

티안트렌 양이온 자유라디칼 과염소산염과 N-아릴벤젠술폰아미드  
및 N-아릴-p-톨루엔술폰아미드의 반응. 5-(p-N-아릴술폰  
아미드페닐)티안트렌이온 과염소산염과 5-(p-N-아릴-p-톨루엔  
술폰아미드페닐)티안트렌이온 과염소산염의 합성

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Reactions of Thianthrene Cation Radical Perchlorate with  
N-Arylbenzene- and N-Aryl-p-toluenesulfonamides. Synthesis  
of 5-(p-N-Arylbenzenesulfonamidophenyl)- and 5-(p-N-Aryl-  
p-toluenesulfonamidophenyl)thianthrenium Perchlorate

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요약. 티안트렌 양이온 자유라디칼 과염소산염은 p-톨루엔술폰아니리드, 벤젠술폰아니리드, N-(2-메틸페닐)벤젠술폰아미드, N-페닐-p-톨루엔술폰아니리드와 같은 N-아릴술폰아미드와 반응하여 각각 5-(p-N-p-톨루엔술폰아미도페닐)티안트렌이온 과염소산염(1a), 5-(p-N-벤젠술폰아미도페닐)티안트렌이온 과염소산염(1b), 5-(4-N-벤젠술폰아미도-3-메틸페닐)티안트렌이온 과염소산염(1c), 5-(p-N-페닐-N-p-톨루엔술폰아미도페닐)티안트렌이온 과염소산염(1d)을 준다. 한편 1d는 티안트렌 양이온 자유라디칼과 다시 반응하여 이과염소산염(1e)을 생성한다.

1a~1e의 구조는 아세트아니리드와의 반응생성물인 5-(p-아세트아미도페닐)티안트렌이온 과염소산염과 매우 비슷하다. 그러나 두 반응의 양 관계에서 상이한 점은 술폰아미드와의 반응이 단일 메카니즘으로 진행되지 않음을 암시한다.

**ABSTRACT.** Thianthrene cation radical perchlorate reacts with N-arylsulfonamides such as p-toluenesulfonanilide, benzenesulfonanilide, N-(2-methylphenyl)benzenesulfonamide, and N-phenyl-p-toluenesulfonanilide to give 5-(p-N-p-toluenesulfonamidophenyl)-(1a), 5-(p-N-benzenesulfonamidophenyl)-(1b), 5-(4-N-benzenesulfonamido-3-methylphenyl)-(1c), and 5-(p-N-phenyl-N-p-toluenesulfonamidophenyl) thianthrenium perchlorate (1d), respectively. In the meantime, 1d reacts further with thianthrene cation radical to form diperchlorate (1e).

The structure of 1a~1e is very similar to 5-(p-acetamidophenyl)thianthrenium perchlorate which has been obtained from the reaction with acetanilide. However, the discrepancy in the stoichiometry between two reactions indicates that the reaction with sulfonamide appears not to proceed with a single mechanism.

## INTRODUCTION

Although organic cation radicals are now known to react with a variety of nucleophiles,<sup>1</sup> there has been no report about the reactions with sulfonamides. It is rather interesting to know how the reactions with thianthrene cation radical proceed because one can think of three kinds of reactions from the reactions of thianthrene cation radical with sulfonamides: (a) Nucleophilic attack of amino group to form a compound with structure such as  $\text{>S}^{\oplus}\text{-NHSO}_2^-$ , which is analogous type of reactions of thianthrene cation radical with amines such as *t*-butylamine and dimethylamine.<sup>2</sup> (b) Nucleophilic attack of aryl group of N-arylsulfonamides to the thianthrene cation radical, which is an analogous reaction to the reaction with acetanilide.<sup>3</sup> (c) An electron transfer reaction between thianthrene cation radical and sulfonamide, which results in the formation of thianthrene and sulfonamide cation radical. With these in mind, the reactions of thianthrene cation radical perchlorate with N-aryl-substituted sulfonamides were first undertaken. We have now reported the results obtained from these reactions.

## EXPERIMENTAL

Thianthrene was prepared from benzene and sulfur by using Dougherty and Hammond's method<sup>4</sup>, which was improved by Jeong.<sup>5</sup> mp (EtOH) 156.5~157°C (*lit.*<sup>4</sup> 158.8~159°C).

*p*-Toluenesulfonyl chloride was prepared from the reaction of *p*-toluenesulfonic acid with phosphorus pentachloride according to the literature.<sup>6</sup> mp (CHCl<sub>3</sub>-pet. ether) 68~70°C (*lit.*<sup>6</sup> 67.5~68.5°C). Benzenesulfonyl chloride was from Merck (Art. 800470).

*p*-Toluenesulfonamide was synthesized from the reaction of *p*-toluenesulfonyl chloride (10

mmol) in 40 ml of benzene with aniline (21 mmol), followed by refluxing for 10 min. Amine hydrochloride was filtered off and the filtrate was dried under reduced pressure. Crude *p*-toluenesulfonamide was recrystallized from ethanol, mp 97~98°C (*lit.*<sup>7</sup> 103~104°C). PMR (CDCl<sub>3</sub>)  $\delta$ : 2.33 (*s*, 3H, methyl) and 7.0~7.9 (*m*, 9H, aromatic). IR (KBr) cm<sup>-1</sup>: 3200 (NH stretch) and 1160 (SO<sub>2</sub> stretch).

Benzenesulfonamide was obtained from the reaction of benzenesulfonyl chloride with aniline in the same way as *p*-toluenesulfonamide. mp (EtOH) 109~109.5°C (*lit.*<sup>7</sup> 110°C). PMR (CDCl<sub>3</sub>)  $\delta$ : 6.7~8.2 (*m*, 10H, aromatic). IR (KBr)cm<sup>-1</sup>: 3200(NH stretch) and 1160 (SO<sub>2</sub> stretch).

N-(2-methylphenyl)benzenesulfonamide was prepared from the reaction of benzenesulfonyl chloride (2.6 ml, 20 mmol) and *o*-toluidine (2.14 g, 20 mmol) in the presence of 3 ml of pyridine. The mixture was heated for 15 min in a steam bath, followed by washing with water to remove pyridine and pyridine hydrochloride. Crude product was recrystallized from aq. ethanol. mp 124~125°C (*lit.*<sup>8</sup> 122~123°C). PMR(CDCl<sub>3</sub>)  $\delta$ : 2.0 (*s*, 3H, methyl) and 7~8 (*m*, 9H, aromatic).

N-phenyl-*p*-toluenesulfonamide was prepared by the addition of diphenylamine (3.38 g, 20 mmol) to *p*-toluenesulfonyl chloride (3.81 g, 20 mmol) containing 3 ml of pyridine. The mixture was worked up as in N-(2-methylphenyl)benzenesulfonamide. Crude compound was recrystallized from a mixture of CHCl<sub>3</sub>-ethanol. mp 142~142.5°C (*lit.*<sup>9</sup> 142°C). PMR (CDCl<sub>3</sub>)  $\delta$ : 2.35 (*s*, 3H, methyl) and 6.8~7.7 (quintet, 14H, aromatic). IR (KBr)cm<sup>-1</sup>: 1600, 1490, 1350, 1160.

Thianthrene cation radical perchlorate was prepared according to the known method.<sup>5</sup>

Acetonitrile was Kanto Chemical Co. Extra

pure and dried on  $P_2O_5$  by refluxing for three hrs, followed by distilling twice. It was stored over molecular sieve (Merck 4 Å, Art. 5708) in a septum capped bottle. Acetic anhydride and hexane were Shinyo Pure Chemical Co. guaranteed reagent and distilled before use. Carbon tetrachloride and ether were Junsei Chemical Co. Extra pure reagent. Perchloric acid (70%), toluene and o-toluidine were Wako Pure Chemical Industries guaranteed reagent.

Aniline (EP) and diphenylamine (GR) were obtained from Kanto Chemical Co. Chloroform was Ishizu Pharmaceutical Co. Extra pure reagent. All solvents were distilled before use. Column chromatography was performed with Merck silica gel (35~70 mesh ASTM, Art. 7733)

Thin layer chromatography was carried out with Merck Kiesel 60 PF<sub>254</sub> silansiert (Art. 7751) and the plate was made by dipping the glass plate (3×8 cm) into the slurry in the mixture of methanol and chloroform (2:1 v/v). The chromatogram was visualized using mineral ultraviolet lamp (UVSL 25 Ultraviolet Products Inc. San Gabriel, Calif., U. S. A.)

Ultraviolet spectra were obtained using Beckmann UV-VIS Spectrophotometer (Model 5260). Infrared spectra were obtained using Perkin-Elmer Infrared Spectrophotometers (Model 283 and 710 B). PMR spectra were recorded using Varian EM 360 A Spectrometer and chemical shifts were measured in values using TMS as an internal standard.

All melting points were taken with Fisher-Jone's melting point apparatus and uncorrected. Elemental analyses were performed at Department of Chemistry, The University of New Mexico.

**Reaction of Thianthrene Cation Radical Perchlorate ( $Th^{+} ClO_4^{-}$ ) with p-Toluenesulfonamide.** To the solution of 1.557 g (4.93

mmol) of  $Th^{+} ClO_4^{-}$  in 25 ml of acetonitrile was added 1.444 g (5.84 mmol) of p-toluenesulfonamide. The dark purple color of  $Th^{+} ClO_4^{-}$  disappeared in 10 min and the reaction mixture became pale brown. Thin layer chromatography (benzene) of the reaction mixture showed three spots, corresponding thianthrene ( $R_f$ , 0.76), p-toluenesulfonamide ( $R_f$ , 0.13) and an unknown ( $R_f$ , 0). After the solvent was removed under vacuum, the residue was column chromatographed (1.9×13 cm).

Elution with hexane gave 0.462 g (2.14 mmol) of thianthrene. Elution with benzene gave 0.242 g (0.98 mmol) of p-toluenesulfonamide and 0.05 g of a sticky material. Elution with acetone gave 1.506 g of an unknown compound, identified as 5-(p-N-p-toluenesulfonamidophenyl)thianthrenium perchlorate (Ia). mp(dec) 287~288 °C (DMSO-acetone-H<sub>2</sub>O). IR (KBr)  $cm^{-1}$ : 1100 ( $ClO_4$ ) and 1170 ( $SO_2$  stretch). UV (EtOH)  $\lambda_{max}$ : 315(shoulder), 264, 220(shoulder) nm. PMR (DMSO-d<sub>6</sub>)  $\delta$ : 2.37 (s, 3H, methyl), 7.0~8.5 (m; 16H, aromatic).

*Anal.* Calcd. for  $C_{25}H_{20}ClNO_6S_2$ : C, 53.42; H, 3.59; N, 2.49. Found: C, 55.55; H, 3.39; N, 2.55.

**Reaction of  $Th^{+} ClO_4^{-}$  with Benzenesulfonamide.** To the solution of 1.392 g (4.408 mmol) of  $Th^{+} ClO_4^{-}$  in 20 ml of acetonitrile was added 1.653 g (4.51 mmol) of benzenesulfonamide. The reaction was completed in 10 min and the color of the reaction mixture became pale red. The reaction mixture was worked up as in the previous reaction.

Elution with hexane gave 0.291 g (1.34 mmol) of thianthrene. Elution with benzene gave 0.347 g (1.49 mmol) of benzenesulfonamide. Elution with ether gave 0.023 g (0.099 mmol) of thianthrene-5-oxide. Elution with acetone gave 1.657 g of a perchlorate salt, identified as 5-(p-N-benzenesulfonamidophenyl)thianth-

renium perchlorate(1 b). mp (acetone-EtOH) 234~235 °C. IR (KBr)  $\text{cm}^{-1}$ : 1100 ( $\text{ClO}_4$ ) and 1160 ( $\text{SO}_2$  stretch). UV (EtOH)  $\lambda_{\text{max}}$ : 320, 264, and 220 (shoulder) nm. PMR ( $\text{DMSO}-d_6$ )  $\delta$ : 7.0~9.0 (*m*, 17 H, aromatic).

*Anal.* Calcd. for  $\text{C}_{24}\text{H}_{18}\text{ClNO}_6\text{S}_3$ : C, 52.60; H, 3.31; N, 2.56. Found: C, 53.38; H, 3.60; N, 2.49.

The compound was sensitive to the light, becoming violet.

**Reaction of  $\text{Th}^+ \text{ClO}_4^-$  with N-(2-Methylphenyl)benzenesulfonamide.** To the solution of 1.463 g (4.63 mmol) of  $\text{Th}^+ \text{ClO}_4^-$  in 20 ml of acetonitrile was added 1.313 g (4.64 mmol) of N-(2-methylphenyl)benzenesulfonamide. The reaction was completed in 48 hrs and the color of the reaction mixture became pale violet. The reaction mixture was worked up as in the previous reaction, followed by column chromatography (2×15 cm).

Elution with hexane gave 0.349 g (1.61 mmol) of thianthrene. Elution with benzene followed by ether gave 0.576 g (2.04 mmol) of N-(2-methylphenyl)benzenesulfonamide. Finally elution with acetone gave 1.940 g of a sticky unknown compound, which was recrystallized from a mixed solvent ( $\text{DMSO}-\text{CH}_2\text{Cl}_2$ -ethanol-ether) to give white solid, identified as 5-(4-N-benzenesulfonamido-3-methylphenyl)thianthrenium perchlorate(1c). mp(dec) 246~247 °C. IR(KBr)  $\text{cm}^{-1}$ : 1100 ( $\text{ClO}_4$ ) and 1170 ( $\text{SO}_2$  stretch). UV (EtOH)  $\lambda_{\text{max}}$ : 316, 290, 260 and 220 (shoulder) nm. PMR ( $\text{DMSO}-d_6$ )  $\delta$ : 2.08 (*s*, 3 H, methyl), 6.6~8.7 (*m*, 16 H, aromatic) 10.0(*s*, 1 H, amine).

*Anal.* Calcd. for  $\text{C}_{25}\text{H}_{19}\text{ClNO}_6\text{S}_3$ : C, 53.42; H, 3.59; N, 2.49. Found: C, 53.27; H, 3.67; N, 2.38.

**Reaction of  $\text{Th}^+ \text{ClO}_4^-$  with N-Phenyl-*p*-toluenesulfonamide.** To the solution of 1.072 g (3.40 mmol) of  $\text{Th}^+ \text{ClO}_4^-$  in 18 ml of aceto-

nitrile was added 1.111 g (3.44 mmol) of N-phenyl-*p*-toluenesulfonamide. The color of the reaction mixture became pale violet after 30hrs stirring. The reaction mixture was worked up as before and the residue was chromatographed on silica gel column (1.9×7.5 cm). Elution with hexane gave 0.236 g (1.09 mmol) of thianthrene. Elution with benzene, followed by ether gave 0.447g (1.38 mmol) of N-phenyl-*p*-toluenesulfonamide. Elution with acetone gave a residue which turned a foamy solid under reduced pressure and did not look like a single compound. This acetone fraction was rechromatographed. Elution with chloroform, followed by acetone gave 0.792 g and 0.583 g of perchlorate salts, respectively.

The former was carefully recrystallized from a mixture of methylene chloride and ethanol. mp 129. 5~131 °C. UV (EtOH)  $\lambda_{\text{max}}$  320(shoulder), 290 (shoulder), 265, and 226 (shoulder) nm. IR(KBr)  $\text{cm}^{-1}$ : 1100 ( $\text{ClO}_4$ ) and 1170 ( $\text{SO}_2$  stretch). Pmr( $\text{CDCl}_3$ )  $\delta$ : 2.45(*s*, 3 H, methyl), 7.0~9.0 (*m*, 2 H, aromatic).

*Anal.* Calcd. for  $\text{C}_{31}\text{H}_{24}\text{NClO}_6\text{S}_3$ : C, 58.34, H, 3.79; N, 2.19. Found: C, 58.45; H, 4.02; N, 2.21.

This compound was identified as 5-(*p*-N-phenyl-N-*p*-toluenesulfonamidophenyl)thianthrenium perchlorate(1 d).

In the meantime, the crude compound was recrystallized from acetonitrile solution. In this case PMR spectrum of the crystal showed a singlet at  $\delta$  2.08 which was due to acetonitrile occluded in the crystal. mp (acetonitrile) 158~159.5 °C. PMR ( $\text{DMSO}-d_6$ )  $\delta$ : 2.08 (*s*, 3 H, methyl), 2.45 (*s*, 3 H, methyl), 7.0~9.0 (*m*, 21 H, aromatic).

Of two compounds from acetone fraction, the latter was recrystallized from acetonitrile and had mp 184~185 °C. IR (KBr)  $\text{cm}^{-1}$ : 1100 ( $\text{ClO}_4$ ) and 1170 ( $\text{SO}_2$  stretch). UV (EtOH)

$\lambda_{max}$ : 290, 264, and 225 nm. PMR (DMSO- $d_6$ )  
 $\delta$ : 2.40 (s, 3H, methyl), 7.0~8.8 (m, 28 H, aromatic).

*Anal.* Calcd. for  $C_{43}H_{31}NCl_2O_{10}S_5$ : C, 54.14; H, 3.28; N, 1.47. Found: C, 54.07; H, 3.35; N, 1.70.

The compound was assigned to be N,N-di-(p-(5-thianthrenium perchlorate)phenyl)-p-toluenesulfonamide(1e).

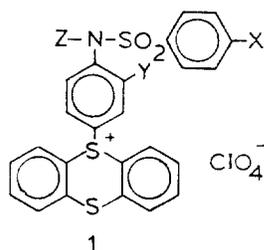
**Reaction of  $Th^+ \cdot ClO_4^-$  with 1d.** To the solution of 0.604 g (1.91 mmol) of  $Th^+ \cdot ClO_4^-$  in 3 ml of acetonitrile was added 1.185 g (1.86 mmol) of 1d. The reaction mixture was protected from the light by wrapping the flask with aluminum foil and stirred for 5 days at room temperature. The color of the reaction mixture was pale violet. This mixture was worked up as usual manner and the residue was column chromatographed (1.9×5.5 cm).

Elution with benzene gave 0.150 g (0.69 mmol) of thianthrene and elution with ether gave 0.010 g (0.04 mmol) of thianthrene 5-oxide. Elution with acetone gave 0.274 g of solid with a sticky material, which was recrystallized from acetonitrile to give 1e. All spectral data was exactly identical with those of the product obtained from the reaction described in the previous experimental section.

### RESULTS AND DISCUSSION

N-Arylbenzene- and N-aryl-p-toluenesulfonamides react with thianthrene cation radical perchlorate in acetonitrile to give a class of compound as shown below rather than nitrogen-sulfur bonding compounds.

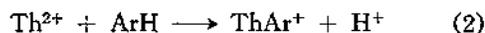
This can be accounted for by weak nucleophilicity of nitrogen of the sulfonamides. The sulfonium salts (1a~1e) were identified by the spectroscopic methods (IR, PMR, UV) and elemental analyses. The amounts of reactants and products of each reaction are tabulated in the



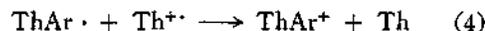
	1a	1b	1c	1d	1e
X	CH <sub>3</sub>	H	H	CH <sub>3</sub>	CH <sub>3</sub>
Y	H	H	CH <sub>3</sub>	H	H
Z	H	H	H		

Table 1.

The table shows that the number of moles of thianthrene formed in each reaction is much less than a half moles of thianthrene cation radical perchlorate. Furthermore, if thianthrene 5-oxide is assumed to be produced from the reaction with water, the same number of moles of thianthrene as that of thianthrene 5-oxide is also produced according to the stoichiometry of the reaction with water.<sup>10</sup> Therefore, elimination of thianthrene resulted from reaction with water makes these reactions more unfit to the stoichiometry represented by either disproportionation mechanism (eq 1 and 2)



or a two-step reaction analogous to parts of an electrochemical ECE process (eq 3 and 4)

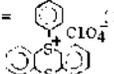


In the meantime, the amount of the sulfonium perchlorate (1a~1e) was more than that expected from the stoichiometry represented by

either eq 1 and 2 or eq 3 and 4. The sulfonium salt was obtained from acetone fraction and dried on  $P_2O_5$  desiccator under vacuum but perchloric acid could not be removed under low vacuum through an aspirator. Accordingly one possible candidate causing overweight of the sulfonium salt except for 1d which is a chloroform fraction may be said perchloric acid formed during the course of the reaction.

It has been reported<sup>3</sup> that the reactions with some aromatics such as anisole, phenol, toluene, and acetanilide gave the corresponding *p*-substituted thianthrenium perchlorate in good yield according to eq 1 and 2. In contrast, Parker and co-worker<sup>11</sup> studied anisylation of thianthrene cation radical using electrochemical techniques and suggested a different mechanism. Apart from the detailed mechanism, the structure of the sulfonium salts obtained in these reactions are similar to the sulfonium salt previously obtained from the reaction with acetanilide. Furthermore, it has been well-known that hydrogen on nitrogen of acetanilide is more basic than that of the corresponding sulfonamide.<sup>12</sup> Nevertheless, reaction with acetanilide did not give nitrogen-sulfur bonding sulfonium salt. By the analogy with this result, one may rationalize the failure of nitrogen-sulfur bonding in the reaction with sulfonamide. However, the fact that the stoichiometry of these reactions can not be explained cleanly as that of acetanilide reaction indicates that other reactions may occur concurrently. One may think of the possibility of an electron transfer as in the reaction with *N,N*-dimethylaniline, which has afforded not only *p*-substituted thianthrenium perchlorate in poor yield, but also *N,N,N',N'*-tetramethylbenzidine as a major product. The formation of the latter must without doubt have occurred by oxidative dimerization of *N,N*-dimethylaniline. How-

Table 1. Summary of the reaction of thianthrene cation radical perchlorate with *N*-arylbenzene- and *N*-Aryl-*p*-toluenesulfonamides.

Th <sup>+</sup> · <sup>a</sup>	Reactants (mmol)	Products (mmol)		
		Th <sup>b</sup>	Thc <sup>c</sup>	d
4.93	X=CH <sub>3</sub> , Y=OH (5.84)	2.14	0.22	1e (2.52)
4.41	X=Y=2-H (4.51)	1.34	0.13	1b (3.37)
4.63	X=2-H, Y=CH <sub>3</sub> (4.64)	1.62	0.04	1c (2.31)
3.44	X=CH <sub>3</sub> , Y=H.	1.09	0.02	1d (1.24)
	Z=  (3.44)			1e (0.61)
1.93	X=CH <sub>3</sub> , Y=H, Z=  (1.26)	0.59	0.04	1e (1.51)

\*Numbers in parentheses are the number of moles.

<sup>b</sup>Thianthrene cation radical perchlorate, <sup>c</sup>Thianthrene, <sup>d</sup>Thianthrene 5-oxide, <sup>e</sup>5-(*p*-*N*-Arylbenzenesulfonamidophenyl)- and 5-(*p*-*N*-aryl-*p*-toluenesulfonamidophenyl)thianthrenium perchlorate, Recovery from acetone fraction after column chromatography, followed by vacuum-dry.

ever, to our knowledge, no report on either the radical cation of sulfonamide or the anodic oxidation of sulfonamide has been made. Therefore, it is rather difficult to make a prediction about the possibility of an electron transfer in sulfonamide reactions.

Reaction with *N*-phenyl-*p*-toluenesulfonamide afforded two kinds of perchlorate salts (1d and 1e), which were very sensitive to light and the compounds became tinged with red. Fading in the color of the cation radical occurred much slower in the reaction with perchlorate (1d) than *N*-phenyl-*p*-toluenesulfonamide. The fact that the formation of monoperochlorate (1d) is followed by that of the diperochlorate (1e) indicates that electron density of non-bonding electrons on nitrogen of monoperochlorate is still strong enough to delocalize into phenyl ring although sulfur atom *i. e.*, electron-

deficient center, is attached to *para* position of the other phenyl ring. This in turn, suggests that thianthrenium ion may be a poor electron-withdrawing group. If this is true, acidity of each sulfonamide used in this reaction may be close to that of the corresponding thianthrenium perchlorate. This possibility will be examined later.

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12.  $C_6H_5SO_2NH_2$ ,  $K_a=10^{-10}$ .  $C_6H_5CONH_2$ ,  $K_a=10^{-14} \sim 10^{-15}$ .  $K_a$  of N-Aryl sulfonamide is expected to be greater than  $10^{-10}$ .