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Reactions of Thianthrene Cation Radical Perchlorate with N-(p-Methoxyphenyl)benzene - and Methanesulphonamides

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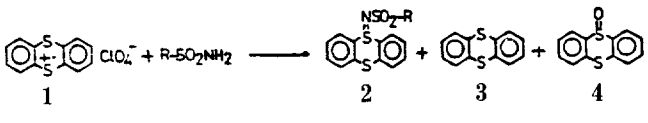
Reactions of thianthrene cation radical perchlorate (**1**) with N-(*p*-methoxyphenyl)benzenesulphonamide (**14**) in acetonitrile at room temperature afforded various products: thianthrene (**3**), N-(*p*-hydroxyphenyl) benzenesulphonamide (**16**), benzenesulphonamide (**18**), hydroquinone (**20**); 5-(5-benzenesulphonamido-2-methoxyphenyl)-thianthrenium perchlorate(**21**), 2-benzenesulphonamido-2'-hydroxy-5,5'-dimethoxybiphenyl(**24**), 2-benzenesulphonamido-2', 5'-dihydroxy-5- methoxybiphenyl(**25**), and a traceable amount of *p*-quinone(**23**). The formations of part of (**3**) and (**21**) can be explained by either disproportionation or half-regeneration mechanism but those of the remainders by diverse reactions of sulphonamidyl radical (**27**) derived from (**14**) (through single electron transfer, followed by deprotonation processes). Similar results were observed from the reaction with N-(*p*-methoxyphenyl)methanesulphonamide (**15**).

Introduction

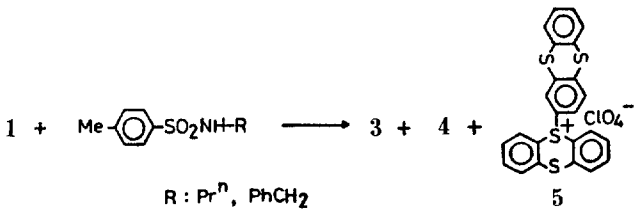
Reactions of thianthrene cation radical perchlorate (**1**) with arene- and alkanesulphonamides at room temperature in acetonitrile have shown various aspects, depending on the substituents at nitrogen. That is, reactions with N-free sulphonamides afforded N-sulphonylsulphilimines (**2**) along with thianthrene (**3**) and thianthrene 5-oxide (**4**) after being elapsed with a couple of months[1] (Scheme 1).

Reactions with N-alkylsulphonamides, which were expected to increase the nucleophilic reactivity of amino group due to electron-donating effect of alkyl group, however, did not afford any product containing the sulphonamide moiety even in three months of reaction time. The sulphonamides were almost quantitatively recovered and (**1**) turned to (**3**), (**4**), and thianthreniumylthianthrene perchlorate (**5**)[1] (Scheme 2).

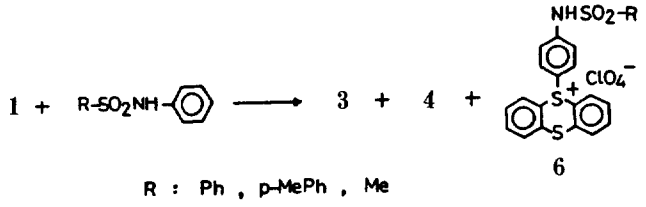
Sulphonamides with N-aryl group reacted smoothly with (**1**) to give 5-(*p*-N-arene- and alkanesulphonamidophenyl)-thianthrenium perchlorate (**6**) in good yields[2] (Scheme 3)



Scheme 1



Scheme 2

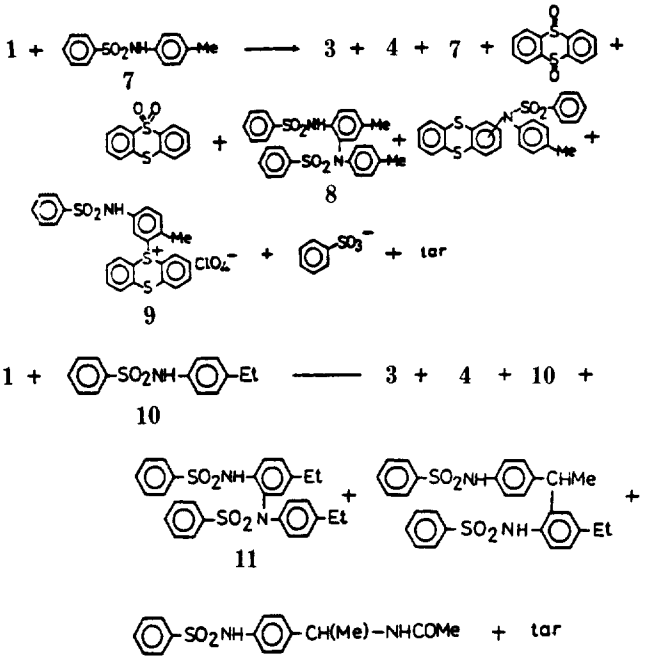


R : Ph , p-MePh , Me

Scheme 3

which were analogous type of compounds with 5-(*p*-acetamidophenyl)thianthrenium perchlorate obtained from the reaction of (1) with acetanilide.[3]

When (1) was reacted with sulphonamides with para substituted N-phenyl group such as N-(*p*-tolyl)benzenesulphonamide (7)[4] and N-(*p*-ethylphenyl)benzenesulphonamide (10)[4], various products were isolated (Scheme 4).



Scheme 4

Of these products shown in Scheme 4, compounds (8) and (11) were explained by a coupling reaction between two canonical forms of the corresponding sulphonamidyl radicals, (12) and (13), which could be formed by an electron transfer between (1) and the sulphonamides, (7) and (10), yielding (3) and cation radicals of (7) and (10), followed by deprotonation of the sulphonamide cation radicals, respectively.

Sulphonamidyl radicals have been mainly generated by photolysis of N-halosulphonamide[5] and oxidations of N-alkyl or -arylsulphonamides by sodium persulphate[6] or hydrogen atom abstractions from N-monoalkylsulphonamides by *t*-butoxy radical[7] also afforded the corresponding sulphonamidyl radicals. All of these belong to N-alkylsulphonamidyl radicals except for 2-biphenylsulphonamidyl radical which was generated by treatment of N-phenyl 2-biphenylsulphonamide with sodium persulphate.[6] However, [*c,e*][1,2]-thiazine 5,5-oxide, which was expected to be formed by attack of a radical center on nitrogen of 2-biphenyl-N-sulphonamidyl radical to the biphenyl ring was not formed. Only a complex mixture was formed. Therefore, isolations of

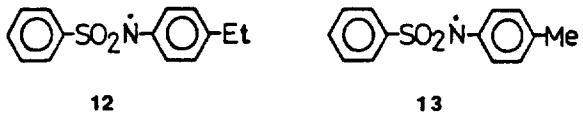


Figure 1

Table 1. Products obtained from the Reaction of (1) with N-(*p*-methoxyphenyl)benzenesulphonamide (14)

Reactants mmol		Products mmol (%)							
(1)	(14)	(3)	(14)	(16)	(18)	(20)	(21)	(23)	(24)+(25)
4.434	4.424	4.008	3	0.100	0.744	0.136	0.128		0.041g
		(90.4)	(68)	(2.3)	(16.8)	(3.1)	(5.8)		

Percent yield of (3) is based on (1) and that of (21) is based on the stoichiometry in which 2 moles of (1) is assumed to give 1 mole of (3) and 1 mole of (21). The others are based on (14). (23): contaminated with some of (14) recovered and only identifiable by its characteristic smell and n.m.r. peaks at 6.80 ppm.

Table 2. Products obtained from the Reaction of (1) with N-(*p*-methoxyphenyl)methanesulphonamide (15)

Reactants mmol		Products mmol (%)						
(1)	(15)	(3)	(4)	(15)	(17)	(19)	(22)	(23)
6.150	6.460	5.686	0.129	4.264	0.233	0.526	0.293	
		(92.5)	(4.1)	(66.0)	(3.6)	(8.1)	(4.5[a])	
							(9.5[b])	

Percent yields of (3) is based on (1) and that of (4) is based on the stoichiometry in which 2 moles of (1) gives 1 mole of (3) and 1 mole of (4). [a] Percent yield based on (1) in such a way as in (4). [b] Percent yield based on (15). (23): contaminated with some of (15) recovered and only identifiable by its characteristic smell and n.m.r. peaks at 6.80 ppm.

(8) and (11) were the first example for the isolation of the products formed from the N-arylsulphonamidyl radicals.

In order to gain a further insight into single electron transfer between (1) and sulphonamides, study on reactions with sulphonamides with a methoxy group at para position of N-phenyl group was undertaken. We now report the results obtained from these reactions.

Results

At a glance, it can be said that the rate of the reaction of (1) with sulphonamides with a substituent at para position of N-phenyl group is drastically influenced by the substituent as manifested by the results in which the reaction of (1) (4.434 mmol) with (14) (4.424 mmol) was completed in less than 10 min., but that of (1) (4.420 mmol) with (7) (8.750 mmol) was completed in a week.[4] In addition, the difference of the reactivities of two sulphonamides, (7) and (14) to (1) results in diverse products in each reaction, which connot be simply understood in terms of electronic effects of the corresponding substituents. Products obtained from the reactions with (14) and (15) are tabulated in Table 1 and 2.

All of the products were identified based on spectroscopic

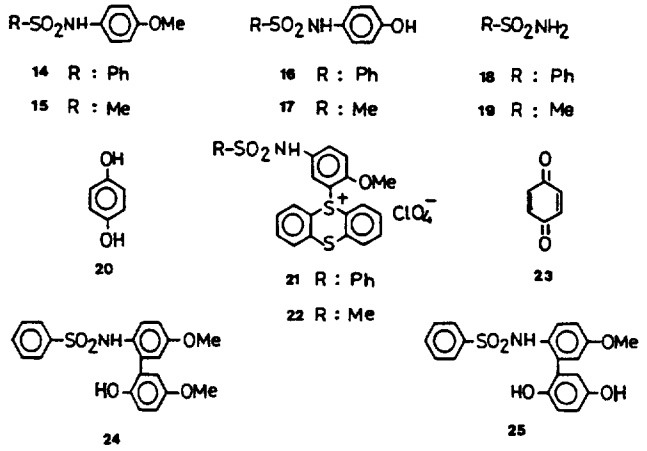


Figure 2

data and by the comparison with the physical properties of the authentic samples. Of the products in Table 1, a mixture of (**24**) and (**25**), obtained from ether fraction of column chromatography as brown solids was identified based on the following data: two singlets at 3.77 ppm and 3.81 ppm indicate the presence of two methoxy groups and broad i.r. peaks at 3660 to 3350 cm^{-1} and 3350 to 3060 cm^{-1} suggests the presence of OH and NH groups, respectively. Mass numbers (*m/z*) 385 and 371 were in agreement with molecular weight of (**24**) and (**25**), respectively.

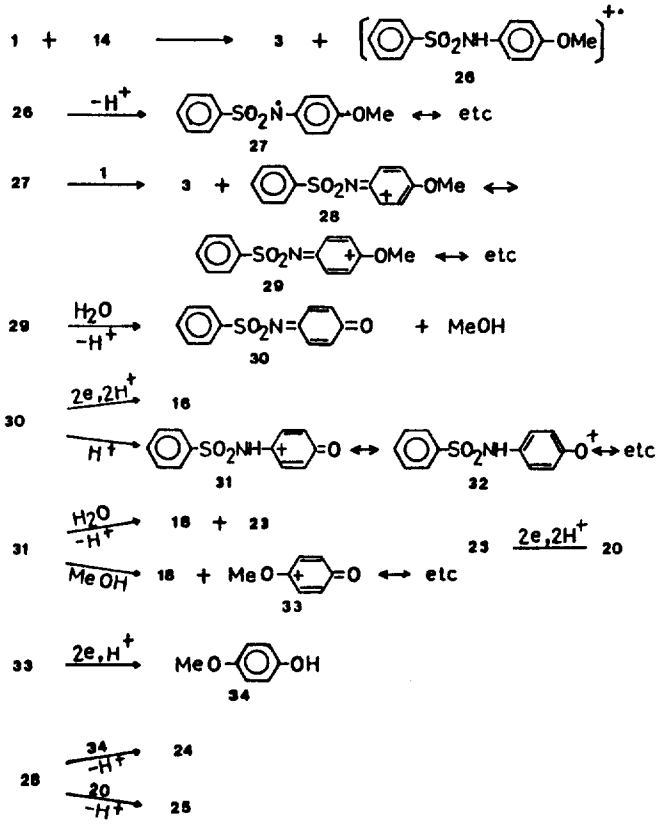
N.M.R. spectra of the sulphonium salts, (**21**) and (**22**) showed a multiplet corresponding to two protons, C(4)H and C(6)H of thianthrene moiety at 8.5 ppm and another multiplets due to the remaining aromatic protons between 6.55 ppm and 8.20 ppm. The splitting pattern of these protons in thianthrene moiety was quite well in accord with those exhibited by other 5-(arene)thianthrenium perchlorates, *i.e.* 5-(*p*-acetamidophenyl)thianthrenium perchlorate[3] and 5-(*p*-benzenesulphonamidophenyl)thianthrenium perchlorate.[2]

Discussion

Reactions of (**1**) with the sulphonamides, (**14**) and (**15**) afforded (sulphonamido)thianthrenium perchlorates, (**21**) and (**22**) in 5.8% and 4.5%, respectively, which means that nucleophilic substitution of the sulphonamides to (**1**) occurs although there is considerable steric hindrance by the presence of a methoxy group at para position of N-phenyl group of the sulphonamides.

The bonding position between sulphur of thianthrene moiety and N-phenyl group was determined based on the fact that methoxy group is stronger than benzenesulphonamido group in the electron-donating ability. However, the mechanism of the formations of these products is uncertain. Presumably disproportionation or half-regeneration mechanism, as in the reactions of (**1**) with some other nucleophiles[12], may be involved.

Since (**3**) was isolated in 90.4% and 92.5% yields in each reaction, and (**21**) and (**22**) were the only products containing thianthrene moiety excluding (**4**), possibly formed by the reaction with water remained in the dried solvent, it is thought that main reaction is initiated by single electron transfer from the sulphonamides, (**14**) and (**15**), to (**1**) to



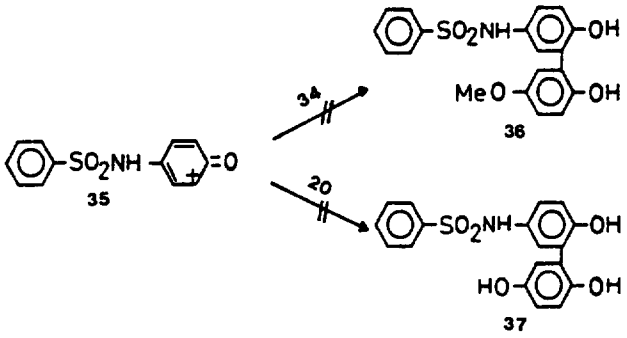
Scheme 5

generate cation radicals of (**14**) and (**15**), respectively and (**3**).

Scheme 5 shows the proposed pathways for the formations of (**16**), (**18**), (**20**), (**23**), (**24**), and (**25**) in the reaction with (**14**).

The sulphonamide cation radical (**26**) loses a proton to give sulphonamidyl radical (**27**), which is further oxidized by (**1**) to afford the corresponding cations. Among them, (**29**) reacts with water to give methanol and N-benzenesulphonyl-*p*-quinone imine (**30**) as a key intermediate leading to either N-(*p*-hydroxyphenyl)benzenesulphonamide (**16**) by two successive one-electron reduction or benzenesulphonamide (**18**) and *p*-quinone (**23**) by protonation to give (**31**), followed by hydrolysis. The formation of hydroquinone (**20**) can also be explained by two successive one-electron reduction of (**23**) as described in the literature.[13] But the detailed mechanism is uncertain because the reduction mechanism is so sensitive to the solvents, acidity of the medium, and the concentration of the reducing agent. At this moment, it is uncertain what the single electron-donor is in these reduction processes. Nevertheless hydrolysis of (**17**) to yield (**20**) is unlikely because it has been known to be very difficult process under acidic conditions.[14] Similar reductions were observed earlier by Adams and co-worker[10] who obtained (**16**) by the treatment of quinone imine (**30**) with hydriodic acid or hydrochloric acid in chloroform or water. In addition, *p*-quinone (**23**) and benzenesulphonamide (**18**) were obtained by hydrolysis of (**30**) at elevated temperature.[10] However, no details on the mechanism have been reported.

One noteworthy thing among the series of the proposed pathways is the involvement of water to give quinone imine (**30**) and methanol, and benzenesulphonamide (**18**) and



Scheme 6

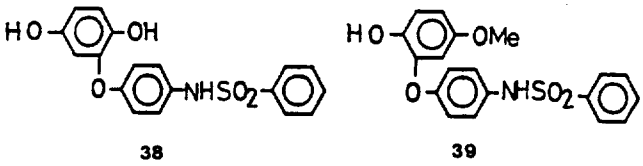
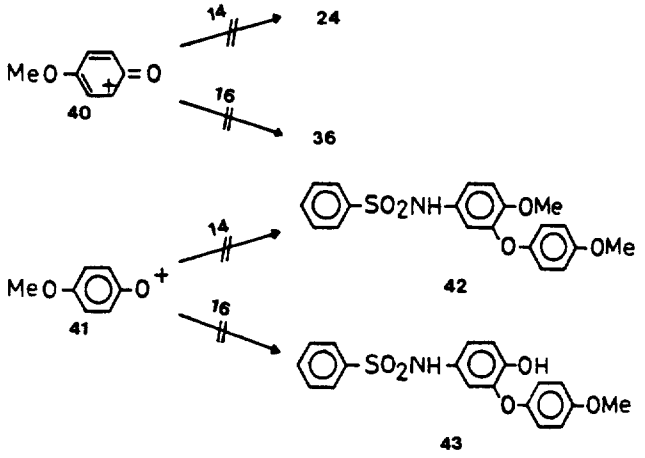


Figure 3

p-quinone (**23**). The anhydrous conditions were maintained through the reaction and some residual moisture, if it exists, in the solvent at the begining was expected to be eliminated by the fast reaction with (**1**) to give (**4**).[15] Nevertheless products resulted from hydrolysis were produced. Therefore, the cations (**29**) and (**31**), formed by the oxidation of sulphonamidyl radical (**27**) and protonation of (**30**), respectively, must be very reactive to catch up water somehow. If this is so, one may also anticipate methanolysis in place of hydrolysis because methanol is produced in the process of forming (**30**), of which mechanism is analogous to that of the formation of (**23**) from *p*-methoxyphenol (**34**).[16]

Reaction of (**31**) with methanol, followed by a bond cleavage between nitrogen and carbon atoms of *p*-quinone moiety leads to (**18**) and (**33**). If the cation (**33**) is reduced, (**34**) can be formed. Actually (**34**) was not detected. Instead, a mixture, exhibiting mass numbers (*m/z*) 385 and 371, which correspond to the molecular weight of (**24**) and (**25**), respectively, was isolated. N.M.R. and i.r. data are also in accord with those expected from both compounds. We propose tentatively that compounds (**24**) and (**25**) are formed by electrophilic aromatic substitution of (**28**) to *p*-methoxyphenol (**34**) and hydroquinone (**20**), respectively. Electrophilic substitution of protonated quinone imine (**35**) to either (**34**) or (**20**) to give (**36**) or (**37**), respectively (Scheme 6) is ruled out owing to the mass spectral data. That is, mass number (*m/z*) 357 corresponding to the molecular weight of (**37**) was not observed. If the reactions shown in Scheme 6 are really involved, compound (**37**) is expected to be formed preferably on twofold grounds: concentration of (**20**) is higher than that of (**34**), and (**20**) is expected to be more reactive than (**34**) to electrophilic substitution due to the stronger electron-donating ability of OH group.

Furthermore, if protonated (**30**) is involved, phenyl ethers (**38**) and (**39**) are expected to be formed by the reactions of (**32**) with (**20**) and (**34**), respectively as shown in the results in which 4-methanesulphonamidophenyl 4-hydroxyphenyl ether was obtained from the reaction of protonated methanesulphonyl-*p*-quinone imine with phenol.[17] However, no such products, (**38**) and (**39**) were detected.



Scheme 7

Table 3. Products from the Reaction of Quinone Imine (**30**) with 70% Perchloric acid in the Presence and Absence of Sulphonamide (**14**)

Reactants mmol			Products mmol (%)					
(**14**)	(**30**)	$HClO_4$	(**14**)	(**16**)	(**18**)	(**20**)	(**23**)	tar
4.367	2.439	6	4.162	0.650	1.037	0.318	0.194	0.239g
			(95.3)	(26.7)	(42.5)	(13.0)	(8.0)	
	2.831	6		0.309	1.616	0.817	0.268	0.018g
				(10.9)	(57.1)	(28.9)	(9.5)	

Percent yields are based on quinone imine (**30**) except for (**14**).

By the same token, possibilities of reactions of (**40**) and (**41**), which are cannonical forms of (**33**), with sulphonamides, (**14**), and (**16**) to give biphenyls, (**24**) and (**36**), and phenyl ethers, (**42**) and (**43**) are ruled out although molecular weight of (**24**) and (**36**) are 385 and 371, respectively (Scheme 7).

If (**24**) and (**36**) are formed according to the mechanism shown in Scheme 7, reactions of (**40**) with either (**20**) or (**34**) are expected to occur in advance on the electronic and steric grounds of substituents.

In order to ascertain the involvement of quinone imine (**30**) as an intermediate, (**30**) was treated with sulphonamide (**14**) in the presence of 70% perchloric acid in acetonitrile. The results are tabulated in Table 3.

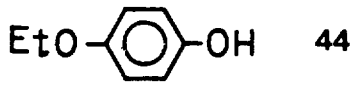
Quinone imine (**30**) decomposes in the presence of 70% perchloric acid and its decomposition products are the same compounds as those obtained from the reaction of (**1**) with sulphonamide (**14**) except for the coupling products, (**24**) and (**25**) and thianthrenium perchlorate (**21**). By the addition of (**14**) under similar conditions were obtained the same compounds as those obtained without (**14**). In either case, no (**24**) and (**25**) were formed. This results support the assumptions that quinone imine (**30**) acts as an intermediate and the coupling products, (**24**) and (**25**), cannot be formed by an electrophilic attack of protonated (**30**) to *p*-methoxyphenol (**34**) and hydroquinone (**20**), respectively, although quinone imine (**30**) is known to be readily protonated.[16]

Table 3 shows that yield of (**18**) is much greater than the summation of the yields of two compounds, (**20**) and (**23**), whether (**14**) is added or not. This result can be rationalised

Table 4. Products from the Reaction of Quinone Imine (**30**) with 70% Perchloric acid in the Presence of 95% EtOH in Acetonitrile

Reactants mmol			Products mmol (%)					
(**30**)	$HClO_4$	EtOH	(**16**)	(**18**)	(**20**)	(**23**)	(**44**)	tar
4.044	12	15.8	0.798 (19.7)	2.678 (66.2)	0.409 (10.1)	4.6×10^{-2} (1.1×10^{-3})	0.69 (17.1)	0.128g

Percent yields are based on quinone imine (**30**).



44

Figure 4

by the fact that *p*-quinone (**23**) is transformed to not only (**20**) but also various unidentified black tar in the presence of perchloric acid.

In order to gain an insight into hydrolysis of quinone imine (**30**), 70% perchloric acid was added to a mixture of (**30**) and 95% ethanol. Results are summarized in Table 4.

Surprisingly the yield of (**23**) decreased drastically but *p*-ethoxyphenol (**44**) was isolated in considerable amount. It is reasonable to expect somewhat the decreased yield of (**23**) owing to the competitive reaction between ethanol and water in the reaction with (**31**). However, the fact that essentially no (**23**) was formed in spite of the generation of quite a (**20**) implies that reduction of (**23**) occurs very fast. Moreover, the formation of (**44**), presumably formed by the same mechanism as in the formation of (**20**), strongly supports the assumption in which *p*-methoxyphenol (**34**) is involved in the formation of (**24**).

Experimental

I.r. spectra were recorded on a Perkin-Elmer 283 infrared spectrometer. N.M.R. spectra were measured on Varian EM 360A spectrometer and chemical shifts were measured in δ relative to an internal standard Me_4Si. U.V. spectra were obtained from Beckman 5270 spectrometer. Melting points were recorded using Fisher-Jones melting point apparatus and are not calibrated. Elemental analyses were relied on the Institute of Chemical Technology, Dae Jeon, Korea and mass spectra were taken from Korea Advanced Institute of Science and Technology, Seoul, Korea.

Thianthrene (**3**) was synthesized from according to the literature[8] and thianthrene cation radical perchlorate (**1**) was prepared by the method of Rundel and Scheffer.[9] Acetonitrile was dried by refluxing on phosphorus pentoxide for four hours, followed by distillation over calcium hydride after refluxing 4h. Distillate was stored over molecular sieve (4Å) in a septum-capped bottle. Column chromatography was performed with Merck Silica gel (70-230 mesh, 0.05-0.2 mm). Thin layer chromatogram was purchased from Merck (Cat. No. 5715). All sulphonamides used were prepared according to the literature method: N-(*p*-methoxyphenyl)benzenesulphonamide (**14**): m.p. 94.5-95.5 °C (from aqueous MeOH); ν_{max}(KBr), 3405(OH), 3260(NH), 1315(SO_2), and 1155 cm^{-1} (SO_2); δ_H($CDCl_3$), 3.75 (3H, s, OMe), 6.40-6.90 (4H, dd, ArH), and 7.10-7.70 (6H, m, NH and ArH).

N-(*p*-Methoxyphenyl)methanesulphonamide (**15**): m.p. 117-118.5 °C (from EtOH); ν_{max}(KBr), 3259(NH), 1316(SO_2), and 1148 cm^{-1} (SO_2); δ($CDCl_3$), 2.93 (3H, s, Me), 3.76 (3H, s, OMe), and 6.70-7.30 (5H, m, NH and ArH).

General Procedure for the Reactions of Thianthrene Cation Radical Perchlorate (1) with Sulphonamides, (14) and (15). To an appropriate amount of (**1**) dissolved in dried acetonitrile was added an equimolar amount of sulphonamide at room temperature. The reaction flask was wrapped with aluminum foil to protect the reaction mixture from light. Progress of the reaction was monitored by either t.l.c. or disappearance of purple color due to (**1**). After the reaction was completed, small amount of distilled water was added and the aqueous solution was concentrated under reduced pressure, and saturated with brine, which was extracted with diethyl ether. The ether layer was evaporated to dryness and the residue was dried on P_2O_5, followed by column chromatography on silica gel.

Reaction of (1) with N-(*p*-Methoxyphenyl)benzenesulphonamide (14). To a solution of (**1**) (1.400g, 4.434 mmol) in acetonitrile (60 m*l*) was added (**14**) (1.165g, 4.424 mmol). The dark purple color of the solution changed to dark brown within 5 min: Chromatography (15 cm × 3 cm) with hexane (500 m*l*) gave (**3**) (0.867g, 4.008 mmol), while elution with benzene (200 m*l*) gave (**14**) (0.876g, ca. 3 mmol) containing a trace amount of *p*-quinone (**23**). Elution next with chloroform (300 m*l*) gave pale brown solids (0.117g, 0.744 mmol), identified as benzenesulphonamide (**18**): m.p. 153-154 °C (lit.[11], 156 °C) (from chloroform-hexane). Elution with ether gave sticky materials (0.098g) which were rechromatographed on silica gel column (15 cm × 1 cm) with methylene chloride to give N-(*p*-hydroxyphenyl)benzenesulphonamide (**16**) (0.025g, 0.100 mmol) and hydroquinone (**20**) (0.015g, 0.136 mmol). Continuous elution with ether gave brown materials (0.041g), a mixture of 2-benzenesulphonamido-2'-hydroxy-5,5'-dimethoxybiphenyl (**24**) and 2-benzenesulphonamido-2',5'-dihydroxy-5-methoxybiphenyl (**25**): m.p. (decomp.) 116-119.5 °C: ν_{max}(KBr) 3360-3350OH), 3350-3060(NH), 1315(SO_2), and 1150 cm^{-1}(SO_2); δ($CDCl_3$-DMSO-d_6), 3.77(s), 3.81(s), and 6.50-7.90(m); λ_{max}(MeOH), 295,270 (shoulder), 210 nm: *m/z* 385 (M^+, 5.6%), 371 (M^+, 9.4, 263 (0.4), 156(1.3), 123(12.0), 110(1.8), 78(59.6), 77(100), 64(5.0).

Finally elution with acetone (100 m*l*) in the first chromatography gave a brown sticky material (0.074g, 0.136 mmol), which was decolorised with charcoal in hot methanol, and allowed to stand at 0 °C for 10 days to give granular solids, identified as 5-(5-benzenesulphonamido-2-methoxyphenyl)-thianthrenium perchlorate (**21**): m.p. (decomp.) 218.5-219 °C (from aqueous EtOH); ν_{max}(KBr), 3170(NH), 1159(SO_2), 1130-1010 (ClO_4^-), and 620 cm^{-1}(ClO_4^-); δ($CDCl_3$-DMSO-d_6), 3.19 (3H, s, OMe), 6.55-8.20 (9H, m, NH and ArH), 8.5 [2H, m, C(4)H and C(6)H of thianthrene ring]; λ_{max}(MeOH) 308,220 nm; (Found; C, 52.2; H, 2.0; N, 3.2. $C_{25}H_{20}ClNO_7S_3$ requires C, 51.95; H, 2.4; N, 3.6%).

Reaction of (1) with N-(*p*-Methoxyphenyl)methanesulphonamide (15). To a solution of (**1**) (1.942g, 6.150 mmol) in acetonitrile (55 m*l*) was added (**15**) (1.300g, 6.460 mmol). Upon addition of (**15**), dark purple color of the solution turned brown and much of white solids were formed. Chromatography (15 cm × 3 cm) with hexane (200 m*l* × 3) gave (**3**) (1.230g, 5.686 mmol). Elution next with chloroform

(180 m*l*) afforded (**4**) (0.030g, 0.129 mmol) and (**15**) (0.858g, 4.264 mmol). Elution with ether (75 m*l*) gave a brown sticky material (0.136g), which was rechromatographed on silica gel (15 cm × 1 cm) with ether to give methanesulphonamide (**19**) (0.050g, 0.526 mmol) and N-(*p*-hydroxyphenyl)methanesulphonamide (**17**) (0.058g, 0.233 mmol). Finally elution with ethyl acetate, followed by acetone gave a dark sticky material (1.034g), which was washed with water to give 5-(5-methanesulphonamido-2-methoxyphenyl)thianthrenium perchlorate (**22**) (0.151g, 0.293 mmol): m.p. 151.5–152.5 °C (from aqueous EtOH) (Found: C, 46.7; H, 3.4; N, 2.6. $C_{20}H_{18}ClNO_7S_3$ requires C, 46.6; H, 3.5; N, 2.7%; ν_{max}(KBr), 3190(NH), 1355(SO_2), 1150(SO_2), 1100–1050(ClO_4^-), and 620 cm^{-1}(ClO_4^-); δ($CDCl_3$–DMSO-d_6), 2.23 (3H, s, Me), 3.88 (3H, s, OMe), 6.58–8.17 (9H, m, NH and ArH), and 8.4[2H, m, C(4)H and C(6)H of thianthrene ring]; λ_{max}(MeOH), 305,262 (shoulder), 220 nm.

Preparation of N-Benzenesulphonyl-*p*-quinone imine (30).[10] To a stirred suspension of finely powdered (**16**) (10g, 40 mmol) in glacial acetic acid (40 m*l*) was added lead tetraacetate (17.6g, 40 mmol) for over 15 min at room temperature. Crystallization occurred in 10 min. Two drops of ethylene glycol were added in 30 min. After 15 min, additional 0.5 m*l* of ethylene glycol was added again. Stirring was continued for 10 min, followed by setting in an ice-water bath prior to filtration. Recrystallization from cyclohexane-chloroform gave orangish yellow crystals (**30**) (4.2g, 17 mmol, 43%): m.p. (decomp.) 133–134 °C (lit.[10], 134 °C); ν_{max} (KBr) 3029–3081 (Vinyl C-H), 1314(SO_2), 1145(SO_2), and 1645 cm^{-1} (C=O); δ($CDCl_3$–CCl_4) 6.59 (2H, d, =CH-CO-CH=), 6.82 (1H, d, =CH-), 7.40–8.09 (5H, m, ArH), and 8.15 (1H, d, =CH-).

Reaction of Quinone Imine (30) with 70% Perchloric Acid. To a stirred solution of (**30**) (0.700g, 2.831 mmol) in acetonitrile (50 m*l*) was added 70% perchloric acid (0.52 m*l*, 6 mmol) at room temperature. The orangish yellow color of the solution changed to dark brown in 48h. After being stirred for an additional three days, the reaction mixture was worked up as usual. Chromatography (12 cm × 1.9 cm) with benzene (80 m*l*) afforded (**23**) (0.029g, 0.268 mmol). Methylene chloride (100 m*l*) fraction gave (**18**) (0.254g, 1.616 mmol) and (**16**) (0.077g, 0.309 mmol). Next ether (280 m*l*) fraction gave (**20**) (0.090g, 0.817 mmol): m.p. 170–172 °C (lit.[11], 173–174 °C). Finally elution with acetone gave a black tar (0.018g).

Reaction of Sulphonamide (14) with Quinone Imine (30) in the Presence of 70% Perchloric Acid. To a stirred solution of (**14**) (1.150g, 4.367 mmol) and (**30**) (0.603g, 2.439 mmol) in acetonitrile (60 m*l*) was added 70% perchloric acid (0.52 m*l*, 6 mmol) at room temperature. The orangish yellow color of the solution changed to dark brown. The reaction mixture was then worked up as usual. Chromatography (12 cm × 1.9 cm) with benzene (200 m*l*) gave (**23**) (0.021g, 0.194 mmol). Elution with methylene chloride (320 m*l*) gave (**14**) (1.096g, 4.162 mmol), (**18**) (0.163g, 1.037 mmol), and (**16**) (0.162g, 0.650 mmol). Next elution with ether (100 m*l*) gave (**20**) (0.035g, 0.318 mmol). Finally elution with acetone gave a black tar (0.239g).

Reaction of Quinone Imine (30) with 70% Perchloric Acid in the Presence of 95% Ethanol in Acetonitrile. To a stirred solution of (**30**) (1.000g, 4.044 mmol) and 95% ethanol (1.00 m*l*, 15.8 mmol) in acetonitrile (50 m*l*) was added 70% perchloric acid (1.09 m*l*, 12 mmol). The orangish yellow color of the solution changed to dark brown in 9h. When t.l.c. did not show the presence of (**30**), the reaction mixture was worked up and chromatographed (10 cm × 2.0 cm). Elution with chloroform (80 m*l*) gave (**23**) (0.005g, 0.046 mmol). Next fraction (80 m*l*) gave a brown sticky material (0.095g, 0.69 mmol). Decolorization, followed by evaporation of the solvent to dryness afforded *p*-ethoxyphenol (**44**): m.p. 62–63 °C (lit.[1], 66–67 °C); ν_{max}(KBr) 3330(OH), and 1105 cm^{-1}(C-O); δ(CCl_4) 1.20–1.60 (3H, t, Me), 3.70–4.20 (2H, q, CH_2), and 6.70 (4H, s, ArH); λ_{max}(MeOH) 290,223 nm. Continuous elution with chloroform (100 m*l*) gave (**18**) (0.421g, 2.678 mmol). Subsequent elution with ether (70 m*l*) gave a mixture of (**16**) (0.199g, 0.798 mmol) and (**20**) (0.045g, 0.409 mmol). Finally elution with acetone gave a black tar (0.128g).

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