i.e., **15** and **17**, cannot be explained by either a disproportionation or a half-regeneration mechanism which is well-known mechanisms in the reaction of **1** with some nucleophiles.¹

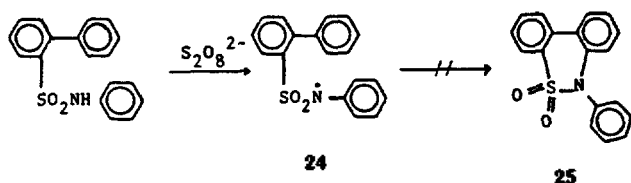
The structural assignment of **18**, analogous to **9**, was rather difficult because not only the yield was low but also it showed two sharp peaks due to perchlorate ion at 1120 and 1070 cm⁻¹ on its IR spectrum, which was prominently contrast with a broad, intense peak in the same region shown by many thianthrenium perchlorates.¹⁰ But in connection with this research we studied the reaction of **1** with **21** and obtained analogous IR and $^1\text{H NMR}$ spectra¹¹ to those of **18**.

The formation mechanism of **18** is uncertain. However, it can be explained by either a prior disproportionation or a half regeneration mechanism as in other cases.¹⁰

The formation of **16** can be rationalized by a coupling reaction between two radical species (**23a**, **23b**) which suggest that **10** is oxidized by **1** to form 1-methyl-4-benzenesulfonylamino benzene cation radical (**22**) as shown in Scheme 5.



To our knowledge, chemistry of sulfonamide cation radical has not been reported although oxidations of some sulfonamides by the oxidants such as manganese dioxide¹² and lead tetraacetate¹³ have been studied. Deprotonation of **22** gives rise to *N*-(*p*-tolyl)-benzenesulfonamidyl radical (**23**) which may be stabilized by resonance hybridizations. Sulfonamidyl radicals have been mainly generated by photolysis of *N*-halosulfonamide¹⁴ and oxidations of *N*-alkyl or -arylsulfonamides by sodium persulfate¹⁵ or hydrogen atom abstractions from *N*-monoalkylsulfonamides^{14(b)} by *t*-butoxy radical also afforded the corresponding sulfonamidyl radicals. Of these works, there is only one report regarding the *N*-arylsulfonamidyl radical¹⁵: [c,e] [1,2]thiazine 5,5-dioxide (**25**) was expected to be formed by way of 2-biphenylsulfonamidyl radical (**24**) from the reaction of *N*-phenyl 2-biphenylsulfonamide with sodium persulfate as shown in Scheme 6.

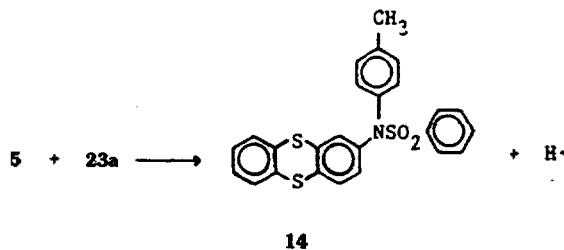


Scheme 6

Apart from the results from *N*-free and -alkyl analogs, only complex mixture was obtained. Therefore, isolation of **16** is the first demonstration of the product formed from *N*-arylsulfonamidyl radical.

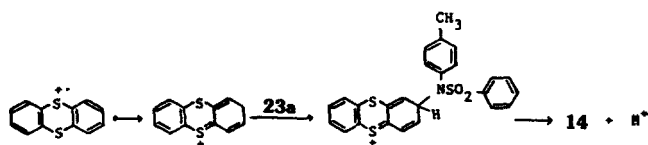
The formation of **14** can be rationalized by a sulfonamidyl radical (**23**) substitution to **5** as in the formation mechanism of the sultams in oxidation of biphenyl-2-sulfonamides.¹⁵

We do not know the substitution position of thianthrene moiety to which radical **23** is bonded. However, we prefer the structure represented by **14** simply because a large steric hindrance is expected to be avoided at 2 position of thianthrene ring as shown in Scheme 7.



Scheme 7

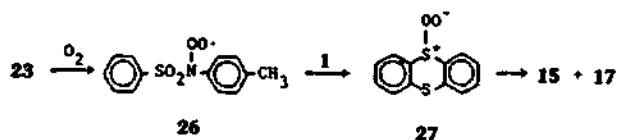
One may speculate the combination reaction between **1** and **23a** to lead **14** as shown in Scheme 8.



Scheme 8

This possibility, at present moment, cannot be excluded for the formation mechanism of **14**.

The formation of thianthrene 5,5-dioxide (**15**) and cis-thianthrene-5,10-dioxide (**17**) suggest also the involvement of a peroxy radical as we have previously proposed in the reactions of **1** with di-*t*-butyl peroxide,¹⁶ azo-bis-isobutyronitrile,¹⁷ acetyl cyanide,¹⁸ and azo-bis-2-phenoxy-2-propane.¹⁹ We believe that compounds **15** and **17** are not formed in the reactions in which no peroxy radical is produced during the course of the reaction. Therefore, Scheme 9 is proposed for the formation mechanisms of **15** and **17**.

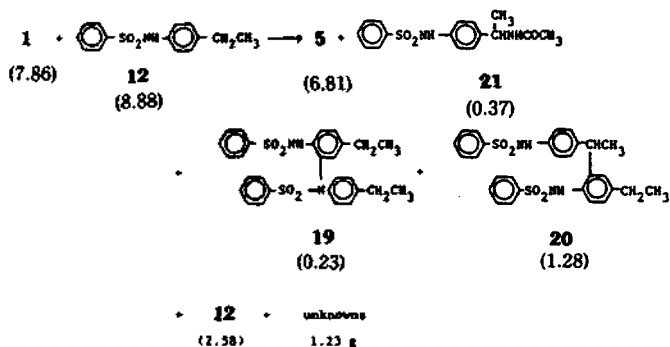


Scheme 9

Thianthrenesulfinyl oxide (**27**) was proposed as an intermediate in the reaction of **1** with superoxide.²⁰ Ando *et al.*²⁰ did not obtain **15** and **17**. Originally Foote *et al.*²¹ proposed sulfinyl oxide as an intermediate in the photooxidation of sulfides by singlet oxygen from which sulfoxide, sulfone, and sulfide were obtained and the yield of each compound varied depending on the reaction conditions. Hence the fact that Ando *et al.* did not detect **15** and **17** in their reaction is not unexpected. Since **1** does not react with triplet oxygen, the formation of **27** can be explained by assuming an intermediate, **26**, which, to our knowledge, has not been reported. However, one report shows that sulfonamidyl radical behaves unusually in the presence of oxygen. That is, Neale *et al.*^{14(b)} generated *N*-methylethanesulfonamidyl radical by photolysis of the corresponding *N*-chloro compound. The sulfonamidyl radical added to styrene but no addition product was obtained in the presence of oxygen. This result indicates that trapping of the sulfonamidyl radical by oxygen is faster than the addition reaction. Therefore, the assumption of peroxy radical, **26**, is reasonable.

(b) Reaction with **12**

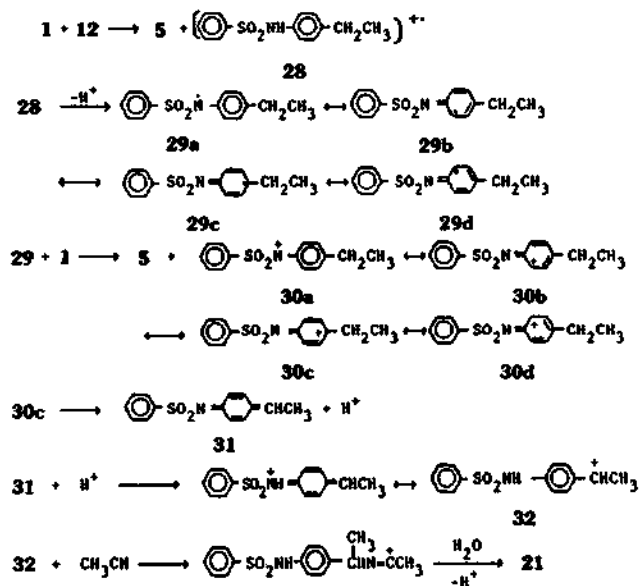
The results are summarized in Scheme 10.



Scheme 10

Compounds **19** is analogous to compound **16**, which are identified by NH stretching band at 3290 cm⁻¹ and a singlet corresponding to one proton at 6.84 ppm, exchangeable with D₂O. Compounds **20** and **21** are compounds which are not produced in the reaction of **1** with **10**. The structure of **21** was identified by the spectral data and an elemental analysis (vide supra) as well as comparison with those of the authentic sample. Since acetamido group of **21** is thought to be from

acetonitrile, one may think generation of benzylic cation (**32**) as shown in Scheme 11 via oxidation and a series of protonation-deprotonation processes.

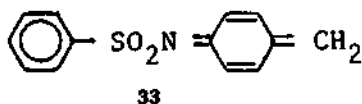


Scheme 11

It is unlikely that **30** is directly generated from **28** by loss of a hydrogen atom. In such a case, only one mole of **1** is used for the reaction of one mole of **12** through the reaction. Since 1.23 g of unknown compounds are thought to be originated from **12** in view of ^1H NMR and IR data, relatively small amounts of **12** are expected to be remained. On the other hand, two moles of **1** should be used for one mole of **12** according to Scheme 11. Therefore, unreacted **12** should be twice greater in the latter than in the former. The experimental result in which 2.58 mmol of **12** is recovered is more consistent with the latter than the former.

The intermediacy of **31** in Scheme 11 is interesting because this type of benzenesulfonimide has not been prepared although quinone imides have been attracted much attention.^{12,13(a),21}

The formation of **20** can also be explained by an electrophilic substitution of **32** to **12**. Reaction of **1** with **10** does not give the analogous compounds to **20** and **21**. This difference between two analogs, **10** and **12** may be due to the stability of the corresponding intermediates, **33** and **31**, in which **31** is more stable than **33**.

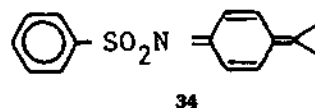


(c) Reaction with 13

Apart from the reactions with **10** and **12**, this reaction gave very complicated reaction mixture from which only **5** and unreacted **13** were identified. Compound **5** is normally eluted from n-hexane or benzene. So sufficient amounts of these solvents were used to remove **5** but even acetone fractions showed the presence of **5**. This observation indicates that acetone fraction has unknown compound(s) containing thianthrene moiety, which decompose(s) during the process of chromatography. ^1H NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$) of acetone

fraction showed a doublet at 1.2 ppm, a singlet at 2.15 ppm, a singlet at 2.65 ppm, and a multiplet at 7.69 to 8.3 ppm. Attempted recrystallizations of acetone fractions from various solvents were unsuccessful. Treatment with 5% aq. NaOH, followed by refluxing afforded also **5** and several unidentified products. Chloroform, methylene chloride, and methanol fractions gave products, which did not show the presence of isopropyl group on ^1H NMR spectra.

By the analogy with an intermediate, **31**, **34** is



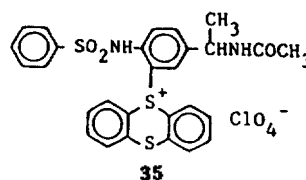
expected to be formed readily, compared with **31** but in this case deisopropylation seems to be a facile reaction.

In conclusion, reactions of **1** with 1-alkyl-4-benzenesulfonylaminobenzenes are sensitive to the nature of alkyl groups. Further investigations of these reactions are in progress.

Acknowledgement. The authors gratefully acknowledge the financial support of Korea Research Foundation in this work.

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- Compound **21** was prepared via an independent route and a reaction of **21** with **1** was investigated. From this reaction was obtained a compound in good yield of which structure was assigned to be **35** based on spectral data and the result of an elemental analysis. IR of this compound showed two sharp peaks at 1120 and 1070 cm^{-1} and ^1H NMR spectrum showed the same type of peaks as that obtained from **18** between 6.5 and 9.0 ppm.



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A Stereoselective Synthesis of (Z,Z)-3,13-Octadecadien-1-yl Acetate, and Its (E,Z)-Isomer, the Sex Pheromone of the Cherry Tree Borer, *Synanthedon hector* Butler

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Received February 2, 1988

A mixture of (Z,Z)-3,13-octadecadien-1-yl acetate(1) and its (E,Z)-isomer(2), the sex pheromone of the cherry tree borer, *Synanthedon hector* Butler was synthesized. (Z)-11-Octadecen-1-ol(3) was prepared from 1,10-decandiol. The Wittig reaction of the above aldehyde(3) with carboethoxymethylenetriphenylphosphorane, or the Wadsworth-Emmons reaction of the above aldehyde(3) with the anion of triethylphosphonoacetate gave ethyl (Z,Z)-2,13-octadecadienoate and its (E,Z)-isomer. Deconjugative protonation of ethyl (Z,Z)-2,13-octadecadienoate and its (E,Z)-isomer with potassium hexamethyldisilazide followed by aqueous ammonium chloride work-up afforded stereoselectively ethyl (E,Z)-3,13-octadecadienoate and its (Z,Z)-isomer, respectively, of which stereoselectivity was adjusted to give the product in the required ratio. Exposure of the above deconjugated ester to excess lithium aluminium hydride resulted in formation of the penultimate (Z,Z)-3,13-octadecadien-1-ol and its (E,Z)-isomer. Acetylation of the desired alcohols afford the final products, (Z,Z)-3,13-octadecadien-1-yl acetate(1) and its (E,Z)-isomer(2).

Introduction

The sex pheromone of the cherry tree borer, *Synanthedon hector* Butler, was isolated and identified as a mixture of (Z,Z)-3,13-octadecadien-1-yl acetate(1) and its (E,Z)-isomer(2) (Figure 1) by Yaginuma *et al.*¹ and Voerman *et al.*². The cherry tree borer, *Synanthedon hector* Butler, is one of the most important pests of peach and various deciduous fruit trees in Korea³ and Japan⁴. Also sex pheromones of the less peach tree borer, *Synanthedon pictipes*⁵ Grote Robinson and the peach tree borer, *Sanninodea exitiosa*⁵ Say were identified as (Z,Z)-3,13-octadecadien-1-yl acetate(1) and its (E,Z)-isomer(2).

Generally, *Synanthedon* species (Lepidoptera: Sesiidae) were found to be attracted by a mixture of the (Z,Z)-isomer 1 and the (E,Z)-isomer 2, which suggest that relatively low species-specificity of the pheromone component of Sesiidae. Recently, the highly purified (Z,Z)-isomer 1 was shown to be attractive to the smaller clear wing, *Synanthedon tenus*⁶, which is the pest in Japanese persimmon orchards. Even 0.5% contamination of the (E,Z)-isomer 2 inhibited⁶ the attractancy of the (Z,Z)-isomer 1.

Several syntheses⁷ of the (Z,Z)-isomer 1 and the (E,Z)-isomer have been reported in the literature.

A mixture (1:1) of the (Z,Z)-isomer 1 and the (E,Z)-isomer 2 was known to be an effective trap bait for the male cherry tree borer, an economic pest in Korean peach orchards. We have devised a convenient synthesis of the mixture of the (Z,Z)-isomer 1 and the (E,Z)-isomer 2 employing the Wittig or Emmons reaction followed by deconjugative protonation as the key step, which were adjusted to give the products in the required ratio.

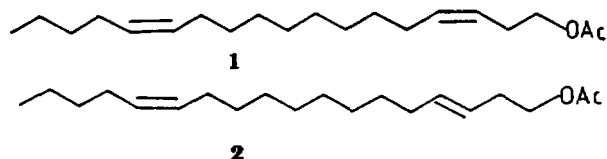


Figure 1