Reduction of Isophorone Oxide. Isophorol oxide was obtained in a 95% (2.79 g) yield and GLC analysis showed that the ratio of cis-and trans isophorol oxide was 13:87.; bp 103-106°C (5 mm) (lit.[14] bp 97-99 °C (4 mm)); ^{1}H NMR (Neat) 0.99 (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.63 (t, 2H, CH_2), 2.18 (m, 1H, OH), 2.88 (s, 1H, H), 4.14 (m, 1H, H); n_D^{20} 1.4632 (lit.[14] n_D^{20} 1.4635).

Reduction of 3,4-Epoxy-4-Methyl-2-Pentanone. 1.9g (82%) of 3,4-epoxy-4-methyl-2-pentanol was obtained: bp 52-55°C (4mm) (lit.[14] bp 58-60 (6mm)); ^{1}H NMR (Neat) 1.2-1.4(m, 9H, CH_3), 2.50 (d, 1H, H), 3.48 (m, 1H, OH), 3.95 (s, 1H, H): n_D^{20} 1.4193 (lit.[14] n_D^{20} 1.4180).

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A Route for Sulfuranyl Radical by an Electron Transfer from Sodium Naphthalenide to a Triarylsulfonium Salt[1]

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Reaction of 5-(2-thianthreniumyl)thianthrene perchlorate with sodium naphthalenide in the presence of benzenethiol in tetrahydrofuran at −78°C proceeded via a formation of a sulfuranyl radical to give thianthrene (66%), 2-phenylthiothianthrene (33%), phenyl 2-(2-thianthrenylthio)phenyl sulfide (traceable amount), and some unknowns, along with naphthalene and very small amount of 1,4-dihydronaphthalene.

Sulfuranyl radicals have been mainly suggested in reactions involving radical substitution at sulfur.[2] However, little is known about generation of sulfuranyl radical *via* an electron transfer to arylsulfonium salts. McEwen and co-worker[3] studied reactions of triarylsulfonium salts with sodium alkoxides, and rationalized their results on the basis of an electron transfer from alkoxides to the sulfonium salts, yielding sulfuranyl and alkoxy radicals. Since triarylsulfuranyl radicals are too reactive to be detected by ESR techniques, and in particular, it is necessary to obtain clearly information about sulfuranyl radicals which might be involved in the reactions of triarylsulfonium salts with organolithiums[4] or thiolates[5], investigations on reactions of triarylsulfonium salts with an good electron donor are needed.

Results and Discussion

We have chosen sodium naphthalenide (**1**) as an electron donor and carried out the reaction of **1** with 5-(2-thianthreniumyl)thianthrene perchlorate (**2**). By treatment of **2** with **1** in tetra-hydrofuran (THF) under nitrogen at −78°C were obtained naphthalene, thianthrene (**3**), and a great number of unidentified products. Since one of the reasons for the complexity was conceived of diverse reactions of radicals formed by the decomposition of sulfuranyl radical, the same reaction was carried out in the presence of benzenethiol so as to quench the possible secondary radical reactions. The results are summarized in Table 1.

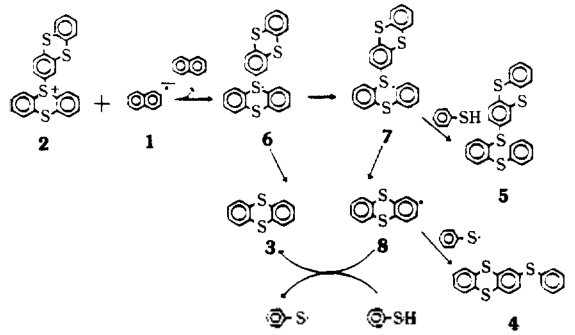
The fact that only a trace amount of 1,4-dihydrona-

Table 1. Reactants and Products in the Reaction of 1 with 2 in the Presence of Benzenethiol under N_2 at $-78°C$

Reactants (mmol)			Products (%)[a]		
1	**2**	PhSH	**3**	**4**	**5**
2.08	1.32	1.17	66	33	trace

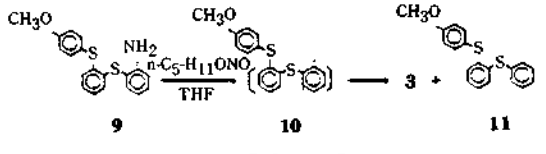
[a]mole % based on **2**. Apart from those products, naphthalene, a trace amount of 1,4-dihydronaphthalene, and some unknown liquids were isolated. But no **2** was recovered.

phthalene was formed suggests that reaction of **1** with **2** proceeds much faster than that of **1** with benzenethiol. Thus it is expected that the concentration of sodium benzenethiolate is very low and **4** cannot be formed by either simple nucleophilic aromatic substitution on **2** or a sulfurane mechanism. The high yield of **3** compared to that of **4** supports also our view. The unknown liquid obtained from the earlier benzene fraction showed several unresolved broad peaks on a gas chromatogram and only aromatic proton NMR signals from which only small amount of a white solid was isolated and identified to be **5** by mass spectral data (*vide infra*). However, the unknowns from the later benzene fraction and acetone fraction showed many overlapped peaks on gas chromatograms, and aromatic and aliphatic proton NMR signals. The gas chromatograms and the NMR spectra of the unknowns showed peaks at the same retention times and chemical shifts as those of corresponding fractions obtained from the reaction of **3** and **1** under the same condition. Therefore, it can be said that the unknowns are originated by the decomposition of **3**. Scheme 1 is proposed for the explanation for data in Table 1.



Scheme 1

Since the generation of radical (**7**) via independent route failed, indirect evidence for the involvement of the pathway (**7** → **3** + **8**) was obtained by diazotization of 2-aminophenyl 2-(4-methoxyphenylthio)phenyl sulfide (**9**) (Scheme 2) as in the literature.[6] The formation of **3** (23%) can be accounted for by intramolecular homolytic substitution on the sulfur atom of the 4-methoxyphenylthio group of **10**.[7] This result, therefore, indicates that the proposed pathway (**7** → **3** + **8**) is possible. However, the fact that 4-methoxyphenyl 2-(phenylthio)phenyl sulfide (**11**) (60%) which is a hydrogen abstraction product was formed predominantly suggests that decomposition of sulfuranyl radical (**6**) occurs more rapidly to form **3** and **8** than **7**. This in turn gives rise to high yields of **3** and **4**. The formation of small amount of **5** also can be explained on the basis of the thread of connection. Otherwise, high yield of **5** should be formed, especially in the presence of benzenethiol.



Scheme 2

Experimental Section

Materials and Equipment. Thianthrene[8], 4-methoxyphenyl 2-nitrophenyl sulfide[9], 2-aminophenyl 4-methoxyphenyl sulfide[9] were prepared by the standard methods and had melting points agreeing with the literature. The cation radical perchlorate of thianthrene[10] was prepared and assayed as described in the literature. Tetrahydrofuran (THF) was Merck reagent grade and was dried by distillation from calcium hydride before use. Acetonitrile was Kanto Extra pure and was refluxed over phosphorus pentoxide for 2 h, followed by distillation twice and stored over molecular sieve (4A). All other solvents were distilled before use. Column chromatography was performed with Merck silica gel (70-230 ASTM mesh, 0.05-0.2 mm). Infrared spectra (IR) were obtained using Perkin-Elmer Model 283 spectrometer. Nuclear magnetic resonance spectra (NMR) were obtained using Varian EM 360 A NMR spectrometer. Chemical shifts (δ) are given in parts per million (ppm) downfield from Me_4Si; coupling constants (J) are expressed in Hz. Mass spectra (MS) were recorded on a Simadzu GC/MS OP 1000 at a 70 eV ionization potential. Gas chromatographic analyses were performed on a Hitachi Model 164 (SE-30, column temperature 300°C, carrier gas flow rate, 1.6 Kg/cm^2). Elemental analyses were carried out by the Institute of Chemistry and Chemical Technology, Dae Jeon, Korea. Melting points were measured on a Fisher-Johns melting point apparatus and are reported uncorrected.

5-(2-Thianthreniumyl)thianthrene Perchlorate (**4**). A solution of 1.500g (4.75 mmol) of thianthrene cation radical perchlorate and 1.500g (6.94 mmol) of **3** in 40 m*l* of dry acetonitrile was refluxed for 24 h. After the solvent was removed, the residue was chromatographed on silica gel column. Elution was performed with benzene, followed by chloroform. Finally acetone fraction afforded 1.575g (2.97 mmol, 63%) of **2**: mp 153-154°C (EtOH-Et_2O); IR(KBr) 1100, 620(ClO_4^-) cm^{-1}; λ_{max}(EtOH). 270, 229 nm; NMR (DMSO-d_6) 6.86-7.97 (m, 13H), 8.41-8.70 (m, 2H); *Anal.* Calcd. for $C_{24}H_{15}O_4ClS_4$: C, 54.28; H, 2.84; S, 24.15; Cl, 6.68. Found: C, 54.19: H, 3.02; S, 23.96; Cl, 6.53.

Determination of the concentration of sodium naphthalenide (**1**). A solution of 1.474g (11.5 mmol) of naphthalene and 0.499g (21.7 mmol) of sodium turnings in 60 m*l* of dry THF was stirred at room temperature under nitrogen for 40 min., after the dark green color of **1** had appeared. The dark green solution was then cannulated to the flask, which was quenched with water, followed by the extraction with chloroform (60 m*l* × 3). The chloroform layer was dried over potassium carbonate, followed by the evaporation to dryness. The residue was chromatographed on silica gel. Elution with *n*-hexane gave a mixture of naphthalene and 1,4-dihydronaphthalene. Elution was continued until no fluorescent spot corresponding to those compounds was observed on a thin layer chromatogram. The mixture consisted of two compounds, after the solvent was removed, was subjected to the NMR analyses, showing the formation of 2.08 mmol of **1** at the foregoing condition.

Reaction of **2** with **1**. A solution of **1** prepared as in the method described above was added dropwise to a mixture of **2** (0.680g, 1.28 mmol) and 0.132g (1.20 mmol) of benzenethiol in 60 m*l* of THF over 15 min. period at -78°C under nitrogen. The mixture was additionally stirred for 1.5 h and then warmed to room temperature. After the mixture was treated with water, THF was evaporated on a rotary evaporator. The aqueous layer was extracted with chloroform (60 m*l* × 3), which then was dried over potassium carbonate. The residue obtained from removal of chloroform was chromatographed on silica gel column. Elution with *n*-hexane gave 1.162 g (9.07 mmol) of naphthalene and a trace amount of 1,4-dihydronaphthalene, which was identified by comparison with their NMR spectra with those of the authentic samples. Continuous elution with *n*-hexane gave 0.184 g (0.85 mmol, 66%) of **3** and 0.137 g (0.42 mmol, 33%) of **2**-phenylthiothianthrene **(4)**: mp 106-106.5°C (MeOH); IR (KBr) 3100, 1594, 1578, 1559, 1490, 1470, 1462, 1450, 1374, 1270, 1120, 1034, 890, 830, 754, 712, 704 cm^{-1}; λ_{max}(MeOH) 278 nm; NMR ($CDCl_3$) δ 7.58-7.01 (m); *Anal.* Calcd. for $C_{18}H_{12}S_3$: C, 66.66; H, 3.73. Found: C, 66.32; H, 3.50. Elution with benzene gave 0.235 g of a mixture of unknowns showing six major peaks (R_t: 0.7, 1.0, 1.4, 1.9, 5.7, and 11.0 min.) on a gas chromatogram. NMR spectrum of this mixture showed only aromatic proton signals. By the treatment of the unknown mixture with methanol at an ice-water temperature, was obtained small amount of a white solid, identified as phenyl 2-(2-thianthrenylthio) phenyl sulfide **(5)**: mp 50-56°C; λ_{max}(MeOH) 263 nm; MS, m/e (*rel. int.*) 433 (15.1), 432 (18.8), 431 (61.3), 295 (10.6), 294 (21.2), 294 (100), 290 (35.6), 217 (16.1), 216 (94.5), 215 (19.3), 214 (16.7), 184 (59.9), 171 (16.9), 139 (12.3). Later benzene fraction, followed by acetone fraction gave 0.048 g and 0.067 g of unidentified liquids, respectively.

2-Mercaptophenyl 4-Methoxyphenyl Sulfide **(12)**. A solution of 19.80 g (85.60 mmol) of 2-aminophenyl 4-methoxyphenyl sulfide in 55 m*l* of aqueous hydrochloric acid (1:1, V/V) was diazotized with 7.70 g (111.60 mmol) of sodium nitrite in 15 m*l* of water at 10°C. The diazonium salt in the solution was added dropwise to a solution of 21.60 g (134.76 mmol) of potassium ethyl xanthate in 45 m*l* of water at 40°C. The resulting mixture was then kept at 80°C for 30 min., followed by cooling to room temperature. The organic layer was separated, followed by dryness over calcium chloride. The residue was taken up by 20 m*l* of ether which was added dropwise to a suspension of 3.35 g (88.26 mmol) of lithium aluminum hydride in 55 m*l* of ether at -10°C and left at room temperature for 12 h. Diluted hydrochloric acid was added to the reaction mixture and the ether layer was separated, followed by evaporation to give 7.50 g of a crude product, which was unable to be purified by the column chromatography. IR band at 2584 (neat, SH) cm^{-1} and a singlet at δ 4.05 indicated the formation of **12**. Without further purification, the crude product was used for the next reaction.

2-Nitrophenyl 2-(4-Methoxyphenylthio)phenyl Sulfide **(13)**. To a stirred solution of 5.10 g (22 mmol) of the crude **12** and 3.10 g (19.7 mmol) of 2-chloronitrobenzene in 30 m*l* of ethanol was added dropwise 21.0 mmol of 30% aqueous sodium hydroxide. The mixture was refluxed for 2 h, followed by overnight in an ice-water bath to give yellow solids. The solids were filtered, followed by recrystallization from methanol to give 1.90 g (5.15 mmol) of **13**: mp 121-122°C; IR (KBr) 1590, 1565, 1558, 1505, 1490, 1448, 1430, 1335, 1304, 1294, 1285, 1274, 1245, 1170, 1100, 1028, 850, 820, 785, 732, 708 cm^{-1}; NMR ($CDCl_3$) δ 8.23 (dd, 1H, J = 0.75, 0.3 Hz), 7.64-6.71 (m, 11H), 3.80 (s, 3H); *Anal.* Calcd. for $C_{19}H_{15}NO_3S_2$: C, 61.77; H, 4.09; N, 3.79. Found: C, 61.54; H, 4.04; N, 3.68.

2-Aminophenyl 2-(4-Methoxyphenylthio)phenyl Sulfide **(9)**. Compound **13** was hydrogenated using 10% Pd-C in THF. Chromatography of the residue, after the solvent was removed, with benzene on silica gel column gave **9** (49%); mp 91-91.5°C (MeOH); IR (KBr) 3376, 3475, 1604, 1584, 1568, 1480, 1440, 1285, 1244, 1170, 1020, 844, 740 cm^{-1}; λ_{max} (MeOH) 302 (shoulder), 236 nm; NMR ($CDCl_3$) δ 7.54-6.75 (m, 12H), 4.13 (s, 2H), 3.83 (s, 3H); *Anal.* Calcd. for $C_{19}H_{17}NOS_2$: C, 67.22; H, 5.05; N, 4.13. Found: C, 67.77; H, 5.15; N, 4.29.

Reaction of **9** with *n*-Pentyl Nitrite. To a solution of 0.350 g (1.03 mmol) of **9** was added 0.200 g (1.71 mmol) of *n*-pentyl nitrite. The mixture was kept at 50°C for 5 h, followed by the evaporation of the solvent in vacuo. The residue was chromatographed on silica gel column using *n*-hexane, giving 0.051 g (0.24 mmol, 23%) of **3** and 0.201 g (0.62 mmol, 60%) of 4-methoxyphenyl 2-(phenylthio)phenyl sulfide **(11)**: mp 70-72°C (MeOH); IR (KBr) 3100, 1608, 1582, 1514, 1458, 1442, 1310, 1270, 1204, 1190, 1046, 845, 766, 704 cm^{-1}; λ_{max}(MeOH) 250, 232 nm; NMR ($CDCl_3$) δ 7.55-6.79 (m, 13H), 3.80 (s, 3H); MS, m/e 324 (M^+, B), 309, 215, 200, 184, 171, 139.

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